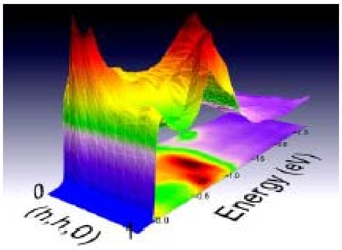
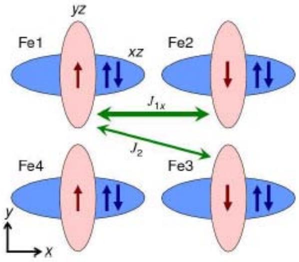
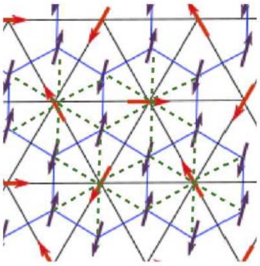
Theoretical Condensed Matter Physics Principal Investigators' Meeting

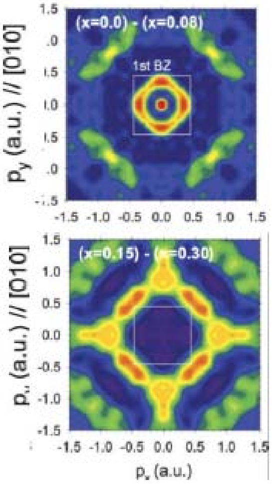
August 20-22, 2012

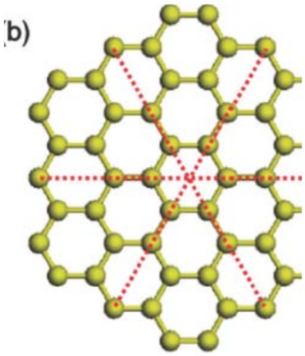
Rockville, Maryland

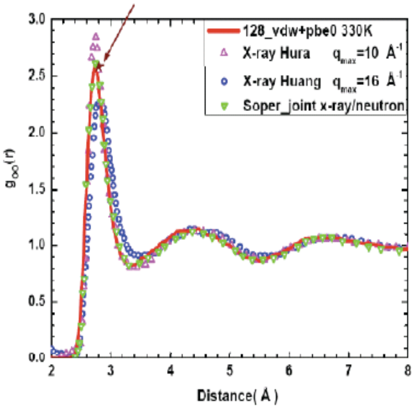


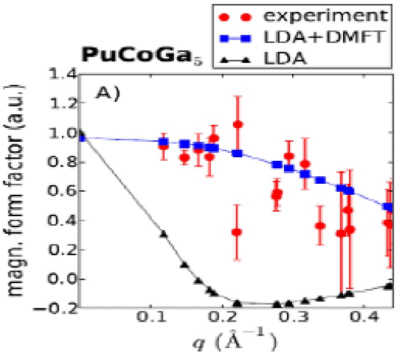












Office of Basic Energy Sciences

Division of Materials Sciences and Engineering

U.S. DEPARTMENT OF ENERGY

Office of Science

On the Cover

Left, upper:	Single particle spectral density of $UCoGa_5$. *A. Balatsky*, Los Alamos National Laboratory
Left, center:	Interpenetrating triangular and honeycomb lattices. *P. Coleman*, Rutgers University
Left, lower:	Dynamic structure factor for liquid water, theory versus experiment. *Roberto Car*, Princeton University
Center, upper:	Image of doped holes in La-Sr-Cu-O obtained from Compton scattering. *A. Bansil*, Northeastern University
Right, upper:	Spin-orbital coupling in iron-based superconductors. *Wei Ku*, Brookhaven National Laboratory
Right, middle:	Graphene structure. *A. MacDonald*, University of Texas
Right, lower:	Magnetic form factor of delta plutonium. *G. Kotliar*, Rutgers University

This document was produced under contact number DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

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Foreword

This volume provides descriptions of supported projects in the Theoretical Condensed Matter Physics (TCMP) Program, Division of Materials Sciences and Engineering (MSED) in the Office of Basic Energy Sciences (BES) of the U.S. Department of Energy (DOE). It is intended to provide material for the first TCMP Principal Investigators' meeting, held August 20–22, 2012, in Rockville, Maryland.

BES supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels and fundamental research that provides the foundations for new energy technologies relevant to DOE's missions in energy, environment, and national security. Condensed matter theory plays a key role in both the discovery of new organizing principles and the clarification of the origin of newly discovered phenomena. There are major efforts in strongly correlated electron systems, quantum transport, superconductivity, magnetism, and optics. Development of theory targeted at aiding experimental technique design and interpretation of experimental results is also emphasized. There is ongoing work in nanoscale science, where links between the electronic, optical, mechanical, and magnetic properties of nanostructures and their size, shape, topology, and composition are poorly understood.

This research area has recently expanded its portfolio in computational materials science through joint programs with the Chemical Sciences, Geosciences and Biosciences Division of BES, the Office of Advanced Scientific Computing in DOE, and the interagency Materials Genome Initiative.

The purpose of the BES biannual PI meetings is to bring together researchers funded by BES to foster an awareness of the research of others in the program, to facilitate the exchange of new results and research highlights, to promote new ideas and collaborations among participants and BES scientific user facilities, and to identify and pursue new scientific opportunities and new frontiers. For BES the PI meetings provide an opportunity to see the entire portfolio/program at one time and to assess the state of the program and chart new scientific directions.

We thank all the meeting participants for their active contributions in sharing their ideas and research accomplishments. We wish to thank Teresa Crockett in MSED and Lee-Ann Kiser at the Oak Ridge Institute for Science and Education (ORISE) for their outstanding work in all aspects of the meeting organization.

Dr. James W. Davenport, Program Manager
Theoretical Condensed Matter Physics
Materials Sciences and Engineering Division
Basic Energy Sciences
Office of Science
U.S. Department of Energy

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2012 Theoretical Condensed Matter Physics
Principal Investigators' Meeting
Materials Sciences and Engineering Division, Office of Basic Energy Sciences
U. S. Department of Energy

Program Chair: Jim Davenport, TCMP Program Manager

SUNDAY, AUGUST 19

6:00 – 8:00	**Registration**

Dinner on Your Own

MONDAY, AUGUST 20

7:00 – 8:00	**Breakfast**
8:00 – 8:30	Linda Horton, Director, Materials Sciences and Engineering Division *BES Program Updates*
8:30 – 9:00	Jim Davenport, Program Manager, Theoretical Condensed Matter Physics *TCMP Program Overview*
Session I	**Superconductivity 1** Chair: Alexei Tsvelik, Brookhaven National Laboratory
9:00 – 9:30	Elbio Dagotto, Oak Ridge National Laboratory, University of Tennessee *Study of Model Hamiltonians for the Iron-Based Superconductors*
9:30 – 10:00	Piers Coleman, Rutgers University *Tetrahedral Model for s± Pairing in the Iron-Based Superconductors*
10:00 – 10:30	Peter Hirschfeld, University of Florida *Theory of Novel Superconductors*
10:30 – 11:00	**Break**
Session II	**Graphene** Chair: Jerry Bernholc, North Carolina State University
11:00 – 11:30	Mei-Yin Chou, Georgia Tech *Physics of Twisted Bilayer Graphene*

11:30 – 12:00	Steven G Louie, Lawrence Berkeley National Laboratory, UC Berkeley *Many-Body Effects in the Excited-State Properties of Graphene and Nanostructured Materials*
12:00 – 12:30	Zhi-Gang Wu, Colorado School of Mines *Electronic and Optical Properties of Graphene Nanomeshes*
12:30 – 1:00	Valeri Kotov, University of Vermont Antonio Castro-Neto, Boston Univ., Graphene Research Center, Singapore *Anisotropic Dirac Liquids and Solids: Strained Graphene and Related Systems*
1:00 – 2:00	**Working Lunch** *Overview of Poster Session I: Presenters with Highlights*
2:00 – 3:30	**Poster Session I**
3:30 – 4:00	**Coffee Break**
Session III	**Transport** Chair: Philip Allen, Stony Brook University
4:00 – 4:24	Anton Andreev, University of Washington, Seattle *Hydrodynamic Description of Electron Transport in High Mobility Semiconductor Nanostructures*
4:24 – 4:48	Hai-Ping Cheng, University of Florida *Molecular Switches*
4:48 – 5:12	Massimiliano Di Ventra, UC San Diego *Incompleteness of the Landauer Formula for Electronic Transport due to Renormalized Viscous Corrections*
5:12 – 5:36	Eugene Mishchenko, University of Utah *Many-Body Effects in Chiral Electron Transport*
5:36 – 6:00	Arthur Voter, Los Alamos National Laboratory *Accelerated Molecular Dynamics Methods*
6:00 – 7:30	**Working Dinner** *Scientific Highlights of the Day: Discussion and Input from Attendees*

Session IV	**Spectroscopy and Time Dependence** Chair: John Rehr, University of Washington, Seattle
7:30 – 7:54	Arun Bansil, Northeastern University *New Scientific Insights Enabled through Realistic Modeling of Highly Resolved Spectroscopies of Complex Materials*
7:54 – 8:18	Gabriel Kotliar, Rutgers University *Theoretical Spectroscopy of Mixed Valence in Plutonium and Its Compounds*
8:18 – 8:42	Inna Ponomareva, University of South Florida *Atomistic Study of Ultrafast Dynamics in Multifunctional Materials in Bulk and Nanoforms*
8:42 – 9:06	Guoping Zhang, Indiana State University *First-Principles Theory of Laser-Induced Ultrafast Magnetization*
9:06 – 9:30	Viatcheslav Dobrovitski, Ames Laboratory *Quantum Dynamics and Control of Individual Spins in Diamond*

TUESDAY, AUGUST 21

7:00 – 8:00	**Breakfast**
Session V	**Science at the Nanoscale** Chair: Dale Koelling, US DOE, Ret.
8:00 – 8:24	Talat Rahman, University of Central Florida *Tuning Optical Properties of Au Chains through Transition Metal Atom Doping*
8:24 – 8:48	Uzi Landman, Georgia Tech *Small is Different: Energetics and Dynamics of Electrons in Materials Nano-scale Confinements*
8:48 – 9:12	Giulia Galli, UC Davis *Semiconducting Nanostructures by Design*
9:12 – 9:36	Priya Vashishta, University of Southern California *Reactive Molecular Dynamics Simulations of Hydrogen Production from Water and Self-Healing Nanostructured Materials for Energy Technology*
9:36 – 10:00	Harold Baranger, Duke University *Quantum Phase Transitions in Nanosystems: Wires, Dots, and Dissipation*
10:00 – 10:30	**Break**

Session VI	**Exotic States of Matter** Chair: Ravindra Bhatt, Princeton University
10:30 – 11:00	Jainendra Jain, Pennsylvania State University *Composite Fermion Pairing beyond 5/2*
11:00 – 11:30	Patrick Lee, MIT *Production and Detection Schemes of Majorana Bound States*
11:30 – 12:00	Allan MacDonald, University of Texas *Transport Properties of Quantum Hall Superfluids*
12:00 – 12:30	Nandini Trivedi, Ohio State University *Quantum Simulations of Orbitally Controlled Physics and Nanoscale Inhomogeneity in Correlated Oxides*
12:30 – 1:30	**Working Lunch** *Overview of Poster Session II: Presenters with Highlights*
1:30 – 3:00	**Poster Session II**
3:00 – 3:30	**Coffee Break**
Session VII	**Correlation & Computing** Chair: Peter Littlewood, Argonne National Laboratory
3:30 – 3:54	Kieron Burke, UC Irvine *DFT and Strongly Correlated Systems*
3:54 – 4:18	Fernando Reboredo, Oak Ridge National Laboratory *Extending the Reach of Computational-Theoretical Methods to Materials at the Energy Frontier*
4:18 – 4:42	Garnett Chan, Princeton University *Quantum Embedding and Many-Electron Wavefunctions for Strongly Correlated Solids*
4:42 – 5:06	Vladimir Antropov, Ames Laboratory *Ab Initio Method for Spin Fluctuation Calculations*
5:06 – 5:30	Cyrus Umrigar, Cornell University *Quantum Chemistry via Walks in Determinant Space*
5:30 – 6:00	**Break**

6:00 – 7:30	**Working Dinner** *Scientific Highlights of the Day: Discussion and Input from Attendees*
Session VIII	**Superconductivity 2** Chair: Alexander Balatsky, Los Alamos National Laboratory
7:30 – 8:00	Eugene M. Chudnovsky, CUNY Lehman College and Graduate School *Lifetime of Skyrmions in Cuprates and Other 2D Ferro- and Antiferromagnetic Lattices*
8:00 – 8:30	Torsten Clay, Mississippi State University *Theory of Layered Organic and Inorganic Materials with Charge-Spin Frustration*
8:30 – 9:00	Dung-Hai Lee, Lawrence Berkeley National Laboratory, UC Berkeley *Superconductivity in Correlated and Spin-Orbit Materials*
9:00 – 9:30	Donna Sheng, California State University, Northridge *Novel Charge and Spin Fractional Quantum Hall Effects and New Emerging Quantum Phases*

WEDNESDAY, AUGUST 21

7:00 – 8:00	**Breakfast**
Session IX	**Oxides** Chair: Sashi Satpathy, University of Missouri
8:00 – 8:30	Warren Pickett, UC Davis *Semi-Dirac Semi-Weyl Semi-Metal: Computational Discovery and Phenomenology*
8:30 – 9:00	David Singh, Oak Ridge National Laboratory *Materials Theory*
9:00 – 9:30	Charles Stafford, University of Arizona *Many-Body Theory of Energy Transport and Conversion at the Nanoscale*
9:30 – 10:00	Wei Ku, Brookhaven National Laboratory *Recent Progress in Treating Electronic Structure of Materials with Disordered Impurities*
10:00 – 10:15	**Break**

Session X	**Physics at the Mesoscale** Chair: Kim Ferris, Pacific Northwest National Laboratory
10:15 – 10:45	ValeriI Vinokour, Argonne National Laboratory *Quantum Mesoscopic Materials*
10:45 – 11:15	Sidney Nagel, University of Chicago *Jamming and the Low-Temperature Properties of Glasses*
11:15 – 11:45	Leonid Glazman, Yale University *Interference of Quantum Phase Slips in One-Dimensional Weak Superconductors*
11:45 – 12:15	Michel Pleimling and Uwe Tauber, Virginia Tech *Non-equilibrium Relaxation and Aging Scaling of Magnetic Flux Lines in Disordered Type-II Superconductors*
12:15 – 1:00	**Working Lunch** *Meeting Feedback, Suggestions for Future Meetings*
1:00	**Sundown**

TCMP PI Meeting

Poster Session I, Monday, August 20, 2:00 – 3:30

1. *Integrated Modeling of Novel Materials*
   Alexander Balatsky, Los Alamos National Laboratory

2. *Mechanistic Aspects of the Nitrogen Cycle: The Action of Copper Nitride Reductase*
   J. Bernholc, North Carolina State University, Raleigh

3. *Surface Electromagnetic Phenomena in Pristine and Atomically Doped Carbon Nanotubes: Fundamentals and Applications*
   Igor Bondarev, Department of Physics, North Carolina Central University

4. *Improved Calculation of Vibrational Mode Lifetimes in Anharmonic Solids*
   Murray S. Daw, Department of Physics & Astronomy, Clemson University

5. *Applications of the Exact Solution of Nonequilibrium Charge-Density-Wave Systems to Pump/Probe Experiments and Cold Atom Experiments*
   J. K. Freericks, Department of Physics, Georgetown University

6. *Fluctuation phenomena in low-dimensional superconductors*
   Victor Galitski, University of Maryland

7. *Bose Glass and Mott Glass of Quasiparticles in a Doped Quantum Magnet*
   Stephan Haas, University of Southern California

8. *Non-plasmonic Mechanism of Light Emission Enhancement from Hybrid Metal-Semiconductor Quantum Heterostructures*
   Arkadii Krokhin, Department of Physics, University of North Texas

9. *Analysis of Electron and Phonon Dynamics in Terahertz Semiconductor Devices within the Framework of a Microscopic Density Matrix Approach*
   Ines Montano, Sandia National Laboratories

10. *Non-equilibrium Physics at the Nanoscale*
    Dirk K. Morr, The University of Illinois at Chicago (UIC)

11. *Condensed Matter Theory*
    Mike Norman, Argonne National Laboratory
    Other Principal Investigators: Alex Abrikosov, Alex Koshelev, Kostya Matveev

12. *Theory of Quantum Oscillations in the Vortex Liquid Phase of High Tc Cuprates*
    Sumilan Banerjee, Shizhong Zhang, and **Mohit Randeria**
    Department of Physics, The Ohio State University

13. *Next Generation Photon and Electron Spectroscopy Theory: Advances in RSGF and GW-BSE Approaches*
John J. Rehr, Department of Physics, University of Washington

14. *A Phase Transition Arising from the Underscreened Anderson Lattice Model: A Candidate Concept for Explaining the Hidden Order in URu2Si2*.
Peter S. Riseborough, Physics Department, Temple University

15. *Theory of the Mott Interfaces*
Sashi Satpathy, Department of Physics, University of Missouri

16. *Phase Separation and FFLO Phases in Fermi Gas of Ultracold Atoms of Spin S with Attractive Potential in a One-Dimensional Trap*
P. Schlottmann, Department of Physics, Florida State University

17. *Important Temperature-Dependences in Approximate Finite-Temperature Density Functionals*
S.B. Trickey, Quantum Theory Project, Departments of Physics and Chemistry, University of Florida, Gainesville

18. *Development of New Methods and Techniques in Theory of Strongly Correlated Systems*
Alexei M. Tsvelik, Brookhaven National Laboratory

19. *Fine Structure of Intersubband Spin Plasmons in a Quantum Well*
Carsten A. Ullrich, Department of Physics and Astronomy, University of Missouri, Columbia, Missouri

20. *Dynamics and Nonequilibrium Effects in Higher-Order and Pump-Probe X-ray Spectroscopy*.
Michel van Veenendaal, Department of Physics, Northern Illinois University

21. *Meta-GGA for Optical Spectra*
V.U. Nazarov and **G. Vignale,** Department of Physics, University of Missouri, Columbia Missouri

22. *Long Ranged Dispersive Interactions in Graphitic Nanostructures*
Lilia M. Woods, Department of Physics, University of South Florida, Tampa, Florida

23. *Magnetization Dynamics at Elevated Temperatures*
Shufeng Zhang, Department of Physics, University of Arizona

24. *Tailoring Magnetism and Spin in Quantum Dots*
Igor Zutic, University at Buffalo, and Andre Petukhov, South Dakota School of Mines and Technology

Poster Session II, Tuesday August 21, 1:30 – 3:00

1. *Modeling for Semiconductor Photo-Catalysis and Solar Water Splitting*
   Philip B. Allen, Department of Physics and Astronomy, Stony Brook University, Stony Brook

2. *Properties of Multiferroic Nanostructures from First Principles*
   Laurent Bellaiche, Department of Physics, University of Arkansas

3. *Internal Geometry, Stability and Design of Quantum Hall States*
   Ravindra Bhatt, Department of Electrical Engineering, Princeton University
   Co-Principal Investigators: F. Duncan M. Haldane, Department of Physics, Princeton University; Edward H. Rezayi, Department of Physics, California State University, Los Angeles; Kun Yang, Department of Physics and National High Magnetic Field Laboratory, Florida State University

4. *Quantum Circuits for Measuring Levin-Wen Operators*
   N.E. Bonesteel, Department of Physics, Florida State University, and D. P. DiVincenzo, Institute for Quantum Information, RWTH Aachen and PGI, Theoretical Nanoelectronics, Forschungzentrum Juelich.

5. *CMCSN: Structure and Dynamics of Water and Aqueous Solutions in Materials Science*
   Roberto Car, Department of Chemistry, Princeton University

6. *Theory of Functionalized Nanostructures*
   James R. Chelikowsky, Center for Computational Materials, Institute for Computational Engineering and Sciences, Departments of Physics and Chemical Engineering, University of Texas at Austin

7. *Theory and Simulation of Defects in Oxide Materials*
   James R. Chelikowsky and **Alexander A. Demkov**, University of Texas at Austin, Steven G. Louie, Lawrence Berkeley National Laboratory and University of California, Berkeley, and Yousef Saad, University of Minnesota

8. *Electronic Structure and Novel Properties in Complex Oxides and Hetero-interfaces*
   Arthur J. Freeman and **Sung-Hyon Rhim**, Department of Physics and Astronomy, Northwestern University

9. *Computational Magnetism: Nanomagnetism and Development of Theoretical Methods*
   Bruce Harmon, Ames Laboratory

10. *Vibrations and Flow Defects in Jammed Packings*
    Andrea J. Liu, University of Pennsylvania

11. *Modeling the Self-Assembly of Ordered Nanoporous Materials*
    Peter A. Monson and Scott M. Auerbach, University of Massachusetts

12. *First-Principles Investigations of the Physics of New Semiconducting Ferroelectrics for Solar Light Absorption and Carrier Separation*
    Andrew M. Rappe, Department of Chemistry, University of Pennsylvania

13. *Metamaterials*
    Costas Soukoulis, **Thomas Koschny**, and Jigang Wang, Ames Laboratory – USDOE and Physics & Astronomy Department, Iowa State University

14. *Potential and Pore-Size Dependent Capacitance of Carbon Pores in Aqueous Electrolytes: Molecular Insights from Simulations and Experimental Validation*
    Alberto Striolo, The University of Oklahoma

15. *High Entropy Alloys a New Class of Structural Materials: Magnetism and Magnetic Interactions.*
    G. Malcolm Stocks, Oak Ridge National Laboratory

16. *First-Principles Studies of Hydrogen Interactions with Storage Materials*
    Chris G. Van de Walle, Materials Department, University of California, Santa Barbara

17. *Exploratory Development of Theoretical Methods*
    Cai-Zhuang Wang, Vladimir Antropov, Bruce Harmon, Kai-Ming Ho, and Viatcheslav Dobrovitski, Ames Laboratory

18. *Charge Patching Method for Electronic Structures and Charge Transports of Organic and Organic/Inorganic Mixed Nanostructures*
    Lin-Wang Wang, Lawrence Berkeley National Laboratory

19. *Modeling Dynamically and Spatially Complex Materials:*
    Accurate Classical Potentials to Mimic BCC Metal Properties
    John Wilkins and **Hyoungki Park**, The Ohio State University

20. *A Hybrid Computational-Experimental Approach for Automated Crystal Structure Solution*
    Christopher Wolverton, Northwestern University

21. *Density Functional Theory for Phase-Ordering Transitions*
    Jianzhong Wu, University of California at Riverside

22. *Topological Insulator Gap in Graphene with Heavy Adatoms*
    Ruqian Wu, Department of Physics and Astronomy, University of California, Irvine

23. *Theory of Defects in Electronic Materials*
    Shengbai Zhang, Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, and Peihong Zhang, Department of Physics, University at Buffalo

Quantum Theory of Semiconductor Photo-Catalysis and Solar Water Splitting

Principal Investigator: Philip B. Allen
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Project Scope

Four solar photons (of energy > 1.23 eV each) are in principle sufficient to drive the splitting of water ($2H_2O \rightarrow 2H_2 + O_2$), creating a versatile storable fuel (H_2) (artificial photosynthesis.) A crystalline semiconductor can serve as the light-absorber, driving heterogeneous catalysis of water splitting at the aqueous interface. The problem, pioneered by Fujishima and Honda in 1972, is to invent an efficient, inexpensive, robust, and scalable system of photo-absorbers and catalytic interfaces. The semiconductor alloy $Ga_{1-x}Zn_xN_{1-x}O_x$ is a promising candidate for the photocatalyst. We model (a) optical and (b) dc transport properties of the bulk alloy, and structure and thermodynamics of the (c) clean, and (d) wet surfaces of this alloy. We want to understand how alloying affects the photo-absorption spectrum and carrier mobility. We want to know the density of bulk and surface carrier traps and their importance for photo-catalysis. How deep are the traps, what are the rates of the carrier recombination processes that compete with energy-harvesting, what are the chemically active interface sites where water oxidation occurs, and what are the electron transfer rates governing delivery of hole carriers to these sites, and then onto the oxidized water intermediates? How do electron carriers separate from holes, and how mobile are they?

Recent progress

$(GaN)_{1-x}(ZnO)_x$ bulk alloy

The thermodynamics (*T versus x* phase diagram) was studied in detail and published in Phys. Rev. B. Density functional theory (DFT) gave energies of various random alloy structures with *N~100* atoms, allowing full relaxation locally from ideal wurtzite positions. The results were fitted with a phenomenological Ising-type (Connolly-Williams cluster expansion) model. The process was iterated so that the

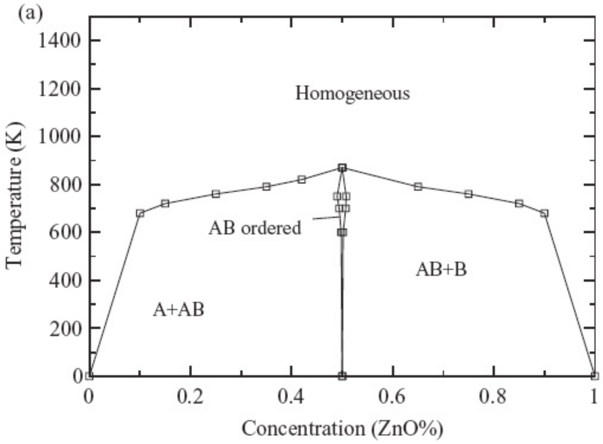

Fig. 1. Predicted $(GaN)_{1-x}(ZnO)_x$ phase diagram

detailed DFT results would sample representative low energy structures. Then the cluster expansion parameters were readjusted and improved. Next, Monte Carlo simulations were done for large cells, at various *x* and *T*. Below 800K, phase separation into an ordered x=0.5 compound and pure end-member GaN or ZnO is found. The ordered compound has not yet been made, and would require non-thermal methods, because lattice diffusion at such temperatures is too slow to allow equilibration. In other words, at typical alloy fabrication temperatures T>1150K, homogeneous alloys are stable at all *x*. Under available annealing schedules, these alloys would not significantly readjust down to low T. However, the structures are by no means totally random. Significant short-range order persists to very high T, and bond-length changes occur which are not intuitively obvious.

Work is now underway to study the electronic structure of large realistic alloy configurations (432 atom cells), generated from the cluster expansion using Monte Carlo simulation, and then relaxed to their ground state structure using DFT.

GaN $(10\bar{1}0)$ / water interface

A student, Jue Wang, working in collaboration with the group of Prof. Fernandez-Serra, has looked in great detail at the behavior of this interface at 340 K, using *ab initio* molecular dynamics (the GGA version of DFT in the SIESTA code was used to compute forces.) Starting from pristine surfaces cleaved from pure water (92 molecules) and pure GaN (120 molecules), the waters rapidly equilibrated. The equilibrated structures had ~83% of the surface Ga atoms hosting dissociated OH^- ions. The corresponding H^+ ions bonded to adjacent surface N atoms.
This result disagrees with our initial thoughts based on a prediction that at T=0, 100% dissociation should occur in a monolayer of water. Apparently, T>0 and adjacent ("bulk") water, combine to stabilize a fraction of undissociated water at the surface. The undissociated waters are closely associated with surface Ga atoms, and are centers of proton emission and absorption, both into the bulk water, and onto adjacent surface-bound OH^- species.

Work is now underway to see whether our earlier T=0 monolayer calculation missed a partially dissociated state because of using too small simulation cells. The answer appears to be no. The re-association of 17% of the ions into molecular H_2O on the surface must be driven by hydrogen bonding to "bulk" water.

Zero-point effects in H_2O and D_2O Ice

Quantum zero-point nuclear vibration normally causes crystals to expand, exactly as thermal vibrations do. Heavier isotopes normally expand less because vibrational

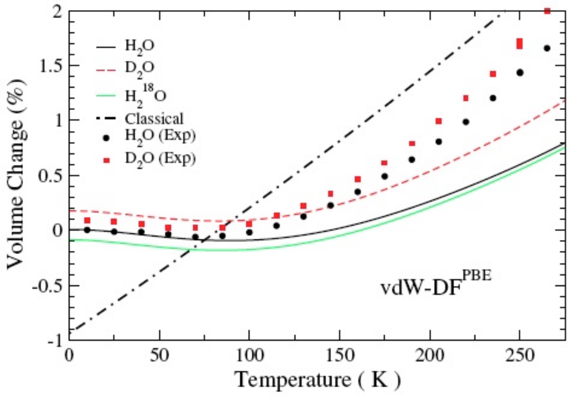

Fig. 2 predicted *versus* experimental thermal and zero-point expansion of ice.

amplitudes are smaller in the quantum regime. The most interesting exception is ice, where D_2O is actually expanded relative to H_2O. We found that the reason is anomalous behavior of OH-stretch vibrations when the H is hydrogen-bonded to a neighboring O. The shorter of the two OH bonds in O-H—O is very covalent, and the longer, hardly covalent but quite ionic. But if the oxygen O-O distance shrinks, the short bond loses some covalency and transfers it to the longer bond. This diminishes the OH-stretch vibrational frequency, thus lowering-zero point energy. Therefore, the higher the zero-point energy, the more the crystal will want to diminish O-O distances to reduce this energy. Since H_2O has higher zero-point energy than D_2O, it has more motive to contract. By the same argument, we expect $H_2{}^{18}O$ not to have such an effect. Our prediction is borne out by experiments performed locally by Peter Stephens. This study was helpful to water-splitting studies for two reasons. First, the role of hydrogen zero-point motion is surely not insignificant in the physics and chemistry of water, and our study helps clarify the importance. In particular, it shows the success of the quasi-harmonic approximation and the need for accurate DFT energies rather than model forces. Second, the computations are a sensitive test of the accuracy of DFT for water. This issue is significant. DFT should be good for covalent and ionic materials, GaN and ZnO for example. But water is a molecular substance. The intramolecular aspect is in the realm where DFT should work. However, intermolecular forces have van der Waals components which are not available (except by accident) to ordinary DFT. This study enabled us to evaluate the effectiveness of new DFT functionals designed to include van der Waals forces.

Future Plans

$(GaN)_{1-x}(ZnO)_x$ bulk alloy

The aim is to learn what is the nature the HOMO and LUMO states. Are they localized at special sites? What is their expected hopping mobility. How would an electron and a hole behave if injected at higher energies than the relevant HOMO or LUMO levels? What would be their diffusivities, and how fast would they thermalize? Our preliminary results suggest that a few 432-atom cells, studied in detail, should enable answers to many of these questions.

Alloy surface and its water interface

It is important to learn about active sites for catalysis. Which sites on the semiconductor-water interface attract photoelectrons or photoholes? How do such sites participate in water oxidation (consuming holes to produce H^+ and O_2) or proton reduction (consuming electrons to produce H_2 from H^+)? This difficult question has perhaps never been answered at the level of quantum theory of electrons. It surely exceeds the ambition of one or two coupled individual-investigator programs. Therefore we have aligned with groups at Brookhaven National Lab (BNL), Yale, and Rochester, with significant expertise in chemical as well as physical theory. A DoE CMCSN (Computational Materials and Chemical Sciences Network) grant provides the glue. All catalysis-related work in the current project takes advantage of this network. One colleague in this network is Prof. Artem Oganov (Stony Brook Geosciences.) He is a leader in structure prediction of inorganic materials, and principal author of the code USPEX, perhaps the premiere code using genetic algorithms for this problem. Future work on surface and interface structure in the current project will attempt to profit from a new version of USPEX designed to do surface and interface prediction. We have preliminary results for an interesting "semipolar" surface $(10\bar{1}1)$ of GaN. The motive for this particular surface is experiments, still unpublished, done at BNL. Alloy powders show evidence that this might be a dominant surface on micron-sized crystallites. GaN is a very important material for optoelectronic applications. There has been much work on many properties, including surface structure. Our preliminary results have identified one new structure, not previously predicted, under nitrogen-rich conditions. It has an unusual N_3 moiety bonded between surface Ga atoms. It is a good example of the advantage of a bias-free genetic algorithm approach. The advantage is, that unusual structures, not intuitively guessable, can be found.

We are about to embark on many projects using the new surface-USPEX code which is nearly developed. This also motivates another project: band unfolding. Surface computations use slabs whose surfaces are separated by bulk layers on one side, and a thick "vacuum" layer on the other. The resulting bands lack a sensible Bloch wavevector k_z in the direction (z) perpendicular to the slab. We are developing computer algorithms which endow the states with their approximate k_z character and allow graphical representations analogous to the ordinary bands of bulk materials.

Publications

1. Li Li, J. T. Muckerman, M. S. Hybertsen, and P. B. Allen, "Phase diagram, structure, and electronic properties of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solutions from DFT-based simulations," Phys. Rev. B **83**, 134202:1-6 (2011).

2. B. Pamuk, J. M. Soler, R. Ramírez, C. P. Herrero, P. W. Stephens, P. B. Allen, and M.-V. Fernández-Serra, "Anomalous Nuclear Quantum Effects in Ice," Phys. Rev. Lett. **108**, 193003:1-4 (2012).

3. J. Wang, L. S. Pedroza, A. Poissier, and M. V. Fernández-Serra, "Water Dissociation at the GaN$(10\bar{1}0)$ Surface: Structure, Dynamics, and Surface Acidity," J. Phys. Chem. C **116**, 14382-14389 (2012).

Electron Interaction Effects in Nanosystems

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Project scope

The research in this program is to investigate effects of electron-electron interactions on the transport and thermodynamic properties of low-dimensional electronic systems: carbon nanotubes, single atom carbon chains, granular and homogeneously disordered superconductors, and superconducting single electron devices. This includes the study of:

- Influence of equilibration of electron fluid on the transport properties of high mobility nanosystems
- Electron correlations in single atom carbon chains
- Boundary effects in the thermodynamic and transport properties of quantum dots based on armchair nanotubes
- Resistance of p-n junctions in armchair nanotubes due to umklapp processes and electron-phonon processes
- Transport phenomena in SNS junctions with p-wave superconductors

Recent progress

Effects of equilibration of electron fluid on the transport properties of high-mobility nanostructures. Electron-electron (e-e) collisions in semiconductors conserve momentum of electron fluid and thus by themselves do not give rise to a finite resistivity. Moreover, if correlations between e-e and electron-disorder scattering are neglected the resistivity of the system also turns out to be unaffected by e-e collisions. Accounting for correlations between e-e scattering and disorder results in a dependence of transport properties of the system on the rate of electron-electron collisions. In the presence of the current, the e-e collisions tend to establish an equilibrium state that is characterized by a nonvanishing hydrodynamic velocity $\mathbf{u}$. This effect is particularly pronounced in high-mobility devices, where the e-e collision mean free path becomes shorter than either the correlation length of a disorder potential or a characteristic device size. In this regime passage of electric current may be described using the hydrodynamic approach. Two types of questions arise in this respect: 1) understanding of transport properties of high mobility electron systems in the hydrodynamic regime, 2) studying the kinetics of equilibration.

Resistivity in the hydrodynamic regime was studied in Ref. [6]. It was shown that the hydrodynamic flow arising in a smooth disorder potential is markedly different from the Stokes flow. The dissipation and resistivity are dominated not by viscous stresses but rather by temperature gradients arising in the electron fluid. Surprisingly, because of this the resistivity turns out to be proportional to the variance of the potential itself rather than that of its gradients. The resistivity may be expressed in terms of the intrinsic parameters of the electron liquid. These results are relevant to transport experiments on high mobility semiconductor nanostructures with strongly interacting carriers, where the hydrodynamic regime can be realized.

The hydrodynamic description of electron transport applies when the mean free path due to e-e collisions is shorter than other length scales in the problem. If this is not the case e-e collisions lead to only partial equilibration of the electron liquid and understanding of transport requires the study of kinetic processes responsible for equilibration. In one-dimensional systems equilibration requires back-scattering processes which involve high-energy hole-type excitations. The microscopic mechanism of equilibration processes and their rate in the regime of strong e-e interactions were studied in Refs. [3, 8, 10, 12]. The influence equilibration processes on conductance of quantum wires was addressed in Ref. [7].

Electron correlation effects in carbon-based electronic devices. The strong correlations between electrons in carbon nanotubes (CNT) have a dramatic influence on their transport and optical properties. The PI studied the following questions: 1) Plasmon decay in strongly correlated armchair nanotubes, Ref. [4], 2) conductance of a Mott pn-junction in an armchair CNT, Ref. [5] (it was shown that the pn-junction may be tuned to a quantum critical point with an intermediate value of conductance) 3) photogalvanic effect in strongly correlated chiral carbon nanotubes, Ref. [11].

Planned research activity 2012-2013

The planned research activity is focused on the following themes.

1. *Transport properties of p-wave superconductors.* Many of the transport properties of unconventional superconductors with p-wave pairing have not been studied. In the following year the PI will study the following topics: 1) mesoscopic fluctuations of critical current in S-N-S Josephson junctions with p-wave superconductors 2) resistivity of boundary between a normal metal and a p-wave superconductor, 3) intrinsic ac Hall effect in p-wave superconductors.
2. *Equilibration of one-dimensional liquids of spin-1/2 particles.* In electron liquids at low density the band width of spin excitations is much smaller than the bandwidth of charge excitations. Therefore the most effective equilibration channel corresponds to a transfer of a spin excitation from the right to the left Fermi point. So far the equilibration theory of on-dimensional liquids has been developed for the spinless case. The PI will work on extending this theory to the spin-1/2 case.

Publications

References

[1] Wei Chen, A. V. Andreev, and G. F. Bertsch, "Conductance of a single-atom carbon chain with graphene leads", Phys. Rev. B **80**, 085410 (2009).

[2] A. V. Andreev, D. T. Son, and B. Spivak, "Hydrodynamics of chiral liquids and suspension", Phys. Rev. Lett. **104**, 198301 (2010).

[3] K. A. Matveev, A. V. Andreev, and M. Pustilnik, "Equilibration of a one-dimensional Wigner crystal", Phys. Rev. Lett. **105**, 046401 (2010).

[4] Wei Chen, A. V. Andreev, E. G. Mishchenko, and L. I. Glazman, "Decay of a plasmon into neutral modes in a carbon nanotube", Phys. Rev. B **82**, 115444 (2010).

[5] Wei Chen, A. V. Andreev, and L. I. Glazman, "Quantum Criticality in a Mott pn Junction in an Armchair Carbon Nanotube", Phys. Rev. Lett. **106**, 216801 (2011).

[6] A. V. Andreev, S. A. Kivelson, and B. Spivak, "Hydrodynamic Description of Transport in Strongly Correlated Electron Systems", Phys. Rev. Lett. **106**, 256804 (2011).

[7] K. A. Matveev and A. V. Andreev, "Equilibration of Luttinger Liquid and Conductance of Quantum Wires", Phys. Rev. Lett. **107**, 056402 (2011).

[8] K. A. Matveev, and A. V. Andreev, "Equilibration of a spinless Luttinger liquid", Phys. Rev. B **85**, 041102(R) (2012).

[9] E. Kirkinis, A.V. Andreev, B. Spivak, "Electromagnetic propulsion and separation by chirality of nanoparticles in liquids", Phys. Rev. E **85**, 016321 (2012).

[10] K. A. Matveev, A. V. Andreev, and M. Pustilnik, "Rate of equilibration of a one-dimensional Wigner crystal", Physica B: (Physics of Condensed Matter) **407**, 1898 (2012), DOI:10.1016/j.physb.2012.01.058.

[11] Raphael Matthews, Oded Agam, Anton Andreev, Boris Spivak, "Manifestations of electron interactions in photogalvanic effect in chiral nanotubes", Phys. Rev. B. **85** 195430 (2012).

[12] K. A. Matveev, A. V. Andreev,"Scattering of hole excitations in a one-dimensional spinless quantum liquid", arXiv:1204.5827, accepted to Phys. Rev. B.

Ab initio spin dynamics in solids

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I. Project Scope

The scope of this project is to describe the spin dynamical effects in magnets using theoretical models and modern first-principles electronic structure methods. Our approach includes calculations of spin dynamical susceptibility using both density functional approach and many-body GW approximation to explain current neutron scattering experiments. We also develop methods beyond linear response approach and perform direct spin dynamical simulation at finite temperatures. One of the goals of this project is to include spin fluctuations beyond mean field description (like LDA, GW and so on) and treat them self-consistently. These developments will allow us to address magnetic many body effects, renormalization of magnetic moments due to quantum spin zero-point motion and finite temperature effects.

II. Recent Progress

We show that the most puzzling features of magnetism of iron superconductors can be naturally reconciled within a rather simple effective spin model with a biquadratic interaction [1], which is consistent with electronic structure calculations. By going beyond the Heisenberg model, our description explains numerous experimental observations, including the peculiarities of the spin-wave spectrum, thin domain walls and crossover from a first- to second-order phase transition under doping. The model also offers insight into the occurrence of the nematic phase above the antiferromagnetic phase transition.

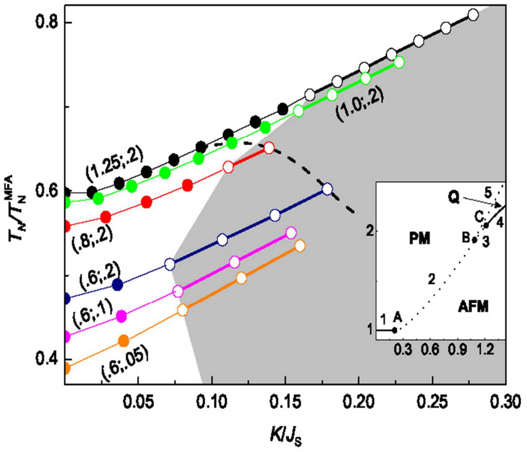

Figure 1 Transition temperature and order of phase transition as a function of biquadratic interaction K obtained by Monte Carlo simulations for $CaFe_2As_2$. Temperature is measured in units of T_N (MFA)=$J_s/3$, which is the second-order T_N in MFA. Each line is labeled by a set of two parameters (J_2/J_1;J_c/J_1). The region of first-order transitions (empty symbols) is schematically highlighted by shading and thicker lines. The dashed line shows the point of inversion of J_{1b}. The inset shows the mean-field phase diagram in a larger area of the same parameters. Solid lines 1 and 4 (dashed lines 2, 3 and 5) denote second-order (first-order) first transition. A and C are tricritical points; B is the triple point. Q denotes the quadrupolar phase.

We suggested a model for the magnetic dynamics of δ-Pu [2] and its alloys in order to show that the dynamical fluctuations of the magnetization density, or spin fluctuations, may be responsible for the anomalies of their observed thermal expansion. We show that due to strong magnetoelastic coupling, spin fluctuations may essentially contribute to the volume strain by giving a negative magnetovolume contribution that is proportional to the squared local magnetic moment and the magnetic Gruneisen constant which is negative in δ-Pu. In the presented model, the local magnetic moment increases as the temperature rises, resulting in the interplay between the positive contributions to the volume strain from the lattice and the negative contribution from spin fluctuations, and finally leads to the Invar anomaly or to the negative coefficient of thermal expansion. Our results agree closely with the measured thermal-expansion data for Pu-Ga alloys.

We also analyze the magnetic stability of the ground state of magnetic systems, taking into account strongly coupled zero-point spin fluctuations [3]. The formalism is applied to the elemental 3d-metals Fe and Ni and to two phases of the 5f-metal Pu. Strong suppression of local magnetism due to spin fluctuations is obtained for xα- Pu. Such inclusion of spin fluctuations changes the character of the magnetism in α-Pu from localized to itinerant.

We developed a new technique to incorporate spin fluctuations into modern band structure calculations. This technique is based on a many body perturbation theory treatment of electron-electron interaction and represents an addition of particle-hole diagrams to the mean field solution obtained by such static methods as LDA, GW, etc. This is a generalization of our previous ab-initio calculations of dynamic spin susceptibility in magnetically ordered or paramagnetic systems and consecutive estimation of particle-hole ladder diagrams, representing electron-magnon interactions. Our results indicate that this method is important for magnetic materials under pressure in general as well as itinerant magnet systems. We show significant improvement of the description of magnetic properties in pure ferromagnetic 3d transition metals under pressure and in iron superconductor compounds.

III. Future Plans

We are planning to continue to develop ab-initio spin fluctuations approach. One of the important goals is to develop self-consistent technique to include spin fluctuations and describe magnetism of itinerant magnets. This will include the direct addition electron-hole diagrams of many body perturbation theory. These diagrams are part of well-known FLEX approximation in the electronic structure theory. We plan first to explore applicability of the electron-hole ladder diagrams for the total energy calculations and for the description of magnetization. Next we will proceed with calculations of the exchange coupling due to spin fluctuations. This exchange coupling has not been described earlier and we expect this contribution to be important near the Fermi level. From a point of view of applications we will apply these methods to the studies of permanent magnet systems, which are being studied actively at Ames laboratory. Our approach will allow us to calculate magnetization, Curie temperature and magnetic anisotropy in these systems with much better accuracy in magnets with itinerant magnetic components. We will also address such issues as temperature dependence of the exchange coupling and magnetic anisotropy in permanent magnets – completely new area for the electronic structure applications.

Next we will use this technique to describe spin fluctuations in disordered magnetic alloys using coherent potential approximation. The theory of dynamic susceptibility for the disordered magnetic alloys will be formulated and computer codes will be developed. After performing testing calculations we will plan to address real world magnetic systems: 3d magnetic alloys, permanent magnets in alloys, newly discovered iron superconductors, graphene systems.

We will also try to address the issue of spin fluctuations in actinides where we believe the inclusion of these fluctuations will correct the ground state of numerous Pu and U systems where density functional theory failed to describe magnetism. In this case we will add spin orbital coupling and/or use full Dirac formalism to describe relativistic effects, which are crucial in 5f systems.

IV. Publications

[1] Consistent model of magnetism in ferropnictides. A. L. Wysocki, K. D. Belashchenko and V.P. Antropov, Nature Physics 7, 485–489 (2011), doi:10.1038/nphys1933.

[2] Effects of spin fluctuations and anomalous thermal expansion of δ-Pu. A. Solontsov and V. P. Antropov, Phys. Rev. B 81, 214402 (2010).

[3] The influence of quantum spin fluctuations on magnetic instability. V. P. Antropov and A. Solontsov, J. Appl. Phys. 109, 07E116 (2011).

[4] Non-linear spin fluctuations and phase transitions in itinerant electron magnets: CMR manganites. A. Solontsov, V.P. Antropov, J. of Magn. Magn. Mater. 324: 21, 3613-3614. Online publication date: 1-Oct-2012.

[5] Phenomenological model of longitudinal spin fluctuations in itinerant antiferromagnets A. Solontsov and V. P. Antropov, Phys. Rev. B 81, 104403 (2010).

[6] Quantum spin effects and magnetic short-range order above the Curie temperature R. Y. Gu and V. P. Antropov, Phys. Rev. B 80, 214405 (2009).

[7] Character of magnetic instabilities in $CaFe_2As_2$. G. D. Samolyuk and V. P. Antropov, Phys. Rev. B 79, 052505 (2009).

Integrated Modeling of Novel Materials

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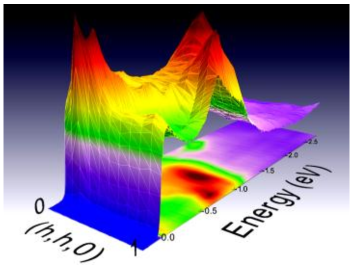
Project Scope

The overarching goal of the project is to provide an understanding of the fundamental physical processes that determine coupling between various degrees of freedom in correlated electronic materials and define nanoscale inhomogeneity as a result of competing interactions. We gain the new insights into physics of the correlated materials with the focus on competing interactions and their consequences as heterogeneities and short length scale domains. We analyze closely spaced energy levels (electronic, phononic, magnetic) belonging to two or more competing phases which interact. These ingredients can lead to ordinary phase transitions, emergent phases, and nanoscale phase separation or spontaneously generated hierarchical spatiotemporal patterns. The research direction is to understand first and then control the outcome of these competitions and to design their functionality Specific materials we choose to apply our methods to include pnictide superconductors, heavy fermion materials and cuprate superconductors.

Recent Progress

Progress has been focused on two areas. The main objective is to develop predictive theory for inhomogeneous states while retaining aspects of strong correlations. We are developing an approach to model effects of strong correlations within the class of hybrid models that would allow us to combine ab initio aspects with the more phenomenological strongly correlated models, see Methods Development below. In parallel, we are developing theory of novel (or in case of URu_2Si_2 old but unsolved mystery) orders that could capture tendencies for inhomogeneous domain structures in correlated matter. We also start to develop theory approach that allows us connect microscopic nanoscale in homogeneities with the macroscopic observables: resistivity, specific heat, thermal conductivity, NMR. Progress is organized around two themes, method developments and detailed studies that reflect our approach.

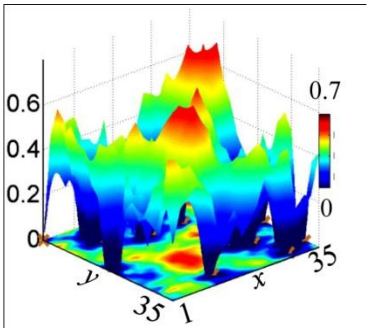


Single-particle spectral density map of a representative actinide system $UCoGa_5$

Methods Developments

- **Ab inito and effective models for strong correlations.** Debate about the significance of the strong correlations and their role in superconducting pairing in actinides and pnictides is ongoing. We have been working on implementing the approach to combine ab initio methods with effective low energy models where we apply strong coupling terms. Applications to a series of actinide systems (superconducting, magnetic or their variants) in the 115 family reveal good correspondence between theory and experiments, and also propose testable predictions. Our broad interest is to implement the approach to other classes of materials as different as cuprates, pnictides, two-dimensional electron gases. [T. Das, J.-X. Zhu, and M. J. Graf, “Spin fluctuations and peak-dip-hump in the photoemission spectrum of actinides.” Phys. Rev. Lett. **108**, 017001 (2012); T. Das, T. Durakiewicz, J. X. Zhu, J. J. Joyce, J. Sarrao, M. J. Graf, “Imaging the formation of high-energy dispersion anomaly in the actinide UCoGa$_5$”. Submitted to Phys. Rev. X (2012); arXiv: 1206.1302.]

- **Step 1: Parameter dependent band structure**. We use ab initio approach like LDA to develop band structure and eigenstates as a functions of parameter z that will parametrize local changes in inhomogeneous states. But at the first step this parameter is to be taken constant. The outcome of this step will be a set of LDA eigenfuctions and eigenvalues, we label as $\{\psi_n(r, z); E_n(z)\}$, n being the eigenvalue index.



Local variation of superfluid density in a non-uniformly distributed impurity concentration.

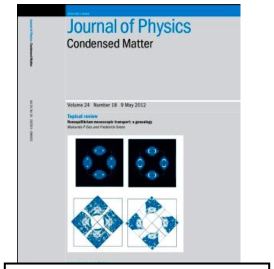
Detailed Studies

- **Fano Lineshape in Kondo hole systems.** To make a contact between local scale inhomogeneity and available characterization tools we have developed a local electronic structure theory in heavy-fermion systems in presence of disorder introduced by impurities, defects, or vacancies. Our theory is based on a minimal two-band Anderson lattice model with finite Coulomb repulsion on the f-orbitals. As an advantage, this model (i) captures both the heavy fermi liquid and Kondo insulator in the pristine system and (ii) a direct treatment of f-orbitals makes its connection to experimental observation more direct especially in the context of Fano lineshape. In particular, it was shown that the Fano lineshape near the Fermi energy is sensitive to the energy location of bound state. [Jian-Xin Zhu, Jean-Pierre Julien, Y. Dubi, and A. V. Balatsky, “Local Electronic Structure and Fan Interference into a Kondo Hole System, ,” Phys. Rev. Lett. **108**, 186401 (2012); E. Bauer et al, PNAS **108** Issue: 45 Pages: 18233-18237 (2011)]

- **Nanoscale Swiss Cheese Models.** We have calculated the superfluid density in PuCoGa5. We solve the Bogoliubov-de Gennes lattice model within the framework of the Swiss Cheese model to explain the aging dependence of the superconducting transition temperature, gap, and superfluid density. Since Pu is radioactive, it decays and creates disorder with time. This disorder is well described by the Swiss Cheese model of holes in the fabric of the unconventional superconductor PuCoGa5. We find good agreement between our Bogoliubov-de-Gennes lattice model calculations and muon-spin rotation measurements on samples 25-day and 400-day old by Ohishi and coworkers. [T. Das, J.-X. Zhu, M. J. Graf. ``Local suppression of the superfluid density of PuCoGa$_5$ in the Swiss Cheese model.” Phys. Rev. B **84**, 134510 (2011)]

- **Low Energy Models.** We have successfully developed low-energy effective models for some d-electron systems (typically for recently discovered iron-based superconductors). This type of models incorporates detailed crystal information from the band structure calculations by performing the tight-binding fitting. [Rong Yu, Jian-Xin Zhu, and Qimiao Si, “Mott Transition in Modulated Lattices and Parent Insulator of (K, Tl)$_y$Fe$_x$Se$_2$ Superconductors”, Phys. Rev. Lett. **106**, 186401 (2011)].

- **Nanoscale Swiss Cheese Models.** We started with the development of a general framework for strong disorder effects in short coherence length superconductors. In a first step, we developed a one-band Bogoliubov-de Gennes (BdG) lattice model within the scenario of the Swiss Cheese model to explain the aging dependence of the superconducting transition temperature, order parameter, and superfluid density in the unconventional superconductor $PuCoGa_5$. Since Pu is radioactive, it decays and creates disorder with time. The suppression of the superfluid density in $PuCoGa_5$ is much stronger than that of the transition temperature or the order parameter, similar to the high-temperature copper-oxide superconductors.



Our results are highlighted on the cover page of J. Phys.: Cond. Mat. in issue 18 (2012)

- **Pairing Symmetry.** The pairing symmetry of superconducting state has then been predicted and confirmed via experiments, within strong and weak coupling models, to be nodeless d-wave like in this newly discovered (K,Tl)Fe_xSe_2 superconductors. Sign-changing d-wave gap lends itself naturally to the sharp feature in neutron scattering spectrum, the so called spin resonance. [T. Das, and A. V. Balatsky, "Stripes, spin resonance and nodeless d-wave superconductivity in Fe_2Se_2-based layered superconductors", Phys. Rev. B **84**, 014521 (2011); *ibid.* "Modulated superconductivity due to vacancy and magnetic order in $A_x\mathrm{Fe}_{2-x/2}\mathrm{Se}_2$ [A=Cs, K, (Tl,Rb), (Tl,K)] iron-selenide superconductor", Phys. Rev. B **84**, 115117 (2011); *ibid.* Testing the sign-changing superconducting gap in the iron-based superconductors with quasiparticle interference and neutron scattering", J. Phys.: Cond. Mat. **24**, 182201 (2012).

- In a related but distinct effort, we focused **on global symmetry of the Hidden Order**. We are developing theory of hidden order as a hybridization wave where hybridization between Ru d and U f bands develops in a mean field fashion with the finite momentum transfer. D-f hybridized nature of the hidden order parameter seem to be consistent with the quasiparticle interference seen in STM and can explain gap like features seen in spectroscopies of URu_2Si_2 below 17K. [Yonatan Dubi and Alexander V. Balatsky, "Hybridization Wave as the "Hidden Order" in URu_2Si_2," Phys. Rev. Lett. **106**, 086401 (2011).] Success of the theory and ongoing experimental efforts represents a significant step forward toward the solution of the problem of "hidden orders" – e.g. pseudogap states, hidden order in URu_2Si_2, nematic order-- the orders that are unconventional and therefore hard to define with simple single particle spectroscopies.

Future Plans

- **Ab initio input for local band structure and real space inhomogeneity.** We will focus on understanding, characterization and simulation of novel properties of materials with nanoscale structure. The relative strengths of various interactions change as we move from the macroscale to the nanoscale. We continue to focus on two specific development of modeling and theory:
- First approach is to use a large enough unit cell in ab initio calculation that would capture at the level of very detailed band structure calculations the inhomogeneous modulated states.

This approach is computationally expensive and has not been attempted to date with the exception of simple two sublattice magnetic structures in antiferromagnetic materials where real space modulation is a simple two sublattice state.

- Another approach is to develop effective low energy model based on the inputs from realistic ab initio calculations and then use this low energy theory to design inhomogeneous models. Specifically, we plan use the following algorithm. Step 1 is a part of ongoing current investigation. Now we are looking at implementing:
  Step 2: Downfolding. In this step we will use downfolded effective bands that are relevant for the observables we are describing.

- **Hidden Order and Pseudogap in URu_2Si_2.** We plan to develop a model for the Hidden Order in in URu_2Si_2 that would allow for the precursor to emerge. For the long history of discussion on nature of the Hidden Order existence of the pseudogap seem to be overlooked. We will develop a phenomenological and microscopic model for the PG in URu_2Si_2.

- **Swiss Cheese models:** In the next step, we will generalize the one-band BdG lattice model to a multiorbital/multiband formulation relevant to a large class of iron-based high-temperature superconductors and heavy-fermion cerium- and plutonium-based superconductors in the presence of random and ordered defects, e.g., impurities vs. vacancy order.

Publications

Alpichshev Zhanybek; Biswas Rudro R.; Balatsky Alexander V.; et al., STM Imaging of Impurity Resonances on Bi2Se3, Phys. Rev. Lett **108** p 206402 (2012). DOI: 10.1103/PhysRevLett.108.206402

T. Das, J.-X. Zhu, M. J. Graf. ``Local suppression of the superfluid density of $PuCoGa_5$ in the Swiss Cheese model.*"* Phys. Rev. B **84**, 134510 (2011)

Zhu Jian-Xin; Julien Jean-Pierre; Dubi Y.; et al.
, Local Electronic Structure and Fano Interference in Tunneling into a Kondo Hole System
Phys. Rev. Lett **108** p 186401 (2012) DOI: 10.1103/PhysRevLett.108.186401

Haraldsen J. T.; Dubi Y.; Curro N. J.; et al., Hidden-order pseudogap in URu2Si2,
Phys. Rev. **B 84** p 214410 (2011), DOI: 10.1103/PhysRevB.84.214410

Hamidian Mohammad H.; Schmidt Andrew R.; Firmo Ines A.; et al.,
How Kondo-holes create intense nanoscale heavy-fermion hybridization disorder
PNAS **108** Issue: 45 Pages: 18233-18237 (2011) DOI: 10.1073/pnas.1115027108

Das Tanmoy; Balatsky A. V.
, Modulated superconductivity due to vacancy and magnetic order in A(y)Fe(2-x/2)Se(2) [A = Cs, K, (Tl,Rb), (Tl,K)] iron-selenide superconductors Phys. Rev. **B 84** p 115117 (2011), DOI: 10.1103/PhysRevB.84.115117

Bauer E. D.; Yang Yi-feng; Capan C.; et al., Electronic inhomogeneity in a Kondo lattice, PNAS Volume: **108** Pages: 6857-6861 , DOI: 10.1073/pnas.1103965108

Rong Yu, Jian-Xin Zhu, and Qimiao Si, "Mott Transition in Modulated Lattices and Parent Insulator of $(K,Tl)_yFe_xSe_2$ Superconductors", Phys. Rev. Lett. **106**, 186401 (2011)

Yonatan Dubi and Alexander V. Balatsky, "Hybridization Wave as the "Hidden Order" in URu_2Si_2," Phys. Rev. Lett. **106**, 086401 (2011).

Electronic Structure, Spectroscopy and Correlation Effects in Novel Materials

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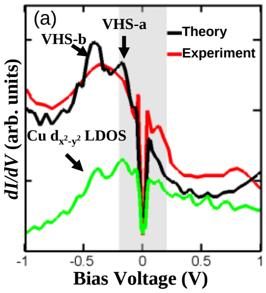
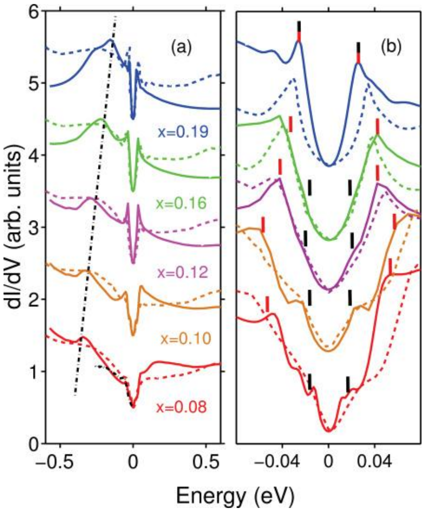
Project Scope

The present research project concerns theoretical studies of electronic structure, spectroscopic response, and correlation effects in a wide variety of novel materials of current interest. Our overarching goal is to undertake realistic modeling of various highly resolved spectroscopies of materials for providing discriminating tests of competing theoretical scenarios, and as a rational basis for future experimentation. We emphasize that spectroscopies do not provide a direct map of electronic states, but act as a complex 'filter' or 'mapping' of the underlying spectrum. This link between electronic states and the measured spectra—the 'matrix element effect'—is in general extremely complex, but a good understanding of this link is crucially important for fully exploiting various spectroscopies. Accordingly, we are working toward formulating and implementing increasingly sophisticated methodologies for making direct connection with angle resolved photoemission (ARPES), resonant inelastic x-ray scattering (RIXS), scanning tunneling microscopy/spectroscopy (STM/STS), magnetic and non-magnetic Compton scattering, and positron annihilation spectroscopies, including some work on neutron scattering and optical spectra. Specific systems considered are cuprates, pnictides, topological insulators, manganites, magnetite, and nano-particles. Although the LDA provides an important baseline, 'beyond LDA' schemes are invoked for modeling the underlying electronic spectrum in correlated materials in order to incorporate the physics of superconducting orders, pseudogaps, impurities and nanoscale heterogeneities, and how matrix element effects can enhance/suppress related signatures in various spectroscopies. The present project thus aims to help fill a critical gap in the available tools for understanding, analyzing and interpreting a wide range of spectroscopies in use today, and to obtain through direct comparisons between theory and experiment new insights into electron correlation effects, Fermi surfaces, magnetism and related issues.

Recent Progress

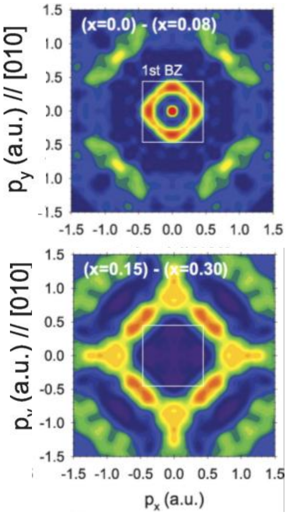
Tunneling Matrix Element, Asymmetries, Pseudogap, Two-gap Physics and Van-Hove Singularity in the Doping Dependent STS Spectra of Bi2212 [PRL 102, 037001 (2009); PRB 85, 214504 (2012)]: The figure compares the first realistic computation (black line) of the STS spectrum in overdoped Bi2212 with the corresponding experiments (red line), and shows that the striking asymmetry of the STS signal between high positive and negative bias voltages (not the low energy electron-hole asymmetry discussed below) arises from the way the electronic states in the cuprate layer couple to the tip to produce the tunneling current, and that with increasing negative bias voltage new tunneling channels associated with d(z^2) and other orbitals begin to open up and yield the large tunneling signal. The asymmetry of the tunneling signal at high energies can thus be understood naturally within the conventional picture without the need to invoke exotic mechanisms, and it cannot be taken as a signature of strong electronic correlations in the cuprates, contrary to what was thought to be the case previously. These results establish clearly that the STS spectrum in the cuprates is not a simple reflection of the LDOS of the Cu-d(x^2-y^2) band, but that it is modified strongly by the tunneling matrix element.



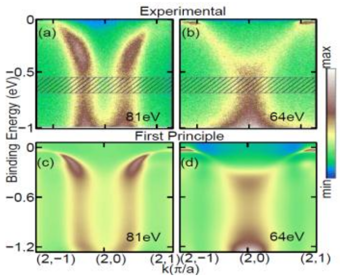


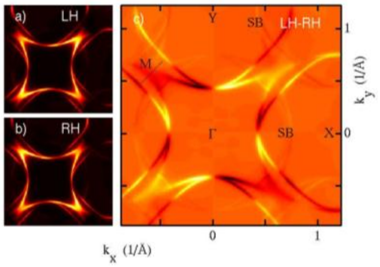
Recently, we have extended the preceding modeling to consider the full doping range. For this purpose, we include strong correlation effects through a GW scheme, which we have shown through analysis of various spectroscopies to produce viable self-energies in the cuprates within an intermediate coupling scenario. Pseudogap physics is modeled by introducing a (π,π) AFM order, which is perhaps the simplest model of the pseudogap as a competing order. The results comparing theory and experiment in the figure [solid lines are theory and dashed lines are experiment; panel (b) is a blow up of the low energy region in panel (a)] show a good overall accord at all dopings *x*. The theory reproduces two gaps and their doping evolution and the characteristic asymmetry of the coherence peaks with doping. The prominent hump in the theory around 200 meV at x=0.19, which moves to higher binding energies with underdoping is a VHS feature. Our study thus gives new insights into the complex role of the VHS in producing various features in the STS spectrum, and into the doping evolution of coherence peaks and the mechanism through which two different gaps emerge.

Doping Evolution of the Hole Wavefunction in La-Sr-Cu-O [Science 332, 698 (2011)]: Compton scattering provides a direct, bulk sensitive image of the electron momentum distribution in a solid. By taking differences between the 2D distributions so obtained as a function of doping, the wavefunction (in momentum space) of the doped hole can be imaged. The results so obtained for a hole in the underdoped system (upper panel) and in the overdoped system (lower panel) in the figure (reds are highs and blues are lows) are seen to differ dramatically. To understand these results, we carried out computations of the momentum density in LSCO using both the band theory framework and appropriate Cu-O clusters, allowing us to obtain key insights into the nature of the experimental spectra. The analysis shows that at low doping level (upper panel), the doped holes go mainly into O-sites, and the location of peaks and symmetry of the momentum density pattern is due to the expected Zhang-Rice singlet composed of Cu d(x^2-y^2) and O-p_x/p_y orbitals. In sharp contrast, in the overdoped system, the doped holes occupy Cu d(z^2) orbital as well, yielding the characteristic new pattern in momentum density where the peaks now occur at the corners of the Brillouin zone (white square). We thus establish clearly that a one-band model is not viable for describing the holes over the full doping range, and that a two-band picture must be invoked.



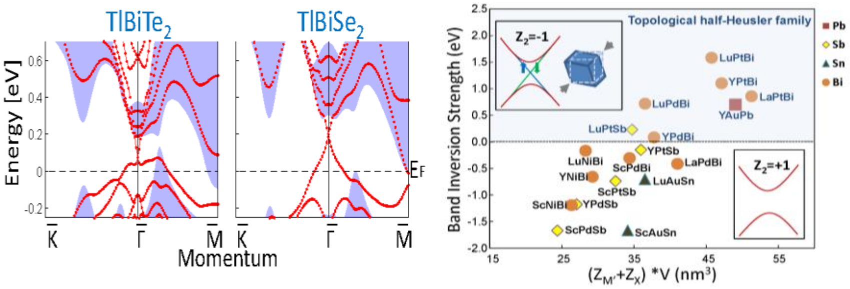
ARPES Spectra of Cuprates—Interplay of Self-energy, Matrix Element and Geometric Effects [PRL 103, 067005 (2009); PRB 80, 214520 (2009); PRL 105, 189702 (2010)]: The figure shows how matrix element and self-energy effects play out to produce quite remarkable manifestations of the high-energy kink or the waterfall effect in Bi2212 at different photon energies. In panel (a) the experimental spectrum has the appearance of a pair of 'waterfalls' with steep slope around 600 meV, while in panel (b) the same sample yields a 'Y-shaped' spectrum. This raises the natural question: Is the waterfall effect an intrinsic property of the electronic spectrum or is it an artifact of the ARPES matrix element? Our study settles this question directly by showing that even though the ARPES matrix element plays a substantial role in shaping the spectra, the experimental spectra cannot be understood without including self-energy effects. We thus establish clearly that the waterfall effect in ARPES is a genuine signature of the high-energy kink in the underlying electronic spectrum.





The figure here highlights another of our ARPES studies, which was designed to address the controversy surrounding the interpretation of the small dichroic signal (i.e. difference in photoemitted intensity for right- and left- circularly polarized light) that has been reported in experiments on Bi2212. The question is: To what extent is the observed dichroic effect a telltale signature of circulating current scenarios? The figure shows the expected dichroic signal in Bi2212 within the conventional band theory picture. The small orthorhombic distortion of the Bi-O plane in Bi2212 is found to be sufficient to more than explain the observed dichroic signals without the need to invoke exotic mechanisms. Our study also suggests that efforts to find support for circulating current scenarios through the measurement of dichroic effects in ARPES will be complicated by the masking effects of geometric mechanisms.

Predicting New Classes of Topological Insulators [PRL 105, 036404 (2010); Nature Materials 9, 546 (2010)]: We have predicted many new classes of topological insulators using more or less standard band theory approaches. As an example, the left panel shows band inversion in a new Tl-based system. Our theoretical prediction that topological phases can be harbored by the ternary Tl-based chalcogenides has since been experimentally verified. In this vein, the right panel shows results of our extensive study of the half-Heusler family, where compounds displaying band inversion at the Γ-point are in the upper half of the figure with Z_2= -1. These results indicate that the half-Heuslers present an exciting new platform for a host of topologically exotic compounds through the inherent flexibility of their lattice parameters, spin-orbit coupling strength, and the magnetic moment tunability, paving the way for the realization of multifunctional topological devices.



Planned activities

Highlights of ongoing/planned activities are: (1) Modeling/analysis of STS signatures of O-vacancies, interstitials, and Zn and Ni impurities in Bi2212 and Bi2201. (2) Modeling ARPES spectra in cuprates and pnictides where effects of superconductivity, pseudogap and kinks are included properly. (3) Analysis and modeling of the high resolution Compton scattering LSCO and NCCO datasets we have available to gain new insights into the doping dependencies of spectral weights, evolution of Fermi surfaces, and to identify possible spectral signatures of exotic physics. (4) Development/implementation of relativistic schemes for modeling STS and ARPES spectra of topological surface states. (5) First principles treatment of alloying effects in the pnictides using our KKR-CPA based approach. (6) Multi-band modeling of STS spectra in the pnictides. (7) Development / implementation of advanced schemes based on light scattering techniques for characterization of Li content and behavior in Li-battery materials. (8) Modeling of RIXS, XAS and XES spectra in complex materials, including work in the time-domain.

Selected Publications (Since 2009- from full list of 58 in Appendix)

1. V. Arpiainen, A. Bansil, and M. Lindroos: "Circular Dichroism in the Angle-Resolved Photoemission Spectrum of the High-Temperature $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductor: Can These Measurements Be Interpreted as Evidence for Time-Reversal Symmetry Breaking?" Phys. Rev. Lett. 103, 067005 (2009).
2. B. Barbiellini, A. Koizumi, P. E. Mijnarends, W. Al-Sawai, Hsin Lin, T. Nagao, K. Hirota, M. Itou, Y. Sakurai, and A. Bansil: "Role of Oxygen Electrons in the Metal-Insulator Transition in the Magnetoresistive Oxide $La_{2-2x}Sr_{1+2x}Mn_2O_7$ Probed by Compton Scattering", Phys. Rev. Lett. 102, 206402 (2009).

3. J. Nieminen, H. Lin, R. S. Markiewicz, A. Bansil: "Origin of Electron-Hole Asymmetry in Scanning Tunneling Spectrum of the High-Temperature $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductor", Phys. Rev. Lett. 102, 037001 (2009).
4. D. Hsieh, Y. Xia, D. Qian, L. Wray, F. Meier, J. H. Dil, J. Osterwalder, L. Patthey, V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan: "Observation of Time-Reversal-Protected Single-Dirac-Cone Topological-Insulator States in Bi_2Te_3 and Sb_2Te_3", Phys. Rev. Lett. 103, 146401 (2009).
5. D. Hsieh, Y. Xia, D. Qian, L. Wray, Dil, Meier, J. Osterwalder, L. Patthey, J. Checkelsky, N. Ong, A. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. Hor, R. Cava and M. Hasan: "A tunable topological insulator in the spin helical Dirac transport regime", Nature 460, 1101 (2009). Highlighted at News and Views: Nature 460, 1090 (2009).
6. Y. Xia, L. Wray, D. Qian, D. Hsieh, H. Lin, A. Bansil, D. Grauer, Y. Hor, R. J. Cava, M. Z. Hasan: "Observation of a large-gap topological-insulator class with a single surface Dirac cone", Nature Physics 5, 398 (2009); Highlighted at News and Views: Nature Physics 5, 378 (2009).
7. S. W. H. Eijt, P. E. Mijnarends, L. C. van Schaarenburg, A. J. Houtepen, D. Vanmaekelbergh, B. Barbiellini, and A. Bansil: "Electronic coupling of colloidal CdSe nanocrystals monitored by thin-film positron-electron momentum density methods", Appl. Phys. Letters 94, 091908 (2009).
8. M. Z. Hasan, H. Lin and A. Bansil: “Warping the cone on a topological insulator”, Physics 2, 108 (2009).
9. H. Lin, R Markiewicz, L.Wray, L. Fu, M.Hasan, A. Bansil, “Single-Dirac cone topological surface states in the $TlBiS_2$ class of topolgical insulators,” Phys. Rev. Lett. 105, 036404 (2010).
10. Hsin Lin, L.A. Wray, Y. Xia, S. Xu, S. Jia, R.J. Cava, A. Bansil, and M.Z. Hasan: “Half-Heusler ternary compounds as new multifunctional experimental platforms for topological quantum phenomena”, Nature Materials 9, 546 (2010).; Article highlighted in News and Views: Nature Materials 9, 536 (2010) and in Research Highlights: Nature Physics 6, 400 (2010).
11. L. A. Wray, S. Xu, Y.-Q. Xia, D. Qian, H. Lin, A. Bansil, Y.S. Hor, R.J. Cava, M.Z. Hasan: “Observation of topological-order in a superconducting doped topological insulator”, Nature Physics 6, 855 (2010).
12. Y. Okada, C. Dhital, Wenwen Zhou, Erik D. Huemiller, Hsin Lin, S. Basak, A. Bansil, Y.-B. Huang, H. Ding, Z. Wang, Stephen D. Wilson, and V. Madhavan, "Direct Observation of Broken Time-Reversal Symmetry on the Surface of a Magnetically Doped Topological Insulator ", Phys. Rev. Lett. 106, 206805 (2011).
13. Y. Sakurai, M. Itou, B. Barbiellini, P. E. Mijnarends, R. S. Markiewicz, S. Kaprzyk, J. -M. Gillet, S. Wakimoto, M. Fujita, S. Basak, Yung Jui Wang, W. Al-Sawai, H. Lin, A. Bansil, and K. Yamada, " Imaging Doped Holes in a Cuprate Superconductor with High-Resolution Compton Scattering ", Science 332, 698 (2011).
14. Su-Yang Xu, Y. Xia, L. A. Wray, S. Jia, J. H. Dil, F. Meier, J. Osterwalder, B. Slomski, A. Bansil, H. Lin, R. J. Cava, and M. Z. Hasan, " Topological Phase Transition and Texture Inversion in a Tunable Topological Insulator", Science 332, 560 (2011); Highlighted at Science 332, 546 (2011).
15. L. A. Wray, S. Y. Xu, Y. Q. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin and M. Z. Hasan, “A topological insulator surface under strong Coulomb, magnetic and disorder perturbations,” Nature Physics 7, 32 (2011); Highlighted at Nature Physics 7, 8 (2011).
16. J.T. Okada, P.H.Sit, Y. Watanabe, Y. Wang, B. Barbiellini, T. Ishikawa, M. Itou, Y. Sakurai, A. Bansil, R. Ishikawa, M. Hamaishi, T. Masaki, P. Paradis, K. Kimura, T. Ishikawa, S. Nanao, “Persistence of Covalent Bonding in Liquid Silicon Probed by Inelastic X-Ray Scattering,” Phys. Rev. Lett. 108, 067402 (2012).
17. Ilija Zeljkovic, Zhijun Xu, J. Wen, G. Gu, R. S. Markiewicz, and J. E. Hoffman, “Imaging the Impact of Single Oxygen Atoms on Superconducting $Bi_{2+y}\,Sr_{2-y}CaCu_2O_{8+x}$”, Science 337, 320 (2012).
18. Su-Yang Xu, M. Neupane, C. Liu, D. Zhang, A. Richardella, L. Wray, N. Alidoust, M. Leandersson, T. Balasubramanian, J. Sánchez-Barriga, O. Rader, G. Landolt, B. Slomski, J. H. Dil, J. Osterwalder, T-R. Chang, H-T. Jeng, H. Lin, A. Bansil, N. Samarth, and M. Z. Hasan, “Hedgehog spin texture and Berry’s phase tuning in a magnetic topological insulator,” Nature Physics, doi:10.1038/nphys2351 (2012).
19. T. H. Hsieh, Hsin Lin, J. Liu, W. Duan, A. Bansil and L. Fu: “Topological Crystalline Insulators in the SnTe Material Class,” Nature Communications, doi:10.1038/ncomms1969 (2012).
20. X. Liu, J. Liu, R. Qiao, Y. Yu, H. Li, L. Suo, Y-S Hu, Y-D Chuang, G. Shu, F. Chou, T-C Weng, D. Nordlund, D. Sokaras, Y. J. Wang, H. Lin, B. Barbiellini, A. Bansil, X. Song, Z. Liu, S. Yan, G. Liu, S. Qiao, T. J. Richardson, D. Prendergast, Z. Hussain, F. M. F. de Groot, W. Yang: “Phase Transformation and Lithiation Effect on Electronic Structure of Li_xFePO_4,” J. Am. Chem. Soc. (2012).

Quantum Phase Transitions in Nanosystems: Wires, Dots, and Dissipation

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project start date: September 1, 2010

Project Scope

Electron-electron interactions cause a variety of quantum phase transitions (QPT) in nanoscale systems; the control and engineering possible experimentally in such systems then allows the QPT to be probed and manipulated in detail in both equilibrium and non-equilibrium contexts. The research in this program addresses such QPT in several settings; the focus is on quasi-one-dimensional (quasi-1D) quantum wires and quantum dots connected to an environment.

In a quasi-1D wire, the positional order of the electrons can vary from extended liquid-like to localized Wigner-crystal-like. In this part of the program, we use quantum Monte Carlo (QMC) techniques to study the nature of the ground state wavefunctions (collaborator: C. Umrigar, Cornell). Within the localized regime, symmetry about the axis of the wire can be broken, and we study the QPT from a linear arrangement to a zigzag phase. In an inhomogeneous wire, we look at the interface between a liquid-like and crystal-like region of relevance to the “0.7 anomaly”.

Quantum dots connected to leads and reservoirs lead to QPT in a variety of situations. For example, we study a quantum dot containing a resonant level connected to dissipative leads. The dissipation in the leads generates an effective Luttinger-liquid-like interaction between the electrons. We study the quantum phase transition as the system is tuned through symmetric coupling by mapping the problem onto a resonant Majorana level.

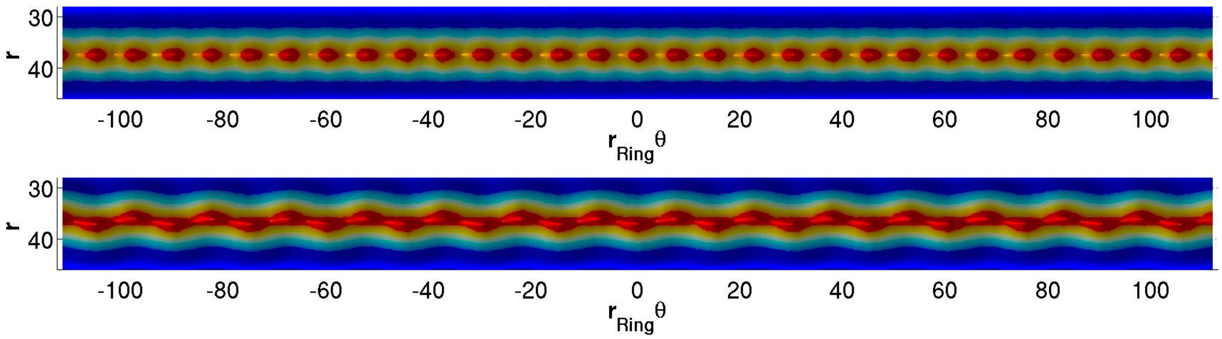
Recent Progress

Linear to Zigzag QPT in Quasi-1D Wires

A model QPT occurs in quasi-1D wires in the regime of low electron density where electrons are localized: at the lowest densities, the electrons form a linear chain in the wire, but as the density increases (but still in the localized regime) symmetry about the axis is spontaneously broken and a zigzag configuration occurs. Previous theoretical work has studied this Ising-like transition in the analytically accessible regimes [1].

We use Quantum Monte Carlo (QMC) techniques to study this QPT in the full range of densities relevant to experiment [2] (with A. Mehta and C. Umrigar). We take Coulomb-interacting electrons with harmonic confinement in the transverse direction; in the longitudinal direction we use either periodic boundary conditions or a ring geometry. A zero temperature wave-function based QMC technique is used: variational Monte Carlo followed by diffusion Monte Carlo in the fixed-node approximation.

The zigzag transition is clearly seen—Fig. 1—directly in the density and pair-density. By using a measure of the amplitude of the zigzag, we see that the transition is sharp. For tighter transverse confinement, the zigzag transition moves to higher density, and eventually is precluded by the transition to extended electrons. The number of gapless modes available should provide a signature of this competition and is currently under study.



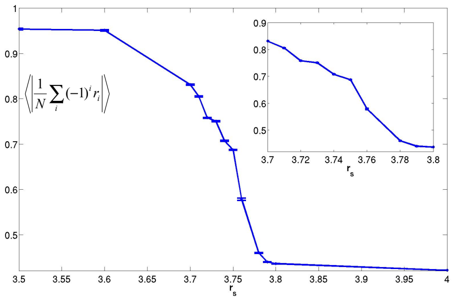


FIG. 1. **Linear to zigzag transition of electrons in a quasi-1D wire.** System: 30 electrons with parabolic transverse confinement ($\omega = 0.1$); ring geometry. Upper panels show the density of electrons for two values of $r_s \equiv 1/2n$, 3.8 and 3.7; note the zigzag which develops at higher density. Left panel shows a "zigzag amplitude" as a function of r_s; note the sudden change in behavior for $r_s \approx 3.77$. For GaAs, the unit of length is 9.8 nm and that of energy is 11.9 meV. [with A. Mehta and C. Umrigar]

Tunable QPT in a Resonant Level Coupled to Interacting Leads

A recent experiment [pub. #5] created a system which emulates tunneling into a Luttinger liquid, by controlling the interaction of the tunneling electron with its environment. In conduction through a resonant level placed into this environment, classic power-law scaling was observed. A schematic of the system is shown in Fig. 2, which we analyze theoretically.

We show that several QPT exist in a model of a resonant level connected to a dissipative environment, transitions which emulate those found in interacting systems such as Luttinger liquids

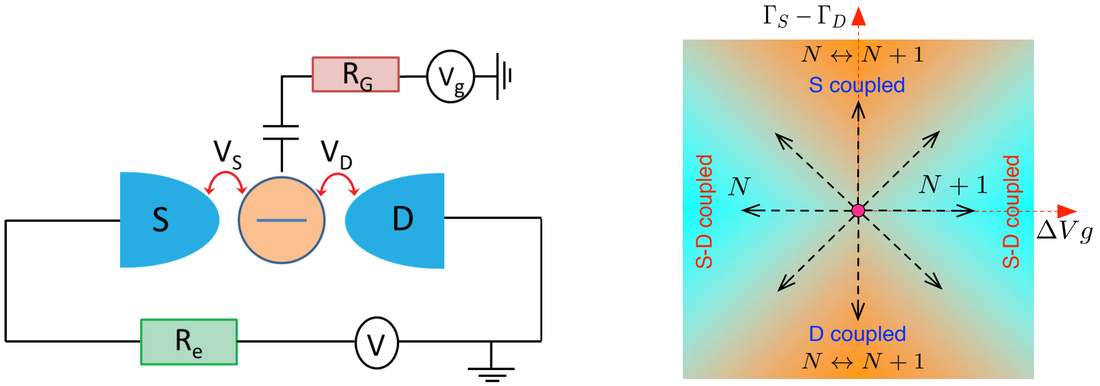


FIG. 2. **Resonant level with dissipative leads: QPT at symmetric coupling.** Left: Schematic of a resonant level coupled to a source, drain, and gate; dissipation is characterized by the two resistors R_e and R_G. Right: Phase diagram as function of energy of the resonant level (tuned by the gate, horizontal axis) and the asymmetry of the source and drain coupling (vertical). On resonance with symmetric coupling leads to competition between the S and D leads and so to a two-channel Kondo state but with interacting fermions. The conductance at the critical point is e^2/h; elsewhere it is 0. (with G. Finkelstein, D. Liu, H. Zheng, and H. Mebrahtu)

or Kondo systems. We study a double barrier resonant level coupled to two dissipative leads (source and drain) as well as to a dissipative gate. The electromagnetic environment couples both to tunneling processes that produce source-drain current and to fluctuations of the total charge of the dot. By using bosonization and unitary transformations, we map this dissipative resonant level model to a resonant level in a Luttinger liquid, being careful to show that the transport properties (current and conductance) of the two models are equivalent. Following methods for analyzing Luttinger liquids at both weak and strong coupling, we obtain the phase diagram. For strong dissipation, a Berezinsky-Kosterlitz-Thouless QPT separates strong-coupling and weak-coupling phases. In the source-drain symmetric case, all relevant backscattering processes disappear at strong coupling, leading to perfect transmission at zero temperature. In fact, a second order QPT occurs as a function of the coupling asymmetry: the two phases correspond to the resonant level merging with the right lead while the left lead decouples, and vice versa. At the critical point, the two leads compete, leading to two-channel Kondo type physics, which we model with a Majorana resonant level coupled to interacting leads.

Future Plans

Electron Localization in the Inhomogeneous Electron Gas: Quantum Point Contacts

As a model of quantum point contacts (QPC), we investigate the behavior of electrons in an inhomogeneous quasi-1D wire—one in which a short low density region is sandwiched between two high density regions. Electrons become strongly localized in the low density constriction region, and previous work has shown that a gap of zero density can open between the localized and liquid-like electrons in the system [3, 4]. We plan to investigate this phenomenon further, in particular the role of exchange-correlation in causing the gap and the possible implications for the “0.7 anomaly” seen experimentally in the conductance.

We model a QPC as a constriction in a quantum ring, and plan to use variational and diffusion Quantum Monte Carlo (QMC) calculations to investigate the effects of different point contact lengths and geometries on the electronic properties of the QPC. A preliminary result is shown in Fig. 3. As the height of the constriction potential increases, the electron density in the constriction decreases. For sufficiently high V_g, an integer number of electrons localize in the constriction. A gap forms in the density between the electrons in the leads and the localized electrons in the constriction, a gap which cannot be accounted for by electrostatics alone.

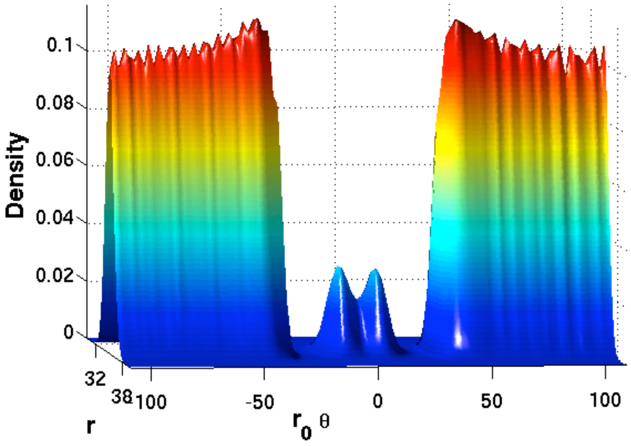


FIG. 3. **Localization in inhomogeneous electron gas.** Electron density as a function of position in a harmonically confined wire (ring) with a low density constriction region. System: $N = 42$ and $V_g = 0.8$. Note the gap that forms between the high-density leads and the 2 localized electrons. [with A. Mehta and C. Umrigar]

Dot+Dissipation: A Building Block for Quantum Simulation

We plan to further develop our collaboration with the experimental group of G. Finkelstein [pub. #5]. These results deepen the close link between effects produced by dissipation and those caused by electron-electron interactions established in earlier work [5]. This link is not surprising since dissipation connected to the electromagnetic environment is caused by electron charge interactions. Thus, coupling to dissipation can be used to emulate what happens in a strongly interacting electron system. Since the type of system we study is very flexible and can be extended, for instance, to several quantum dots connected in a variety of ways to leads and gates, this suggests the possibility of using dissipative systems as a quantum simulator of strongly correlated electronic phenomena.

As a first step, we plan further studies of a single quantum dot, but in the strongly dissipative regime and when the spin degree of freedom is not quenched by a magnetic field. This leads to interesting generalized two-channel Kondo physics.

Publications

1. "Kondo Effect and Mesoscopic Fluctuations," D. Ullmo, S. Burdin, D. E. Liu, and H. U. Baranger, *Pramana* **77**, 769 (2011).
2. "Detecting a Majorana-Fermion Zero Mode Using a Quantum Dot," D. E. Liu and H. U. Baranger, *Phys. Rev. B* **84**, 201308 (2011) [Rapid Comm.].
3. "From Weak- to Strong-Coupling Mesoscopic Fermi Liquids," D. E. Liu, S. Burdin, H. U. Baranger, and D. Ullmo, *EPL* **97**, 17006 (2012).
4. "Mesoscopic Anderson Box: Connecting Weak to Strong Coupling," D. E. Liu, S. Burdin, H. U. Baranger, and D. Ullmo, *Phys. Rev. B* **85**, 155455 (2012) [editor's suggestion].
5. "Quantum Phase Transition in a Resonant Level Coupled to Interacting Leads," H. T. Mebrahtu, I. V. Borzenets, D. E. Liu, H. Zheng, Y. V. Bomze, A. I. Smirnov, H. U. Baranger, and G. Finkelstein, *Nature*, in press (August 2 issue).

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[1] J. S. Meyer, K. A. Matveev, and A. I. Larkin, "Transition from a One-Dimensional to a Quasi-One-Dimensional State in Interacting Quantum Wires," Phys. Rev. Lett. **98**, 126404 (2007).

[2] L. W. Smith, W. K. Hew, K. J. Thomas, M. Pepper, I. Farrer, D. Anderson, G. A. C. Jones, and D. A. Ritchie, "Row coupling in an Interacting Quasi-One-Dimensional Quantum Wire Investigated Using Transport Measurements," Phys. Rev. B **80**, 041306 (2009).

[3] A. D. Gü cü, C. J. Umrigar, Hong Jiang, and H. U. Baranger, "Localization in an Inhomogeneous Quantum Wire," Phys. Rev. B **80**, 201302 (2009).

[4] E. Welander, I. I. Yakimenko, and K.-F. Berggren, "Localization of Electrons and Formation of Two-Dimensional Wigner Spin Lattices in a Special Cylindrical Semiconductor Stripe," Phys. Rev. B **82**, 073307 (2010).

[5] I. Safi and H. Saleur, "One-Channel Conductor in an Ohmic Environment: Mapping to a Tomonaga-Luttinger Liquid and Full Counting Statistics," Phys. Rev. Lett. **93**, 126602 (2004).

Properties of multiferroic nanostructures from first principles

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Project scope:

Multiferroics are materials that can simultaneously possess ferroelectricity (that is, a spontaneous electrical polarization that can be switched by applying an electric field) and magnetic ordering. Such class of compounds exhibits a magnetoelectric (ME) coupling that is of high technological relevance, since it implies that electrical properties are affected by a magnetic field or, conversely, that magnetic properties can be varied by an electric field.

While multiferroics, *in their bulk and (thick) film forms*, have been intensively studied, little is currently known and/or deeply understood about multiferroic *nanostructures* -- e.g., ultrathin films, wires, nanotubes, and three-dimensionally confined multiferroic nanodots. This, despite their technological promise in tuning towards a desired behavior that is not always achievable in a bulk-like material and despite their fundamental promise in yielding novel, exciting effects.

The broad objectives of this award are to gain a deep understanding of multiferroic nanostructures, in general, and to reveal original, exciting phenomena in low-dimensional multiferroics, in particular.

Recent progress:

To achieve these objectives, several research projects on multiferroic nanostructures have been conducted (and are currently conducted) by developing and/or using state-of-the-art techniques from first principles. Collaborations with internationally-recognized groups, including DOE scientists, having vital experimental programs in multiferroics are further strengthened, which allow us to ground our simulations and to fully, deeply understand the complex materials under investigation. It appears that our results are significantly enhancing the current understanding of multiferroics and nanostructures, by revealing their (anomalous) properties, identifying the microscopic features responsible for such properties, and by discovering new phenomena. For instance, we demonstrated strain-driven phase transition towards states with giant axial ratio and large out-of-plane polarization, and revealed dramatic enhancement of magnetoelectric coefficients near this transition, as well as the nearly simultaneous occurrence of a ferroelectric and a magnetic transition near room temperature in BiFeO3 (BFO) thin films. Thanks to DOE support, we also found counter-intuitive dependency of critical transition temperatures with the epitaxial strain and the existence of array of ferroelectric vortices in BFO thin films (both predictions were then experimentally confirmed). We also predicted other new phenomena. Examples include the occurrence of novel chiral states and a gyrotropic phase transition (for which optical activity spontaneously appears) in BFO films, as a result of the formation of interpenetrated arrays of ferroelectric vortices and antivortices. Conductivity was also found to be enhanced at the ferroelectric vortex cores in BiFeO3.

Future plans:

We now envision to develop computational schemes having unprecedented capabilities to (1) model and understand complex properties of multiferroics *solid solutions* (in their low-dimensional forms) and (2) design new multiferroic materials with optimal or original properties.

Many of such compounds and effects are expected to be modeled and studied. Examples include the development of an original method to predict *dynamical* properties of multiferroics, which will allow the investigation of electromagnons and the possibility of finding a material having a negative index of refraction; and the determination of the atomic ordering and/or composition yielding various optimized properties (e.g., piezoelectric and dielectric responses, magnetoelectric coefficients, etc...) in (Bi1-xRx)FeO3 alloys, where R is a rare-earth ion.

Publications:

- 1) ``Dependence of Curie temperature on the thickness of an ultrathin ferroelectric film," Emad Almahmoud, Igor Kornev and L. Bellaiche, Physical Review B 81, 064105 (2010).
- 2) ``Phase diagrams of epitaxial Pb(Zr,Ti)O3 ultrathin Films from first principles," David Sichuga, I. Ponomareva and L. Bellaiche, Physical Review B 80, 134116 (2009).
- 3) ``Low-symmetry phases and loss of relaxation in nanosized lead scandium niobate," J.M. Kiat, C. Bogicevic, F.Karolak, G. Dezanneau, N. Guiblin, W. Ren, L. Bellaiche, R. Haumont, Physical Review B 81, 144122 (2010).
- 4) ``Low-symmetry phases in ferroelectric nanowires," L. Louis, P. Gemeiner, I. Ponomareva, L. Bellaiche, G. Geneste, W. Ma, N. Setter, B. Dkhil, Nano Letters 10, 1177 (2010).
- 5) ``Ferromagnetism in multiferroic BiFeO3 films: a first-principles-based study," D. Albrecht, S. Lisenkov, Wei Ren, D. Rahmedov, Igor A. Kornev and L. Bellaiche, Physical Review B, Rapid Communications 81, 140401 (2010).
- 6) ``Diffuse Phase Transitions in Ferroelectric Ultrathin Films From First Principles," S. Bin-Omran, I. Kornev, I. Ponomareva and L. Bellaiche, Physical Review B 81, 094119 (2010).
- 7) ``Competing phases in BiFeO3 thin films under compressive epitaxial strain," B. Dupe, I. C. Infante, G. Geneste, P.-E. Janolin, M. Bibes, A. Barthelemy, S. Lisenkov, L. Bellaiche, S. Ravy and B. Dkhil, Physical Review B 81, 144128 (2010).
- 8) ``Chiral patterns of tilting of oxygen octahedra in zero-dimensional ferroelectrics and multiferroics: A first principle-based study," David Sichuga, Wei Ren, Sergey Prosandeev, and L. Bellaiche, Physical Review Letters 104, 207603 (2010).
- 9) ``Bridging multiferroic phase transitions by epitaxial strain in BiFeO3," I. C. Infante, S. Lisenkov, B. Dupe, M. Bibes, S. Fusil, E. Jacquet, G. Geneste, S. Petit, A. Courtial, J. Juraszek, L. Bellaiche, A. Barthelemy, and B. Dkhil, Physical Review Letters 105, 057601 (2010).
- 10) ``Size effects in multiferroic BiFeO3 nanodots," Wei Ren and L. Bellaiche, Physical Review B 82, 113403 (2010).
- 11) ``Kittel law in BiFeO3 ultrathin films: a first-principles-based study," S. Prosandeev, S. Lisenkov, and L. Bellaiche, Physical Review Letters 105, 147603 (2010).

- 12) ``Geometric frustration in compositionally modulated ferroelectrics,'' Narayani Choudhury, Laura Walizer, Sergey Lisenkov, L. Bellaiche, Nature 470, 513 (2011).
- 13) ``Lattice dynamics in Ba0.7Sr0.3TiO3: study by THz and IR spectroscopy and ab-initio simulations,'' T. Ostapchuk, J. Petzelt, P. Kuzel, M. Savinov, J. Hlinka, A. Tkach, P. Vilarinho, S Lisenkov, I. Ponomareva and L. Bellaiche, Phase Transitions 83, 955 (2010).
- 14) ``Dynamical Coupling in Pb(Zr,TiO3 Solid Solutions From First Principles,'' Dawei Wang, Jeevaka Weerasinghe, L. Bellaiche and Jirka Hlinka, Physical Review B, Rapid Communications 83, 020301 (2011).
- 15) ``Magnetoelectricity in BiFeO3 films: first-principles-based computations and phenomenology,'' S. Prosandeev, Igor A. Kornev and L. Bellaiche, Physical Review B, Rapid Communications 83, 020102 (2011).
- 16) ``Shape-induced phase transition of domain patterns in ferroelectric platelets,'' A. Schilling, S. Prosandeev, R.G.P. McQuaid, L. Bellaiche, J. F. Scott and J. M. Gregg, Physical Review B 84, 064110 (2011).
- 17) ``Epitaxial Pb(Zr,Ti)O3 Ultrathin Films under Open-Circuit Electrical Boundary conditions,'' David Sichuga and L. Bellaiche, Physical Review Letters 106, 196102 (2011).
- 18) ``BiFeO3 films under tensile epitaxial strain from first-principles,'' B. Dupe, S. Prosandeev, G. Geneste, B. Dkhil, and L. Bellaiche, Physical Review Letters 106, 237601 (2011).
- 19) ``Prediction of the Magnetotoroidic Effect from Atomistic Simulations,'' Wei Ren and L. Bellaiche, Physical Review Letters 107, 127202 (2011).
- 20) ``Enhanced electric conductivity at ferroelectric vortex cores in BiFeO3,'' N. Balke, B. Winchester, W. Ren, Y.H. Chu, A.N. Morozovska, E. Eliseev, M. Huijben, R.K. Vasudevan, V. Nagarajan, P. Maksymovych, J. Britson, S. Jesse, I. Kornev, R. Ramesh, L. Bellaiche, L.Q. Chen, and S. V. Kalinin, Nature Physics 8, 81 (2012).
- 21) ``Coexistence of ferroelectric triclinic phases in highly strained BiFeO3 films,'' Zuhuang Chen, S. Prosandeev, Z. L. Luo, Wei Ren, Yajun Qi, C. W. Huang, Lu You, C. Gao, I. A. Kornev, Tom Wu, Junling Wang, P. Yang, T. Sritharan, L. Bellaiche, and Lang Chen, Physical Review B 84, 094116 (2011).
- 22) ``Phase Transitions in Epitaxial (-110) BiFeO3 Films from First Principles,'' S. Prosandeev, Igor A. Kornev and L. Bellaiche, Physical Review Letters 107, 117602 (2011).
- 23) ``Multiferroic phase transition near room temperature in BiFeO3 films,'' I.C. Infante, J. Juraszek, S. Fusil, B. Dupe, P. Gemeiner, O. Dieguez, F. Pailloux, S. Jaouen, E. Jacquet, G. Geneste, J. Pacaud, J. Iniguez, L. Bellaiche, A. Barthelemy, B. Dkhil and M. Bibes, Physical Review Letters 107, 237601 (2011).
- 24) ``Fermi Resonance Involving Non-linear Dynamical Couplings in Pb(Zr,Ti)O3 Solid Solutions,'' Dawei Wang, E. Buixaderas, Jorge Iniguez, Jeevaka Weerasinghe, Hong Wang and L. Bellaiche, Physical Review Letters 107, 175502 (2011).
- 25) ``Giant surface charge density of graphene resolved from scanning tunneling microscopy and first-principles theory,'' P. Xu, Y. Yang, S.D. Barber, M.L. Ackerman, J.K. Schoelz, Igor A. Kornev, Salvador Barraza-Lopez, L. Bellaiche and P.M. Thibado, Physical Review B 84, 161409(R) (2011).

- 26) ``Giant direct magnetoelectric effect in strained multiferroic heterostructures," P.-E. Janolin, N. A. Pertsev, D. Sichuga and L. Bellaiche, Physical Review B, Rapid Communications 85, 140401 (2012).
- 27) ``Atomic control of strain in freestanding graphene," P. Xu, Y. Yang, S.D. Barber, M.L. Ackerman, J.K. Schoelz, D. Qi, Igor A. Kornev, L. Dong, L. Bellaiche, Salvador Barraza-Lopez, and P.M. Thibado, Physical Review B, Rapid Communications 85, 121406 (2012).
- 28) ``Properties of epitaxial (110) BaTiO3 films from first principles," Zhigang Gui, S. Prosandeev and L. Bellaiche, Physical Review B 84, 214112 (2011).
- 29) ``Finite-temperature flexoelectricity in ferroelectric thin films from first principles," I. Ponomareva, A.K. Tagantsev and L. Bellaiche, Physical Review B 85, 104101 (2012).
- 30) ``Domain structure and in-plane switching in a highly-strained Bi0.9Sm0.1FeO3 film," Weigang Chen, Wei Ren, Lu You, Yurong Yang, Zuhuang Chen, Yajun Qi, Xi Zou, Junling Wang, Thirumany Sritharan, Ping Yang, L. Bellaiche, and Lang Chen, Applied Physics Letters 99, 222904 (2011).
- 31) ``Low-frequency coupled modes in disordered Pb(Zr,Ti)O3 solid solutions from first principles," Jeevaka Weerasinghe, Dawei Wang and L. Bellaiche, Physical Review B 85, 014301 (2012).
- 32) ``A simple law governing coupled magnetic orders in perovskites," L. Bellaiche, Zhigang Gui and Igor A. Kornev, Journal of Physics Condensed Matter, Fast Track Communication 24, 312201(2012).
- 33) ``Strain dependence of polarization and piezoelectric response in epitaxial BiFeO3 thin films," C. Daumont, W. Ren, I.C. Infante, S. Lisenkov, J. Allibe, C. Carretero, S. Fusil, E. Jacquet, T. Bouvet, F. Bouamrane, S. Prosandeev, G. Geneste, B. Dkhil, L. Bellaiche, A. Barthelemy and M. Bibes, Journal of Physics Condensed Matter, Fast Track Communication 24, 162202 (2012).
-34) ``Domain evolution in epitaxial (001) Pb(Zr,Ti)O3 ultrathin films under an electric field applied along the [111] direction," D. Sichuga and L. Bellaiche, Physical Review B 85, 214111 (2012).
- 35) ``A pathway between Bernal and rhombohedral stacked graphene layers with scanning tunneling microscopy," P. Xu, Yurong Yang, D. Qi, S. D. Barber, M. L. Ackerman, J. K. Schoelz, T. B. Bothwell, Salvador Barraza-Lopez, L. Bellaiche, and P. M. Thibado, Applied Physics Letters 100, 201601 (2012).
- 36) ``Ab initio study of the factors affecting the ground state of rare-earth nickelates," Sergey Prosandeev, L. Bellaiche, and Jorge Iniguez, Physical Review B 85, 214431 (2012).
- 37) ``Finite-Temperature Properties of Ba(Zr,Ti)O3 Relaxors From First Principles," A. R. Akbarzadeh, S. Prosandeev, Eric J. Walter, A. Al-Barakaty and L. Bellaiche, Physical Review Letters 108, 257601 (2012).
- 38) ``Revisiting properties of ferroelectric and multiferroic thin films under tensile strain from first principles," Yurong Yang, Wei Ren, Massimiliano Stengel, X. H. Yan and L. Bellaiche, Physical Review Letters, in press (2012).
- 39) ``Magnetic cycloid of BiFeO3 from atomistic simulations," D. Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, Physical Review Letters, in press (2012).
- 40) ``Atomistic Molecular Dynamic Simulations of Multiferroics," Dawei Wang, Jeevaka Weerasinghe and L. Bellaiche, Physical Review Letters, in press (2012).

Theoretical Investigations of Nano and Bio Structures

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Project Scope

This grant addresses fundamental issues in nanoscale science and technology, namely the design of nano- and bio-inspired materials and processes with desired, novel characteristics. The research projects focus on several broad areas, including environmentally important enzymatic reactions, self-assembly mechanisms and structure evolution at surfaces, molecular devices and multi-terminal junctions with novel characteristics. Methodology development is an important part of the research, enabling large-scale simulations of solvated systems, evaluation of free-energy barriers, and calculations of quantum interference effects in electron transport. Our real-space multigrid method is capable of simulating the dynamics of systems containing thousands of atoms on DOE's leadership-class massively parallel supercomputers.

Recent Progress

Mechanistic Aspects of the Nitrogen Cycle: the Action of Copper Nitride Reductase

Copper nitrite reductase (CuNiR) is an enzyme that catalyzes an important step in denitrification, a process in which biologically bound nitrogen is released into the atmosphere as inert nitrogen gas. Human activity has increased the amount of bio-nitrogen via the use of Bosch-Haber process for production of fertilizers and by large-scale cultivation of nitrogen-fixing crops. Excess nitrogen causes many environmental problems, especially in aquatic ecosystems, such as harmful algal blooms and dead zones in the oceans. Denitrification is currently the only proven process for nitrogen removal from water and thus full understanding of the functioning of CuNiR as well as other enzymes involved in denitrification is of high importance.

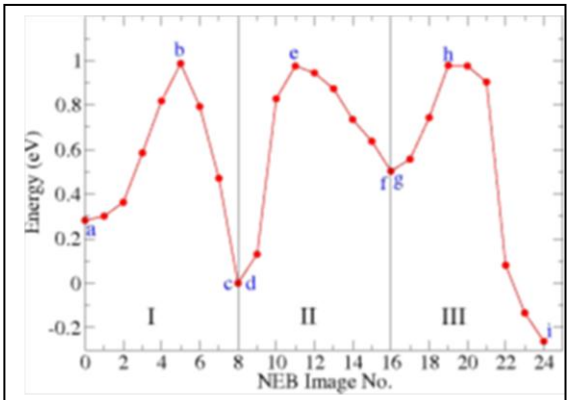

Fig. 1: Energy profile of enzymatic function of CuNiR. Panel I shows substrate (NO_2^-) attachment, II nitrite reduction and III represents removal of the product (NO).

CuNiR catalyzes conversion of NO_2^- to NO. In addition to its role in denitrification this enzyme is also being explored for use as a sensor for nitrite, a widespread pollutant found in food, water and physiological systems. CuNiR is organized as homotrimer with three identical monomers. It contains type I (T1) and II (T2) copper sites, which are connected via cysteine-histidine bridge. The nitrite reduction takes place at the T2 copper, while the T1 copper receives an electron necessary for the catalytic process. While the overall functioning of CuNiR is reasonably well understood, many important aspects of its action remain unknown. Some of them are the origin of two protons taking place in the reaction as well the role

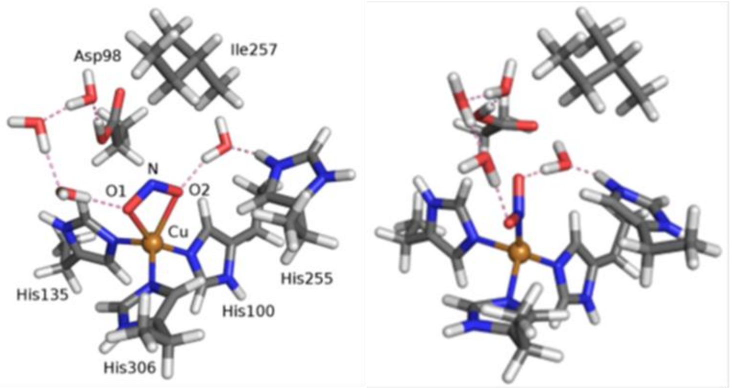

Fig. 2. Attachment of NO_2 before (left) and after (right) electron transfer. Dark grey is carbon, light grey is hydrogen, blue is nitrogen, oxygen is red and copper is gold.

of two experimentally observed features: conformational change of the critical residue Asp98 and the unusual “side-on” attachment of NO to the T2 copper, in which N and O are equidistant to the copper.

To resolve these issues we performed density-functional simulations of catalytic functioning of CuNiR. The nudged elastic band (NEB) technique was used to explore the enzymatic process, including the attachment of NO_2^- and the release of NO. The overall energy profile is displayed in Fig. 1. Our calculations show that the nitrite reduction process has the energy barrier of 0.94 eV, while the initial attachment and release have barriers of 0.70 and 0.47 eV, respectively. A critical step in the catalytic process is electron transfer from T1 copper, which changes the NO_2 attachment to the T2 copper from bidentate (via the oxygens) to monodentate via the nitrogen atom. The optimized structures before and after the electron transfer are shown in Fig 2.

Our calculations also find that the conformational change of Asp98, which was previously detected experimentally, has an important role in the enzymatic process, since it opens and closes the channel to the catalytic copper center. In the resting state, the channel is opened and upon substrate attachment the side chain of Asp98 rotates to close it. The side chain returns back to the open position during the reduction process, which brings it closer to the substrate. The Asp side chain then donates a proton to the substrate, leading to removal of one oxygen from NO_2 and the formation of NO. The open conformation of Asp98 then allows the product to be released and be replaced by a water molecule.

Molecular Self-Assembly on Metal Surfaces

In a joint experimental-theoretical effort with ORNL researchers, we are investigating molecular self-assembly and patterning on metal surfaces. Supramolecular engineering on well-defined surfaces provides access to a multitude of nanoscale architectures, including clusters of distinct symmetry and size. The underlying driving forces that lead to such self-assembled supramolecular structures generally involve both graphoepitaxy and weak directional non-convalent interactions. We show, for the first time, that the balance between very weak CH/π bonding among the ethyne groups of the phenylacetylene molecules and the molecule-surface interactions can enable robust supramolecular self-assembly of well-defined “magic” molecular clusters. The nature of the process is detailed from a corroboration of extensive STM/S and first principles density functional theory calculations that demonstrate cooperative, multi-center CH/π interactions as a dominant factor [9]. These interactions offer an attractive tunability via chemical functionalization and thus may allow new avenues towards rationally designing desired supramolecular shape and size.

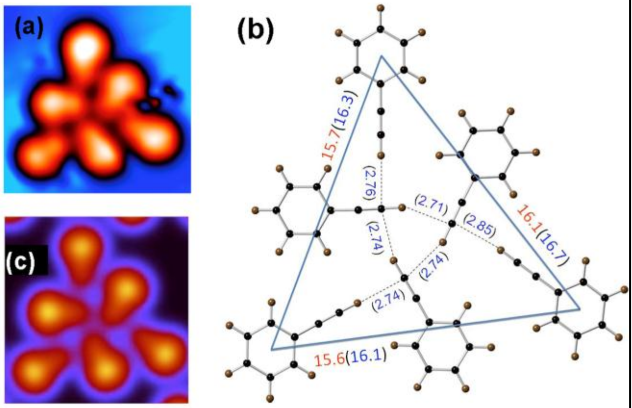

Fig. 3. High-resolution STM image of a hexamer and its calculated structure. (a) STM image. (b) Structural model for 2D-relaxed hexamer. Experimental distances are in red and calculated ones are in brackets. (c) Theoretical STM image for the fully relaxed hexamer on two layers of Au(111).

One of the outstanding paradigms of nanoscience is that of “magic” nanoparticles or molecular assemblies. Weak directional molecular forces are central to self-assembly in general, and are particularly important for the formation of supramolecular structures on surfaces because they provide a balance between intermolecular and molecule-surface interactions, as well as the feasibility of coordination shell saturation. Of the candidate attractive interactions, the hydrogen bonding is by far the most significant because, despite being weak (enthalpy varying from 3 to 7 kcal mol^{-1}) hydrogen bonding maintains well-defined directionality, in contrast to van-der-Waals and ionic interactions. The distinctive properties of the CH/π hydrogen bond are that it can operate in polar solvents and is highly cooperative, due to the ability of the CH/π fragments to act as both a Lewis acid and base.

The building blocks of our investigations are the phenylacetylene molecule and the Au(111) surface.

After low temperature deposition of ~0.1 ML, the molecules assemble themselves into largely disordered clusters within the fcc domains of the Au(111) surface. A surprising transformation occurs when the sample is post-annealed to ~ 120 K for 10 minutes. Most of the molecules on the surface rearrange into a single type of cluster with regular triangular shape and exactly six constituent phenylacetylene molecules, which we call a hexamer in the following.

The hydrogen atom of the ethyne group of each molecule within the hexamer points approximately toward the triple C≡C bond of a central molecule, implying the formation of a CH/π bond. However, although the relative angle between peripheral and central molecules matches the 90^o anticipated for CH/π bonding, that between the central molecules becomes 120^o.

Density functional calculations were performed for the phenylacetylene hexamer optimized over a two-layer slab of Au(111). The relaxed structure (Fig. 3(b)) is in very good agreement with the experimental observations and its size (the average distance between the centers of two peripheral molecules) of 16.4 Å likewise matches the experimental value of 15.8 ± 0.5 Å. Finally, the simulated STM image (Fig. 3(c)) of the hexamer on Au(111) also matches the experiment (Fig. 3(a)) very well. Our results suggest that the favorable formation of the hexamers is driven by a balance between CH/π and surface–molecule interactions. Both the directionality and multi-centricity of the CH/π bond appear to be critical for supramolecular self-assembly, and in fact this self-assembly would not take place in the case of mere van-der-Waals or electrostatic interactions. Z-V spectroscopy has further revealed that the electronic properties of the molecules are modified upon self-assembly, despite of the relatively weak intermolecular interactions. We envision that adding more acetylene groups to the phenyl ring will allow for additional structural flexibility and possibly tunable control over both the shape and the size of supramolecular assemblies, as well as the transition between supramolecular and extended self-assembled structures.

Future Plans

Some of the CuNiR calculations are still in progress and we are currently exploring the role of “side-on” attachment of NO, which has been the subject of several recent investigations. The studies of molecular self-assembly on surfaces are also continuing, and we are investigating the role of charge carrier injection and surface structure on molecular patterns.

As a new project, we plan to develop new methodology for ab initio simulation of atomic motion and reactivity in lithium ion batteries. These batteries are not only important for portable electronics, but are also being increasingly used in the new generation of electric cars. However, the current batteries have significant drawbacks, which include limited temperature range, short lifetime and restrictions on charge and discharge currents. Addressing those will require microscopic understanding of the functioning of these devices, which is currently lacking. At present, no consensus on the mechanism and energetics of Li ion solvation and diffusion in commonly used electrolytes, such as ethylene-carbonate (EC) or propylene carbonate (PC) exists. Almost all computer simulations performed to date have used force fields and yielded differing pictures of Li-ion solvation in carbonate solvents. The main factor hindering the use of *ab initio* approaches is the computational cost of describing the solvent, due to the high number of solvent molecules that need to be included for accurate description of solvation.

We have previously developed a method that enables accurate explicit solvation in *ab initio* calculations at only a small additional cost. This method combines the usual Kohn-Sham (KS) density functional theory (DFT) with orbital-free (OF) DFT, which is used to describe the solvent. The advantage of OF DFT is its low computational cost. Our work has demonstrated that OF DFT has sufficient accuracy, as compared to full KS DFT, to describe interactions between closed-shell water molecules, provided that their internal degrees of freedom are frozen. We have thus devised a multilevel embedding scheme in which the central region is described by KS DFT. This region is surrounded by an extended OF DFT region, in which OF DFT calculations are carried out. Our scheme works very well for simulating reactivity of solvated biomolecules, and we already used it to investigate Cu attachment to prion [2] and Parkinson's disease [7] proteins. We plan to employ a similar strategy for simulating Li diffusion in the electrolyte environment. Support for the proposed project also comes from our earlier simulation of Li diffusion in defected nanotubes, where we found that motion of Li could be described in OF DFT formalism.

Our initial work will focus on parameterizing the charge density of the electrolyte molecules. For water, a relatively simple description was sufficient, provided that it reproduced the overall charge, dipole moment and radial distribution functions (RDFs) of liquid water. In order to separate theoretical limitations from those introduced by parameterization, our initial tests will use superposition of KS-DFT-computed molecular charge densities to evaluate Li ion energetics in OF DFT fashion. If these tests are favorable we will develop a simplified parameterization and simulate the properties of small solvent clusters and their interactions with lithium. The OF DFT results will be compared to full KS DFT simulations.

Once sufficiently accurate models of OF DFT models of EC and PC are available, hybrid KS DFT/OF DFT calculations will be used to study key processes in Li ion battery functioning: Li ion diffusion in electrolyte and its intercalation and reaction with electrodes. The description of the graphite electrodes, which will use the full KS DFT, will require a van der Waals (vdW) corrected functional. For the oxide electrodes, a better description of correlation will be needed. It will first be pursued within the LDA+U formalism, which is straight-forward to implement in our codes.

Publications

1. "First-principles methodology for quantum transport in multiterminal junctions," K. K. Saha, W. Lu, J. Bernholc, V. Meunier, J. Chem. Phys. 131, 164105 (2009).
2. "Insights into prion protein function from atomistic simulations," M. Hodak and J. Bernholc, Prion 4, 13 (2010).
3. "Electron transport in multiterminal molecular devices: A density functional theory study," K. K. Saha, W. Lu, J. Bernholc, V. Meunier, Phys. Rev. B 81, 125420 (2010).
4. "Band gap control of small bundles of carbon nanotubes using applied electric fields: A density functional theory study," G. Kim, J. Bernholc, and Y.-K. Kwon, Appl. Phys. Lett. 97, 063113 (2010).
5. "Negative Differential Resistance in C60-Based Electronic Devices," X. Zheng, W. Lu, T. A. Abtew, V. Meunier, and J. Bernholc, ACS Nano 4, 7205 (2010).
6. "Quantum-Interference-Controlled Three-Terminal Molecular Transistors Based on a Single Ring-Shaped Molecule Connected to Graphene Nanoribbon Electrodes," K. K. Saha, B. K. Nikolic, V. Meunier, W. Lu, and J. Bernholc, Phys. Rev. Lett. 105, 236803 (2010).
7. "Mechanism of copper(II)-induced misfolding of Parkinson's disease protein," F. Rose, M. Hodak, and J. Bernholc, Nature Scientific Reports 1, 11 (2011).
8. "Hybrid quantum simulations of biomolecules: the role of copper in neurodegenerative diseases," J. Bernholc, M. Hodak, W. Lu, and F. Rose, Proceedings of the 2010 Scientific Discovery through Advanced Computing (SciDAC) Conference, pp. 12-22 (2011).
9. "Supramolecular Self-Assembly of π-conjugated Hydrocarbons via 2D Cooperative CH/π Interaction," Q.Li, C. Han, S. Horton, M. Fuentes-Cabrera, B. Sumpter, W. Lu, J. Bernholc, P. Maksymovych, M. Pan, ACS Nano 6, 566 (2012).
10. "A classical molecular dynamics investigation of the free energy and structure of short polyproline conformers", M. Moradi, V. Babin, C. Roland, and C. Sagui J. Chem. Phys. 133, 125104 (2010)
11. "Free energy and structure of polyproline peptides: An ab initio and classical molecular dynamics investigation", M. Moradi, J.-G. Lee, V. Babin, C. Roland, and C. Sagui, Int. J. Quant. Chem. 110, 2865 (2010).
12. "Recipes for free energy calculations in biomolecular systems", M. Moradi, V. Babin, C. Sagui, and C. Roland, in "Biomolecular Simulations: Methods and Protocols", Springer Verlag (Berlin, 2011).
13. "Calculating relative transition rates with driven nonequilibrium simulations", M. Moradi, C. Sagui, and C. Roland, Chem. Phys. Lett. 518, 109 (2011).
14. "Free energies, structural characteristics and transition mechanisms of proline-rich peptides", M. Moradi, V. Babin, C. Roland and C. Sagui, to appear in "In Proline: Biosynthesis , Regulation and Health Benefits" editor, L Stella Mottola (Nova Science Publications, 2012).

Internal Geometry, Stability and Design of Quantum Hall States

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Project Scope

Research in this program, carried out at three institutions in a synergistic fashion, aims at understanding the phase diagram of two-dimensional electrons in the fractional quantum Hall (FQH) regime, at a fundamental and deep level, leading towards the possibility of uncovering the Design Principles for FQH states. This involves the study of different types of Hamiltonians applicable to various two-dimensional materials, currently available, or possible in principle. Much of the current project uses numerical techniques as well as variational many-body wavefunction methods, in conjunction with fundamental theory to achieve the aforementioned goal. Because FQH states are characterized by an energy gap between the ground and excited states (unlike Fermi liquids), numerical approaches on finite size systems using different geometries are found to accurately represent thermodynamic systems. Highlights of the past year and a half have been – (i) a fundamental, new understanding of the role of geometry and anisotropy in the FQH regime; (ii) novel opportunities afforded by materials such as Graphene with Dirac-like spectrum; and (iii) understanding non-Abelian FQH states and quasiparticle tunneling. In addition, serendipitously, a new, hitherto unknown, singularity of the Anderson model of localization was discovered during a trial project with a beginning graduate student.

Recent Progress

Geometry of the FQHE

We uncovered the (previously unsuspected) importance of geometry in the FQHE. This leads to a new way of understanding the origin of FQHE incompressibility [1] in terms of the *shape* of the composite particle that forms a FQHE fluid. Thus, the Laughlin state is not a unique state, but a family of states related by a shear deformation, characterized by a true variational parameter given by a unimodular positive-definite symmetric metric tensor. Consequently, the gauge field to which electrons couple is a linear combination of the electromagnetic field and a geometric curvature gauge field. As a result, a direct incorporation of the collective (magneto-roton) excitation becomes central to phenomenological descriptions of the FQHE. This new approach leads towards a long-wavelength description of the FQHE that is an effective "quantum geometry" theory. A remarkable property of the structure factor S(q) is a duality between small and large q behavior where it is its own Fourier transform [2]. This is reminiscent of duality in quantum gravity theories, and allows several new interpretations, e.g. the long wavelength limit of the collective mode coincides with the short distance fusion of a quasiparticle with a quasihole [3], and is analogous to a graviton.

We investigated the effect of anisotropy (e.g. due to mass or dielectric tensor, or tilted magnetic field) on FQH states, in several numerical studies [4,5,6]. In [4], we used a variational scheme to determine the optimum metric for the Laughlin state in the n=0 Landau level, and performed numerical diagonalization for n=0 and 1 Landau levels to investigate transitions between incompressible and compressible, broken-symmetry states. In [5], we constructed anisotropic versions of Moore-Read and Read-Rezayi states as well, and applied it to cold atomic systems with anisotropic dipolar interactions. In [6], we investigated fast-rotating quasi-2D dipolar Fermi gases in the FQH regime.

New Materials: Tuning the FQH Hamiltonian

The discovery of graphene allowed access to a FQH system differing from conventional semiconductors in several ways, in particular, offering the possibility of tuning both the single particle band structure, and the two-body electron-electron interaction, and with it new possibilities for FQH states. Because the surface of graphene is exposed, unlike the electron gas buried deep inside a semiconductor structure, the e-e interactions can be controlled more substantially by dielectric/metallic screening. We numerically explored [6] the possibility of obtaining different FQH states (including the elusive non-Abelian states) and studied transitions between them. We then generalized the model to include multilayer graphene, including the effect of electric fields [7], and showed that this offers the possibility of in-situ tunability between several different FQH states, e.g. Laughlin and bubble states, or Moore-Read and chiral Fermi liquid states [8]. We also studied [9] the possibility of stabilizing the Read-Rezayi state (a candidate for universal quantum computation). A summary of the work was presented as an invited talk [10].

Another opportunity that graphene affords is the possibility of observing universal low energy behavior of chiral Luttinger liquids. Numerical calculations for graphene using a disc geometry [11] and contrasting it with GaAs-based 2D electron systems [12] show how the edge reconstruction in the semiconductor system can be avoided in graphene, and the underlying universal behavior recovered. A final project was an examination of the effects of the relativistic dispersion in graphene on the effects of e-e interactions vis-à-vis the Landau level splitting [13]; here again graphene allows *two* possibilities at high magnetic fields, unlike the 2D semiconductor counterpart.

Non-Abelian FQH States, and Miscellaneous Results

Non-Abelian FQH states are of great interest as potential candidates for quantum computation. Real systems break particle-hole symmetry due to Landau level mixing, neglected in most numerical studies. A comprehensive study [14] found that LL mixing favors the anti-Pfaffian state at filling $\nu = 5/2$. Calculations in the disc geometry [15] showed that Abelian and non-Abelian quasiparticles have very different tunneling properties, which could be used to distinguish between them in experiments. Bilayers at $\nu = 2/3$ filling was shown to be another potential system with non-Abelian states [16].

Other results include: (i) Hall viscosity and related quantities for the Laughlin and Moore-Read states [17]; (ii) Study of the connection between QHE wavefunctions and correlators of Conformal Field Theories [18]; (iii) Quantum Entanglement Spectrum of QH states, using cuts in real space [19]; (iv) Connection between QH fluids and type-I and II superconductors [20]; and (v) Discovery of a new singularity in the insulating phase of the Anderson model of localization [21].

Future Plans

In the near term, we plan to exploit our new understanding of the geometry of the FQH states to study several physical phenomena. These include:

(i) Effect of spatially inhomogeneous local electric fields (e.g. due to confining potential near edges);
(ii) Hall viscosity (i.e. the stress induced in the QH fluid by non-uniform flow occurring due to non-uniform electromagnetic fields) for multi-component anisotropic FQH systems;
(iii) Conductivity anisotropy in anisotropic QH systems
(iv) Extension of these ideas to compressible liquid states (e.g. at $\nu = ½$), where it might be easier to probe experimentally.

A second frontier of research involves extending numerical methods to larger system sizes using methods such as Density Matrix Renormalization Group. A preliminary exploration [22] shows that DMRG methods are severely restricted for spherical geometry, but may work much better in cylindrical geometry. We therefore plan to study this less-studied geometry in greater detail. If successful, these extensions would prove very useful for the study of the more fragile QH states as well as compressible states.

A third direction we plan to follow is the study of entanglement spectra using real-space cuts, which is turning out to be a powerful tool in determining the topological phase of the ground state of generic Hamiltonians, and is able to discriminate between states that are particle-hole conjugates.

Some other directions we have planned for further study are:

(i) QH phases with more complicated band structures;
(ii) Effect of subband crossing in semiconductor based 2D electron systems;
(iii) Spin and pseudospin structures & textures at QH edges in graphene multilayers;
(iv) Possible new QH phases in cold atom systems, methods for their detection, and interaction driven QH phase transitions.

List of Publications

[1] F. D. M. Haldane, "*Geometrical Description of the Fractional Quantum Hall Effect",* Physical Review Letters **107**, 116801 (2011).

[2] F. D. M. Haldane, *"Self-Duality and Long-Wavelength Behavior of the Landau-Level Guiding-Center Structure Function, and Shear Modulus of Quantum Hall Fluids",* arXiv:1201.0990.

[3] B. Yang, Z.-X. Hu, Z. Papic and F. D. M. Haldane, *“Model Wavefunctions for the Collective Modes and the Magneto-Roton Theory of the Fractional Quantum Hall Effect”,* Physical Review Letters **108**, 256807 (2012).

[4] B. Yang, Z. Papic, E. H. Rezayi, R. N. Bhatt and F. D. M. Haldane, *“Band Mass Anisotropy and the Intrinsic Metric of Fractional Quantum Hall Systems”,* Physical Review **B 85**, 165318 (2012).

[5] R.-Z. Qiu, F. D. M. Haldane, X. Wan, K. Yang and S. Yi, *“Model Anisotropic Quatum Hall States”*, Physical Review **B 85**, 115308 (2012).

[6] R. Z. Qiu, S.-P. Kou, Z. X. Hu X. Wan and S. Yi, *“Quantum Hall Effects in Fast-Rotating Fermi Gases with Anisotropic Dipolar Interaction”*, Physical Review **A 83,** 063633 (2011).

[7] Z. Papic, R. Thomale and D. A. Abanin, *“Tunable Interactions and Fractional Quantum Hall States in Graphene”,* Physical Review Letters **107**, 176602 (2011).

[8] Z. Papic, D. A. Abanin, Y. Barlas and R. N. Bhatt, *“Tunable Interactions and Phase Transitions in Dirac Materials in a Magnetic Field”,* Physical Review **B 84,** 241306 (2011) – Rapid Communication.

[9] D. A. Abanin, Z. Papic, Y. Barlas and R. N. Bhatt, *“Stability of the k=3 Read-Rezayi State in Chiral Two-Dimensional Systems with Tunable Interactions”,* New Journal of Physics **14**, 025009 (2012).

[10] Z. Papic, D. A. Abanin, Y. Barlas and R. N. Bhatt, *“Numerical Studies of the Fractional Quantum Hall Effect in Systems with Tunable Interactions”,* arXiv:1207.7282 (to appear in Proceedings of the Conference of Computational Physics CCP2011, Journal of Physics – Conference Series).

[11] Z.-X. Hu, R. N. Bhatt, X. Wan and K. Yang, *“Realizing Universal Edge Properties in Graphene Quantum Hall Liquids”,* Physical Review Letters **107**, 236806 (2011).

[12] Z.-X. Hu, R. N. Bhatt, X. Wan and K. Yang, *“Universal Edge Physics in Fractional Quantum Hall Liquids”,* arXiv1112.2167 (to appear in Proceedings of the Conference of Computational Physics CCP2011).

[13] Y. Zhang, Y. Barlas and K. Yang, *“Coulomb Impurity under Magnetic Field in Graphene: A Semiclassical Approach”*, arXiv:1201.3100

[14] E. H. Rezayi and S. H. Simon, *“Breaking of Particle-Hole Symmetry by Landau Level Mixing in the $\nu = 5/2$ Quantized Hall State”,* Physical Review Letters **106**, 116801 (2011).

[15] Z.-X. Hu, K. H. Lee, E. H. Rezayi, X. Wan and K. Yang, *“Scaling and Non-Abelian Signature in Fractional Quantum Hall Quasiparticle Tunneling Amplitude”,* New Journal of Physics **13**, 035020 (2011).

[16] E. Rezayi, X.-G. Wen and N. Read, *“Condensation of Fractional Excitations, Non-Abelian States in Double-Layer Quantum Hall Systems and Z4 Parafermions”,* arXiv1007.2022

[17] N. Read and E. Rezayi, *“Hall Viscosity, Orbital Spin and Geometry: Paired Superfluids and Quantum Hall Systems”,* Physical Review **B 84**, 0885316 (2011).

[18] S. H. Simon, E. H. Rezayi and N. Regnault, *“Quantum Hall Wavefunctions Based on S_3 Conformal Field Theories”,* Physical Review **B 81**, 121301 (2010).

[19] S. A. Parameswaran, S. A. Kivelson, E. H. Rezayi, S. H. Simon, S. L. Sondhi and B. Z. Spivak, *“Topology for Quantum Hall Liquids”,* Physical Review **B 85**, 241307 (2012) – Rapid Communication.

[20] J. Dubail, N. Read and E. H. Rezayi, *“Real-Space Entanglement Spectrum of Quantum Hall Systems”*, Physical Review **B 85**, 115321 (2012) – Editor’s Suggestion.

[21] S. Johri and R. N. Bhatt, *“Singular Behavior of Eigenstates in Anderson’s Model of Localization”,* Physical Review Letters (to be published August 10, 2012).

[22] Z.-X. Hu, Z. Papic, S. Johri, R. N. Bhatt and P. Schmitteckert, *“Comparison of Density Matrix renormalization Group Method Applied to Fractional Quantum Hall Systems in Different Geometries”,* arXiv:1202.4697

Surface Electromagnetic Phenomena in Pristine and Atomically Doped Carbon Nanotubes: Fundamentals and Applications

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Project Scope

This theoretical project addresses fundamentals and applications of electromagnetic interactions in quasi-one-dimensional carbon nanomaterials. Ultra-fast quantum processes in pristine and atomically doped carbon nanotubes are being explored in the near-field to learn how to control and reliably manipulate by surface atomic, photonic and excitonic states in these systems. The research program focuses on: (1)physical properties of surface exciton-plasmon resonance excitations in pristine single wall carbon nanotube systems; (2)properties of cavity polariton states in hybrid quantum systems composed of single wall carbon nanotubes doped with single atoms, or ions, or nanotubes coupled to semiconductor quantum dots; (3)exciton energy transfer in single wall carbon nanotube bundles/films, and their related optoelectronic properties. The emphasis is on getting a better understanding of underlying quantum phenomena and providing guidance for future experiments that might result in creation of new research subfields, such as carbon nanophotonics (as opposed to semiconductor nanophotonics) and carbon nanoplasmonics, focused on the development of a new generation of carbon based, high-yield, high-performance, tunable optoelectronic and sensory device components for use in solid state quantum information, quantum communication, energy conversion and storage technologies.

Recent Progress

(A.) Pristine Carbon Nanotubes

Optically excited excitons are theoretically demonstrated to generate and amplify surface plasmons in individual semiconducting carbon nanotubes. Surface plasmons are coherent charge density waves due to the periodic opposite-phase displacements of the electron shells with respect to the ion cores. Charge density waves produce oscillating electric fields concentrated locally throughout the nanotube surface. The entire process can be controlled by a perpendicular electrostatic field [Fig.1(a)]. Our theoretical research shows that the nonradiative exciton-to-plasmon energy transfer, whereby the external electromagnetic radiation absorbed to excite excitons transfers into the energy of surface plasmons, can efficiently mediate and greatly enhance the electromagnetic absorption by pristine semiconducting nanotubes. This enhancement is caused by the buildup of the macroscopic population numbers of coherent localized surface plasmons producing high-intensity local oscillating fields throughout the nanotube surface [Fig.1(b)]. The strong local coherent fields produced in this way can be used in various new technological applications of carbon nanotubes, such as near-field sensing, optical switching, electromagnetic energy conversion, and materials nanoscale modification. [see Figure 1; I.V.Bondarev, Physical Review B 85, 035448 (2012)]

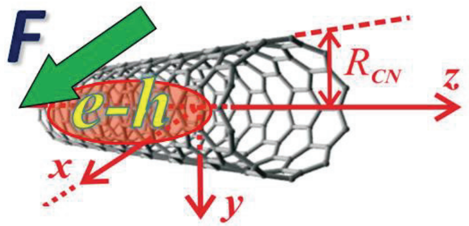
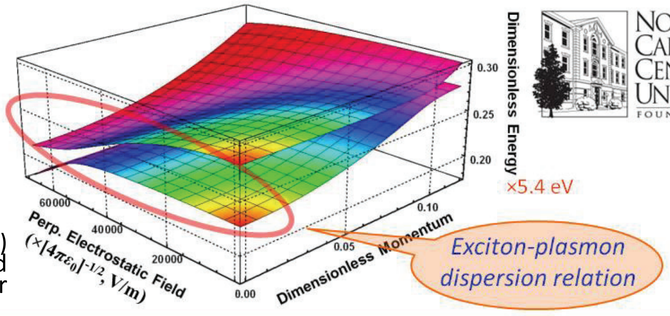


Fig. 1(a): Exciton-plasmon dispersion relation (right) as a function of a perpendicular electrostatic field applied (see above) and longitudinal momentum for the 1st bright exciton in the (11,0) nanotube.



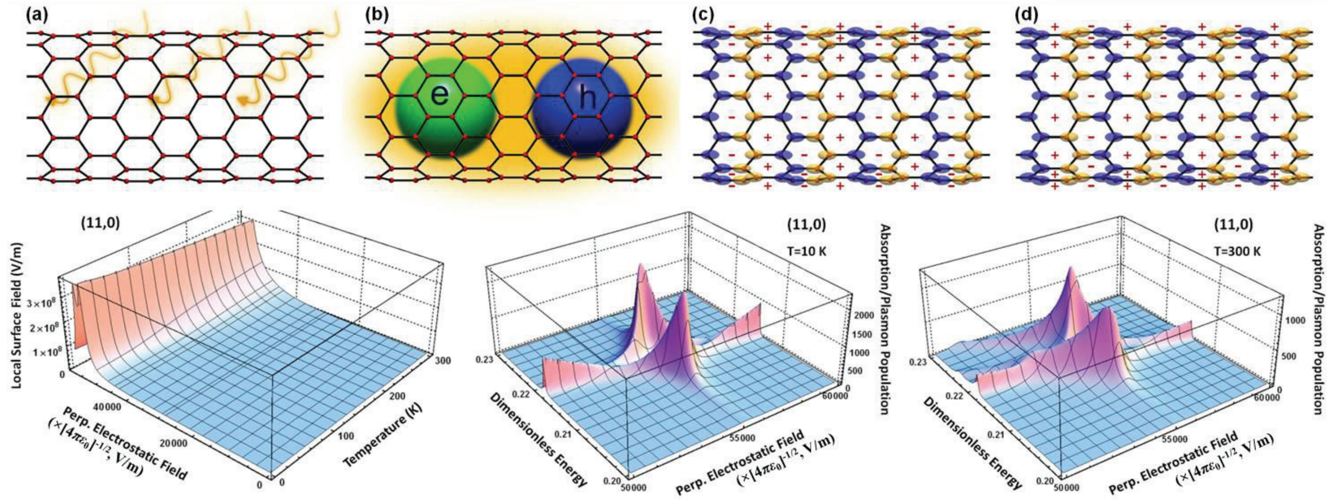
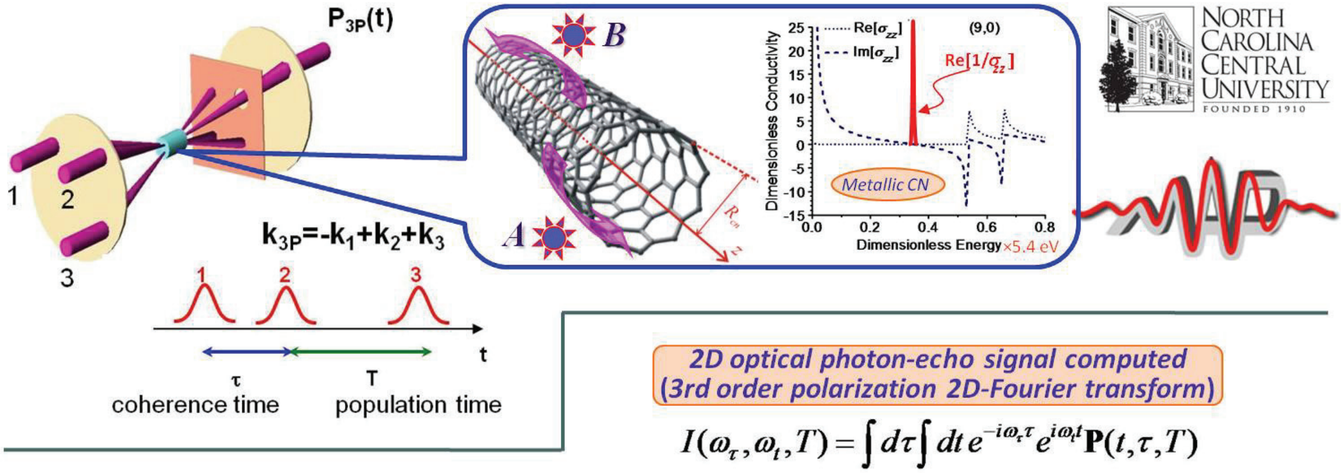


Fig. 1(b): Generation of plasmons by optically excited excitons in individual semiconducting carbon nanotubes (CNs). Calculations for the 1st bright exciton in the (11,0) CN. *Top row, left to right*: Schematic of the plasmon generation process by the optically excited exciton. (a),(b) Exciton excitation by the external electromagnetic radiation. (c),(d) Plasma oscillations (produced by the nonradiative exciton decay) are periodic opposite-phase displacements of the electron shells relative to the ion cores in the neighboring elementary cells (blue and yellow) of the nanotube. Such periodic displacements induce coherent oscillating electric fields (shown by + and − signs) of zero mean magnitude, but non-zero mean-square magnitude, concentrated locally across the nanotube diameter throughout the nanotube length. *Bottom row, left*: Local surface field amplitude as a function of temperature and perpendicular electrostatic field applied; *Middle and right*: Low-*T* and high-*T* plasmon population (also representing increased light absorption by excitons).

I.V.Bondarev, Phys. Rev. B 85, 035448 (2012)

(B.) Hybrid Carbon Nanotube Systems

Hybrid carbon nanotube systems, nanotubes containing extrinsic atomic type species (dopants) such as semiconductor quantum dots, extrinsic atoms, or ions, are promising candidates for the development of the new generation of tunable nanooptoelectronic devices — both application oriented, e.g., photovoltaic devices of improved light-harvesting efficiency, and devices for use in fundamental research including nanophotonics, nanoplasmonics, cavity quantum electrodynamics, and solid-state quantum information. Here, we have studied theoretically a pair of spatially separated two-level dipole emitters, two-level systems (TLS) to model the atomic type dopants mentioned above, in the regime where they are coupled strongly to a low-energy resonant surface electromagnetic mode (the plasmon resonance) of a metallic carbon nanotube. By explicit calculations of non-linear response signals, we show that the 2D photon-echo spectroscopy is a very sensitive tool for detecting and monitoring the bipartite TLS coherences and entanglement in such a hybrid quantum system. Specifically, the CN-assisted bipartite TLS entanglement can be identified unambiguously through the presence of the cross-peaks in the 2D photon-echo spectra. We analyze various experimental situations and formulate practical recommendations for the reliable experimental observation of this unique quantum phenomenon of relevance to the solid-state quantum information science. [see Figure 2; collaborative work with the Munich Advanced Photonics Center (MAP) @ TU-Munich, Germany; M.F.Gelin, I.V.Bondarev, and A.V.Meliksetyan, Chemical Physics Journal (Elsevier) Special Issue on Nanotube Photonics, *at print*]

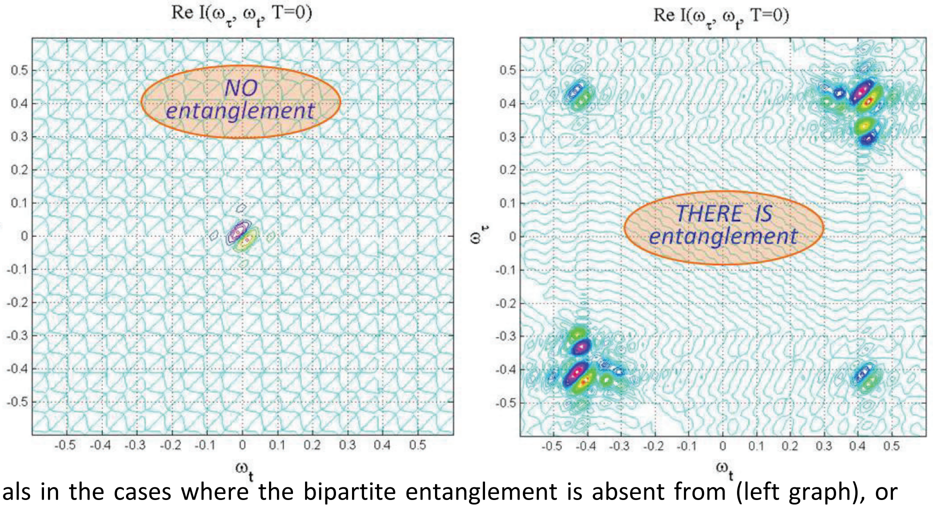


2D optical photon-echo signal computed (3rd order polarization 2D-Fourier transform)

$$I(\omega_\tau,\omega_t,T)=\int d\tau\int dt\, e^{-i\omega_\tau\tau}e^{i\omega_t t}\mathbf{P}(t,\tau,T)$$

Fig. 2: Calculations of the experimental 2D photon-echo signal for hybrid (atomically doped) metallic carbon nanotubes.

Top: Schematic of the optical 2D photon-echo spectroscopy experiment for the detection of the bipartite entanglement between the two spatially separated dipole emitters *A* and *B*, which may be a pair of atoms, ions, or quantum dots, coupled to the same surface plasmon resonance mode of a metallic carbon nanotube (sketch shown in the inset).



Right: 2D optical photon-echo signals in the cases where the bipartite entanglement is absent from (left graph), or present in (right graph) the system. The presence of the cross-peaks on the right panel indicates that the distant dipole emitters are coupled strongly to the same CN surface plasmon resonance and 'talk to each other' via the virtual plasmon exchange, being entangled.

M.F.Gelin, I.V.Bondarev & A.V.Meliksetyan,
Chem. Phys. Special Issue on Nanotube Photonics, at print

Planned activities: 2012-2013

For the second year of this project, we plan to continue our established collaborations with MAP @ TU-Munich, Germany (Maxim Gelin & Wolfgang Domcke) and USF-Tampa, USA (Lilia Woods). A new collaboration is under way with the University College London (UCL), UK (Janet Anders, quantum information theory) to strengthen the quantum information aspect of our research with nanotubes. The activities will be going as follows:

(1.) Quantum theory of exciton energy transfer in single wall carbon nanotube bundles/films, and their related optoelectronic properties, with the emphasis on the controlled absorption, energy conversion and storage applications of nanotube composite materials.
(2.) Quantum electrodynamics of Surface Enhanced Raman Scattering (SERS) by trapped molecules near carbon nanotubes — to take advantage of strong local-field enhancement effect near carbon nanotubes for single-molecule optical sensing.
(3.) Analysis of quantum entanglement in strongly coupled exciton-plasmon excitations and possibility for their Bose-condensation in individual CNs. [*in collaboration with UCL, UK*]
(4.) Theory development for non-linear optical experimental techniques, such as 2D photon-echo spectroscopy and optical double-coherence spectroscopy, for non-linear optical monitoring of near-field quantum effects in pristine (excitons/biexcitons) and hybrid (atoms, ions, quantum dots) CN systems. [*in collaboration with MAP @ TU-Munich, Germany*]
(5.) Computational modeling program code improvement to include: (i)effects of trigonal warping on exciton energies in individual single wall CNs, and (ii)exciton re-scattering effect between constituent tubules in multi-wall nanotube combinations. These improvements are needed, in order to be able to reliably simulate excitonic response spectra of smaller diameter CNs (less than, or ~1 nm), including multi-wall carbon nanotubes. [*in collaboration with USF-Tampa, USA*]

Publications

(1.) I. V. Bondarev, "Single wall carbon nanotubes as coherent plasmon generators"
Physical Review B 85, 035448, (2012).

(2.) I. V. Bondarev, M. F. Gelin, and W. Domcke, "Plasmon nanooptics with pristine and hybrid nanotube systems"
Bulletin of the American Physical Society, Vol. 57, No 1, p. V6.00002.

(3.) I. V. Bondarev and T. Antonijevic, "Plasmon generation by excitons in carbon nanotubes"
Proceedings of the Nanotech 2012 Conference, Vol.1, p. 334.

(4.) I. V. Bondarev, "Nanotube plasmonics"
In: International Conference ”Spins & Photonics Beams at Interface” (September 25–26, 2011, Minsk, Belarus). Book of abstracts, p. 19.

(5.) M. F. Gelin, I. V. Bondarev, and A. V. Meliksetyan, "Monitoring bipartite entanglement in hybrid carbon nanotube systems via optical 2D photon-echo spectroscopy"
Chemical Physics (Elsevier), Special Issue on Photophysics of Carbon Nanotubes and Nanotube Composites, *at print*.

(6.) L. M. Woods, A. Popescu, D. Drosdoff, and I. V. Bondarev, "Dispersive interactions in graphitic nanostructures"
Chemical Physics (Elsevier), Special Issue on Photophysics of Carbon Nanotubes and Nanotube Composites, *at print*.

(7.) I.V.Bondarev, M.F.Gelin, and W.Domcke, "Plasmon nanooptics with individual carbon nanotubes",
Journal of Physics: Conference Series (Dubna-Nano2012 Proceedings), *submitted.*

Correlated Electrons in Reduced Dimensions.

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Project Scope

The study of the quantum Hall effect — a phenomenon which occurs when a two-dimensional electron gas (2DEG) is placed in a strong magnetic field and cooled to ultra low temperatures — continues to provide fundamental insights into the remarkable variety of order possible in strongly correlated quantum systems. For example, the fractional quantum Hall state observed at Landau-level filling fraction $\nu = 5/2$ is conjectured to possess so-called "non-Abelian" order. In states with such order, quasiparticle excitations are characterized by quantum numbers similar to ordinary spin quantum numbers but which, unlike ordinary spin, cannot be distinguished by local measurements. The Hilbert space describing such quasiparticles has a built in resistance to decoherence, and for this reason non-Abelian states have been proposed as ideal physical media for realizing an intrinsically fault-tolerant form of quantum computation (so-called topological quantum computation) which would be carried out by "braiding" the world-lines of quasiparticles in 2+1 dimensional space-time. Another quantum Hall system of current interest is the bilayer $\nu = 1$ system which consists of two parallel 2DEGs each with $\nu = 1/2$. This system exhibits a still poorly understood transition from an incompressible quantum Hall state for small layer spacing to a compressible Fermi liquid of "composite fermions" (electrons bound to two flux quanta) for large layer spacing. This project has focused on the theoretical study of non-Abelian states such as the $\nu = 5/2$ state, addressing in particular how, precisely, one would use such states to carry out topological quantum computation, as well as the possible phases associated with both regular and disordered arrays of "interacting" non-Abelian quasiparticles. In addition, the effects of the strong Chern-Simons gauge fluctuations associated with the composite fermion description of the bilayer $\nu = 1$ state (valid for large layer spacing) on the possible instabilities of that state as the layer spacing is decreased are being studied. Finally, work is being done in the rapidly developing area of "surface codes." Here the essential idea is to use the remarkable properties of topologically ordered matter to carry out fault-tolerant quantum computation using more "conventional" qubits (e.g. superconducting qubits, trapped ions, electron spins in quantum dots, etc.) — an approach which has been shown to have significantly less stringent requirements on qubit coherence and gate accuracy than previous fault-tolerant quantum computation schemes. Particular emphasis is being placed on proposing experiments which can be feasibly carried out today using existing qubit systems and which begin to probe the requirements for carrying out quantum computation using the various known surface codes.

Recent Progress

Valence-Bond Entanglement and Fluctuations in Random Singlet Phases.

The ground state of the uniform antiferromagnetic spin-1/2 Heisenberg chain can be viewed as a strongly fluctuating liquid of valence bonds, while in disordered chains these bonds lock into random singlet states on long-length scales. We have developed a novel method for studying this phenomenon numerically, even in the case of weak disorder, by calculating the mean value of the number of valence bonds leaving a block of L contiguous spins (n_L, the so-called valence-

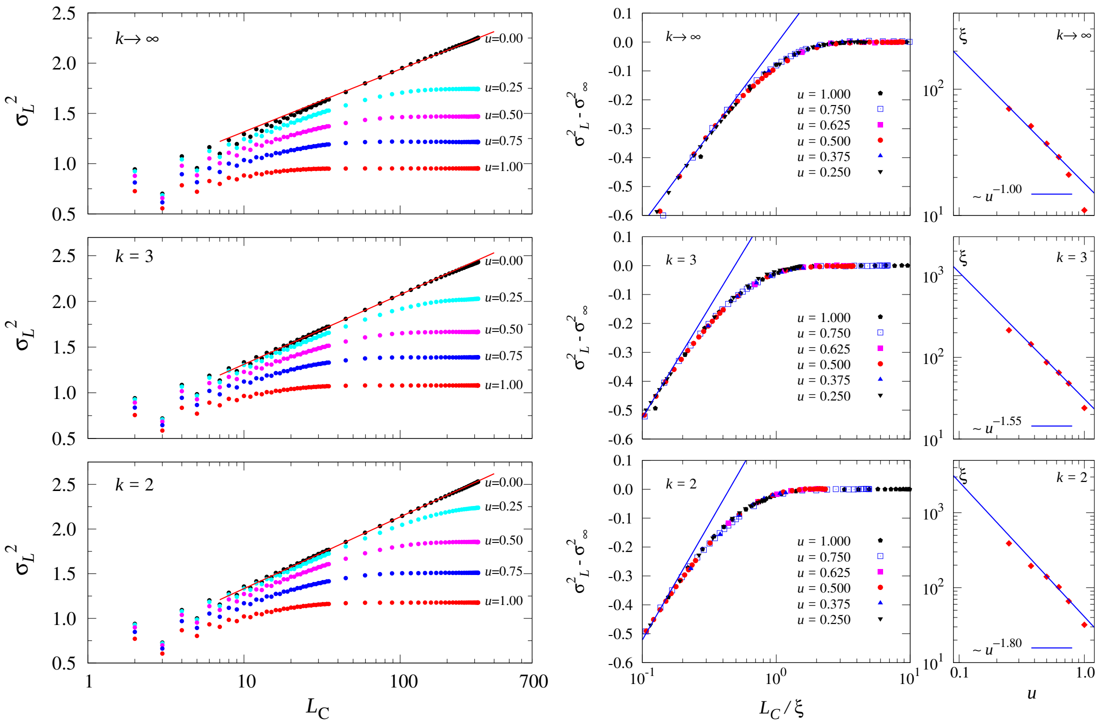

FIG. 1: (Left Column) Log-linear plots of valence-bond fluctuations as a function of conformal distance $L_C = (N/\pi)\sin(L\pi/N)$, for both uniform and random chains for the spin-1/2 Heisenberg chain, (labeled $k \to \infty$ — upper panel), the "golden" chain (labeled $k = 3$ — middle panel) and critical transverse-field Ising model (labeled $k = 2$ — lower panel). (Middle Column) Scaling plots of the valence-bond fluctuations (with the saturation value σ^2_∞ subtracted out), $\sigma^2_L - \sigma^2_\infty$, for $k \to \infty$ (Heisenberg chain), $k = 3$ ("golden" chain), and $k = 2$ (critical transverse-field Ising model) and various disorder strengths u. (Right Column) Log-log plots of the crossover length scale ξ as a function of u for $k \to \infty$, $k = 3$, and $k = 2$.

bond entanglement entropy) as well as the fluctuations in this number (σ^2_L). The fluctuations are particularly useful for studying random singlet state formation. They show a clear crossover from a small L regime, in which they behave similar to those of the uniform model, to a large L regime in which they saturate in a way consistent with the formation of a random singlet state on long length scales.

We have performed Monte Carlo calculations of σ^2_L for a class of models which include the spin-1/2 Heisenberg chain, the critical 1D transverse field Ising model, and the so-called "golden chain" (a model describing a chain of interacting Fibonacci anyons — non-Abelian quasiparticle excitations of certain fractional quantum Hall states). The results are summarized in Fig. 1. For uniform models, σ^2_L was found to scale logarithmically with block size L showing that valence bonds are indeed fluctuating on all length scales (and consistent with analytic calculations based on a field-theoretic mapping). For random models, σ^2_L was found to saturate once L exceeded a disorder-dependent crossover length scale ξ, signaling the expected locking of the valence bonds into a particular random singlet configuration on long length scales. By performing a scaling analysis of σ^2_L we were able to determine the dependence of ξ on disorder strength u, finding $\xi \sim u^\chi$ with model dependent exponent χ. For the spin-1/2 Heisenberg model and the transverse-field Ising model, our results for χ were consistent with those based on a weak-disorder renormalization group approach as well as previous numerical work. For the case of the disordered golden chain we have determined this scaling exponent for the first time, finding that $\chi \sim 1.55$.

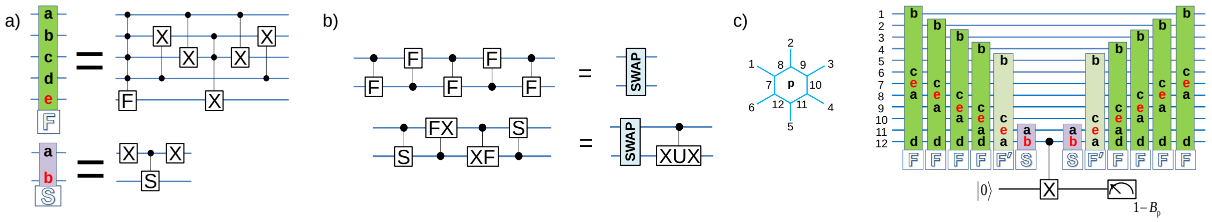

FIG. 2: (a) Two fundamental quantum circuits which carry out specific operations when computing with non-Abelian surface codes — the 5-qubit F-move circuit and the 2-qubit S-move circuit for Fibonacci anyons (the simplest non-Abelian anyons for which braiding is universal for quantum computaiton). (b) Two simplified quantum circuit identities, each requiring only two qubits, which fix the form of the single qubit operations F and S which appear in the fundamental circuits shown in (a). These circuits are suitable for calibrating these operations and can in principle be carried out today using existing quantum computing systems (e.g. superconducting qubits or trapped ions). (c) Full quantum circuits built out of the F-move circuit and the S-move circuit (here the F'-move circuit is obtained by identifying the qubits labeled a and d in the definition of the F-move circuit shown in (a)) that measures the plaquette operator $B_{\mathbf{p}}$ which appears in the Levin-Wen model for Fibonacci anyons for the case of a hexagonal plaquette. These measurement, which our construction shows requires $18n-26$ Toffoli gates (i.e. controlled-controlled-NOT gates), $8n-5$ controlled-NOT gates, and $4n$ single-qubit rotations for an n-sided plaquette, will be required in order to detect errors (in this case states in which $B_{\mathbf{p}}=0$) when using the ground states of the Levin-Wen model as a surface code. These rather demanding requirements become significanty more feasible of it is possible to directly carry out "single step" n qubit Toffoli gates with $n=3,4$ and 5.

Quantum Circuits for Measuring Levin-Wen Operators.

Recent developments in the theory of quantum computation have shown that the error threshold — a measure of the required qubit coherence and quantum gate accuracy needed to carry out arbitrary quantum computations — may be on the order of $\sim$ 1%, a significantly less demanding requirement than earlier estimates of 1 part in 10^5, and close to the accuracy obtained experimentally for a number of physical qubit realizations. This improved threshold is obtained using so-called "surface codes," quantum error-correcting codes which can be viewed as the topologically-ordered ground states of a class of 2D lattice models first introduced by Kitaev. Recently Koenig, Kuperberg, and Reichardt have outlined a scheme for performing quantum compution using "non-Abelian" surface codes. These codes are ground states of Levin-Wen models, generalizations of the Kitaev model for which the excitations are anyons obeying so-called non-Abelian statistics which can be used to carry out arbitrary quantum computation purely by braiding, (something which is not possible using the "Abelian" Kitaev surface code). Motivated by this, we have constructed explicit quantum circuits using standard elements (single qubit rotations, CNOT gates and Toffoli gates) for measuring the commuting set of vertex and plaquette operators that appear in the Levin-Wen model for the case of Fibonacci anyons — the simplest non-Abelian anyons for which universal quantum computation can be carried out by braiding (see Fig. 2). Such measurements will be required in order to detect errors in the quantum error-correcting code defined by the ground states of this model. We were able to quantify the complexity of these circuits with gate counts using different universal gate sets and found that these measurements become significantly easier to perform if n-qubit Toffoli gates with $n=3,4$ and 5 can be carried out directly. In addition to our measurement circuits, we constructed closely related quantum circuits which require only a few qubits and which can feasibly be carried out experimentally in the near future.

Future Plans

Future plans for this project include applying ideas we've developed in earlier work about the interplay between strong gauge fluctuations and possible phase transitions in bilayer quantum Hall systems to other, formally similar, systems, most notably certain "spin-liquid" states conjectured to have a spinon Fermi surface which may undergo a BCS pairing instability at low temperature. In addition, we will continue to investigate the growing number of ideas emerging at the intersection of the theory of topologically ordered states of matter and fault-tolerant quantum computation, particular in the context of "surface codes" (both Abelian and non-Abelian). One important theme of this aspect of the research program will be to focus on finding simplified quantum circuits (i.e. circuits similar to those shown in Fig. 2(b)) which can feasibly be carried out experimentally either today or in the near term, and which begin to explore various aspects of quantum computation with surface codes. As one specific example, we propose borrowing ideas from the study of interferometry of non-Abelian quasiparticles (closely related to current experiments on the $\nu = 5/2$ fractional quantum Hall state) and applying them to quantum computing. Essentially, by *simulating* an anyon interference experiment on a quantum computer one can measure a kind of "flux" which, in the context of quantum error correction, corresponds to an error which needs to be corrected. Our preliminary work in this direction shows that with as few as 6 qubits one can come perform a nontrivial simulation of such an intereference experiment for the case of Fibonacci anyons.

Publications

1. *Quantum Circuits for Measuring Levin-Wen Operators,* N.E. Bonesteel and D.P. DiVincenzo, Submitted to Physical Review B. (arxiv: 1206.6048).

2. *Valence-Bond Entanglement and Fluctuations in Random Singlet Phases,* H. Tran and N.E. Bonesteel, Physical Review B **84**, 144420 (2011).

3. *Monte Carlo Simulations of Anyon Chains,* H. Tran and N.E. Bonesteel, Comp. Mat. Sci. **49**, S395 (2010).

4. *Resources Required for Topological Factoring,* M. Baraban, N.E. Bonesteel, and S.H. Simon, Physical Review A **81**, 062317 (2010).

5. *Topological Quantum Computing with Read-Rezayi States,* L. Hormozi, N.E. Bonesteel, and S.H. Simon, Physical Review Letters **103**, 160501 (2009).

6. *Numerical Analysis of Quasiholes of the Moore-Read Wavefunction,* M. Baraban, G. Zikos, N.E. Bonesteel, and S.H. Simon, Physical Review Letters **103**, 076801 (2009).

7. *Braiding and Entanglement in Non-Abelian Quantum Hall States,* G. Zikos, K. Yang, N.E. Bonesteel, L. Hormozi, and S.H. Simon, International Journal of Modern Physics B **12-13**, 2727 (2009).

Density functional calculations of electron transport

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I. PROJECT SCOPE

The research in this program is about describing conductance through single molecular junctions using density functional theory (DFT). The Landauer formula expresses conductance in terms of the one-body Green's function. However in practice, the exact one-body Green's functions are usually approximated by Kohn-Sham Green's functions from DFT, i.e., the Green's function of the KS orbitals which reproduce the density assuming it is a ground-state density. Therefore, conductance through the Kohn-Sham potential is calculated, rather than the true conductance of the many-body system, and there is no fundamental theorem to guarantee that this is correct.

One goal of the project is to analyze the conditions under which Kohn-Sham conductances are, in fact, accurate or even exact. We have a few preliminary results on the Anderson junction, a single impurity connected to two leads. We hope to generalize our findings to other systems with more complicated internal structure. We also plan to study finite-bias conductance extrapolating our weak-bias results. Another goal of the project is to formulate transport in a real-space context because DFT is a real-space theory. We plan to translate the important concepts and relations often used in lattice models, such as the self-energy, Friedel sum rule, etc. to real space. Our previous result suggests that near a resonance, the Kohn-Sham conductance should be very accurate. This will be a topic to study in this project.

II. RECENT PROGRESS

A. Anderson Junction

We consider electron transport through an Anderson junction. The occupation is exactly solvable by Bethe ansatz, and we can change the strength of interaction by changing the dimensionless variable U/Γ, where U is the on-site Coulomb repulsion and Γ the coupling to the leads. In the strong correlation regime, this model exhibits a Kondo effect. We show that the exact Kohn-Sham functional yields the exact conductance for transport through Anderson junction for all correlation strengths, at zero temperature and in the linear response regime, as shown in Fig. 1. This is because Friedel sum rule applies to this one-channel model, and transmission is a function of occupation on the central impurity site. We solve for the occupations in the Anderson junction using Bethe ansatz, and invert the Kohn-Sham equations to derive

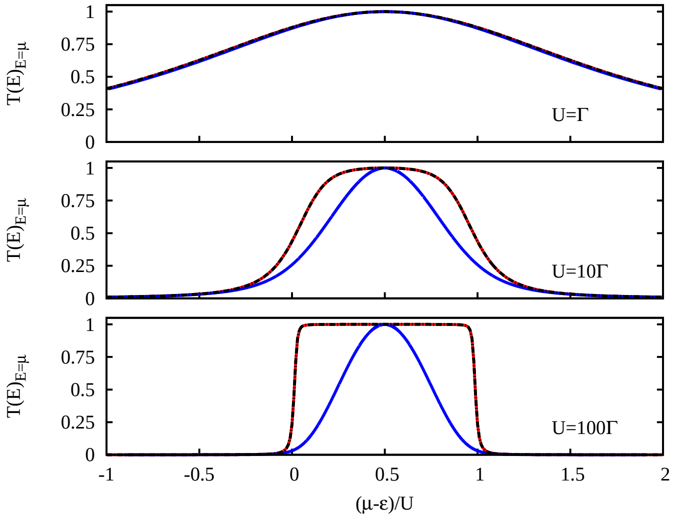

FIG. 1: Zero-temperature transmission at the Fermi energy as a function of ε, the impurity level, for an Anderson junction. The curves are for Bethe ansatz (black), Kohn-Sham DFT with the exact functional (red, coincides with black), and spin-restricted Hartree-Fock (blue). As U increases, HF misses the transmission plateau, but the KS transport is always exact.

exact Kohn-Sham potentials. We find that an important feature of the exact Kohn-Sham potential, namely the derivative discontinuity, must be built in to an approximation in order to capture the Kondo effect in the strong correlation limit. This can be seen in Fig. 2. As found in other problems, the derivative discontinuity is vital to dealing with strong correlation using density functional methods. We give a simple and accurate parametrization of exchange-correlation potential, using reverse-engineering of the exact solution and an exact condition of charge susceptibility at particle-hole symmetry point. This parametrization works through all regimes, from the weakly-correlated limit (where mean-field approaches are accurate) to the strongly-correlated limit (where charge quantization occurs).

Based on the exact solution, we also analyze different approximations. We consider three different kinds of approximation: (1) Smooth functionals, such as restricted Hartree-Fock (RHF). These functionals work well in the weakly-correlated regime, but completely miss the sharp feature at strongly-correlated regime (shown in Fig. 1). (2) Functionals with explicit derivative discontinuity, such as LDA+U type. These functionals work well in the very strongly-correlated regime. (3) Unrestricted approach, such as unrestricted Hartree-Fock (UHF). UHF reduces to RHF for weakly-correlated systems and is accurate, and works much better than RHF at strongly-correlated regime due to symmetry breaking, capturing both the limit and the approach to the limit exactly.

III. PLANNED ACTIVITIES

One immediate generalization of our results with zero-bias Anderson junction is, to see how Kohn-Sham DFT does at finite bias. The complication with respect to the zero-bias case is that the Friedel sum rule no longer applies, and the exact Kohn-Sham functional for zero-bias presumably does not work for finite

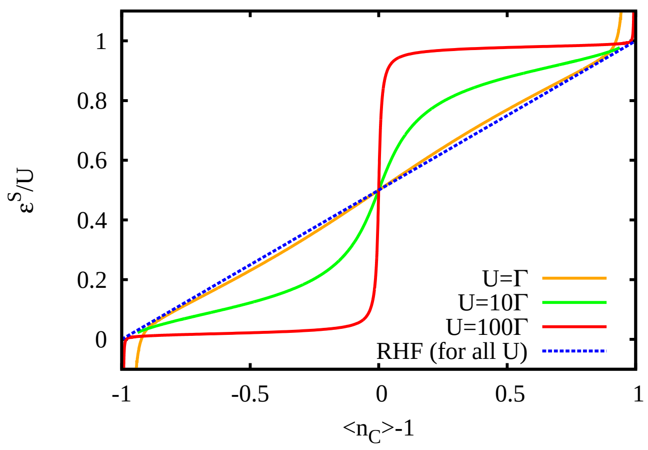

FIG. 2: The exact KS potential ε^{s} calculated from reverse engineering of Bethe ansatz, for Anderson junction. For $U \approx \Gamma$ (weakly correlated), HF is accurate; as U grows, an increasingly sharp step develops, becoming a discontinuity as $U \to \infty$. In real space, this step is in the exchange-correlation potential, which is the functional derivative of the exchange-correlation energy; hence it is called a derivative discontinuity.

bias. An important qualitative feature in the finite bias Anderson junction is the 2/3 plateau in the current vs. bias figure. This is a true many-body effect and cannot be described by Hartree-Fock. Although Bethe Ansatz does not work for large finite bias, we know the co-tunneling approximation is very accurate here (but not exact). We plan to reverse-engineer the results from the co-tunneling approximation, and analyze the special features that a Kohn-Sham potential must have in order to reproduce the 2/3 plateau.

Besides the Anderson junction, we plan to study more complicated systems, such as the two-channel Kondo model, or the interacting resonance lattice model. So far we have a very accurate Kohn-Sham potential (with derivative discontinuity built in) working for one-channel problems such as the Anderson junction. It will be very interesting to see if it works for more-than-one-channel systems. For those systems, transmission is no longer necessarily a simple function of occupation. In such cases, the Kohn-Sham conductance is not expected to be exact, i.e., there should be exchange-correlation corrections. But these models will provide an opportunity to see under what circumstances the Kohn-Sham conductance is accurate. A particular interesting question is to see if Kohn-Sham conductance always becomes accurate near a resonance.

We also are studying the relation between lattice site models and real space models. For example, we can build a one-dimensional real-space double barrier, to mimic the Anderson junction. There we can use real-space techniques, such as density matrix renormalization group (DMRG), to generate exact transmission. We can calculate the Kohn-Sham potential in real space, and compare with the bare external potential, to identify the exchange-correlation potential contribution, as well as comparing Kohn-Sham tunneling rates with true tunneling rates. An important quantity in real space is the transmission phase. It plays a central role in the Friedel sum rule and is related to the density change induced by the impurity (scattering region). Because Kohn-Sham DFT by definition reproduces the density change, there may be a way to analyze transmission through its phase using the Friedel sum rule.

IV. PUBLICATIONS

1. *"Excited states from time-dependent density functional theory"*, P. Elliott, F. Furche, and K. Burke, in "Reviews in Computational Chemistry" Vol. 26. Wiley-Hoboken (2009).
2. *"Charge transfer in Partition Theory"*, M. H. Cohen, A. Wasserman, R. Car, and K. Burke, J. Phys. Chem. A **113**, 2183 (2009).
3. *"Time-dependent density functional theory of high excitations: to infinity, and beyond"*, M. van Faassen and K. Burke, Phys. Chem. Chem. Phys. **11**, 4437 (2009).
4. *"Must Kohn-Sham oscillator strengths be accurate at threshold?"* Z.-h. Yang, M. van Faassen, and K. Burke, J. Chem. Phys. **131**, 114308 (2009).
5. *"Density-potential mapping in time-dependent density-functional theory"*, N. T. Maitra, T. N. Todorov, C. Woodward, and K. Burke, Phys. Rev. A **81**, 042525, (2010).
6. *"One-dimensional Continuum Electronic Structure Calculations with the Density Matrix Renormalization Group"*, E. M. Stoudenmire, L. O. Wagner, S. R. White, and K. Burke, to appear in Phys. Rev. Lett. (2012).
7. *"Exact conditions and their relevance in TDDFT"*, L. O. Wagner, Z.-h. Yang, and K. Burke, in "Fundamentals of Time-Dependent Density Functional Theory", pp. 101-122, Springer (2012).
8. *"The effect of cusps in time-dependent quantum mechanics"*, Z.-h. Yang, N. T. Maitra, and K. Burke, Phys. Rev. Lett. **108**, 063003, (2012).
9. *"Bethe ansatz approach to the Kondo effect within density-functional theory"*, J. P. Bergfield, Z.-F. Liu, K. Burke, and C. A. Stafford, Phys. Rev. Lett. **108**, 066801 (2012).
10. *"Accuracy of density functionals for molecular electronics: The Anderson junction"*, Z.-F. Liu, J. P. Bergfield, K. Burke, and C. A. Stafford, Phys. Rev. B **85**, 155117 (2012).
11. *"Reference electronic structure calculations in one dimension"*, L. O. Wagner, E. M. Stoudenmire, K. Burke, and S. R. White, Phys. Chem. Chem. Phys. **14**, 8581 (2012).

CMCSN: Structure and dynamics of water and aqueous solutions in materials science

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Project Scope

This project aims at developing accurate methodologies to model the microscopic structure and dynamics of water and aqueous solutions from an *ab-initio* perspective, in which the nuclear potential energy surface is generated on the fly from the quantum mechanical ground state of the electrons within density functional theory (DFT). This approach, called *ab-initio* molecular dynamics (AIMD), had considerable success in predicting crucial phenomena, such as large dielectric screening, fast proton transfer and molecular dissociation in solution. In the last decade, however, it became clear that the liquid generated in this way is substantially overstructured with respect to experiment, an outcome stemming from limitations of the adopted DFT approximation, such as the generalized gradient approximation (GGA) for exchange and correlation, and the use of classical mechanics for the nuclei. A goal of this project is to overcome these limitations by seeking improved functional approximations in combination with quantum sampling of molecular configurations to address key experimental results, such as those obtained with x-ray and neutron diffraction, and with deep inelastic neutron scattering (DINS). Other widely used experimental techniques to study water and aqueous solutions exploit core excitation spectroscopies like x-ray absorption (XAS) and Raman scattering (XRS). These studies are of more difficult interpretation, as they require an accurate theory of electronic excitation occurring on the attosecond time scale, in addition to good sampling of molecular configurations. To address this issue the project aims at developing new methodologies based on quasi-particle excitation theory that will be used in conjunction with accurate AIMD configurations.

Recent Progress

Proton momentum distribution

The momentum distribution of the protons extracted from DINS experiments in water and ice deviates substantially from the classical Maxwell distribution. To compute the momentum distribution we introduced an approach based on the sampling of displaced Feynman paths in path integral (PI) simulations [6]. Using concepts introduced in [6] we extracted with improved accuracy the spherical momentum distribution of the protons in a recent DINS experiment in ice at T=271K [2]. The mean kinetic energy of the protons measured in this experiment was ~155 meV, well in excess of the classical thermal value of ~35 meV [2]. The momentum distribution was in good agreement with a quasi-harmonic model suggested by PI-AIMD simulations [5]. A purpose of this study was to quantify the importance of nuclear quantum effects. Classical MD simulations based on empirical force fields, which are adjusted to experiment, should roughly include some of these effects but *ab-initio* simulations require a PI framework to sample correctly the equilibrium properties of water.

Liquid water structure

A proper quantum mechanical framework, although important, is not sufficient to fix the problems of GGA water, which is afflicted by self-interaction errors resulting in excessive proton delocalization and red shifts of the stretching frequencies. In addition, GGA water lacks the effect of attractive van der Waals (vdW) interactions originating from the dynamic correlations of the electronic clouds in the molecules. vdW interactions improve significantly the density of high-pressure ice phases [3]. We have implemented a new functional that we call PBE0-TS, which combines the hybrid functional PBE0 that significantly reduces the self-interaction error, with the Tkatchenko-Scheffler (TS) vdW functional. TS include two-body interactions decaying as R^{-6} with the distance R between a pair of atoms, but the intensity of the pair interactions is governed by coefficients that are functionals of the density and therefore capture environmental effects. The water structure using PBE0-TS in combination with an approximate treatment of the nuclear quantum effects is in excellent agreement with experiments, showing a marked improvement relative to GGA based AIMD, as shown in Fig.1 for the oxygen-oxygen radial distribution function (RDF). The PBE0 implementation used an order N scheme for exact exchange [9].

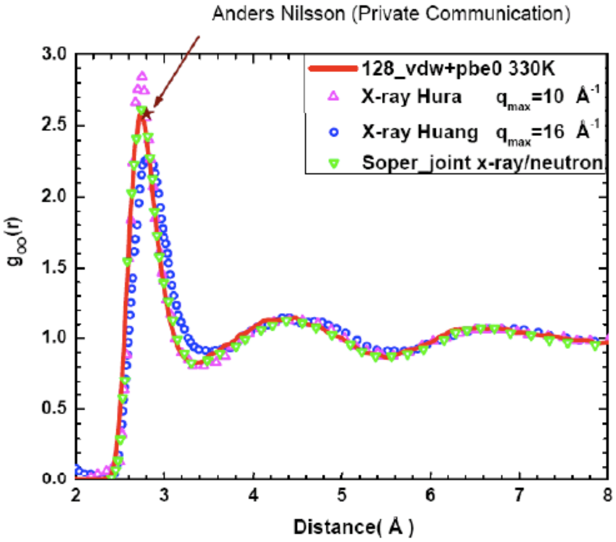

Fig 1: g_{OO} obtained from a PBE0-TS AIMD simulation on a 128-molecule cell at the experimental density. T was set to 330K to account approximately for nuclear quantum effects, as suggested by a previous PI-AIMD simulation. The theoretical RDF (red line) is compared to two x-ray diffraction experiments with different accessible maximum transfer wave vector ($q_{\max}$), Hura et al. and Huang et al., respectively. Interestingly, a new experiment (red star, Nilsson private communication) with $q_{\max} = 23\ A^{-1}$ gives position and height of the first peak in excellent agreement with our calculation. The green triangles show the RDF obtained by Soper with joint refinement of x-ray/neutron diffraction data. All experiments are at ambient conditions.

Comparison with experiment in Fig.1 underlines the importance of large $q_{\max}$ to extract the first peak of g_{OO} from experiment. The figure also indicates the essential correctness of joint refinement of x-ray/neutron diffraction data. From the theoretical standpoint this study allows us to understand in detail the role of corrections to GGA-AIMD on the short (SRO) and intermediate range order (IRO) of the simulated liquid.

X-ray absorption spectra

The X-ray absorption spectra of water and ice have been calculated using a GW approach in which the electron propagator (G) is dressed by the statically screened Coulomb interaction (W), as proposed in [7]. The results are compared to experiment in Fig. 2.

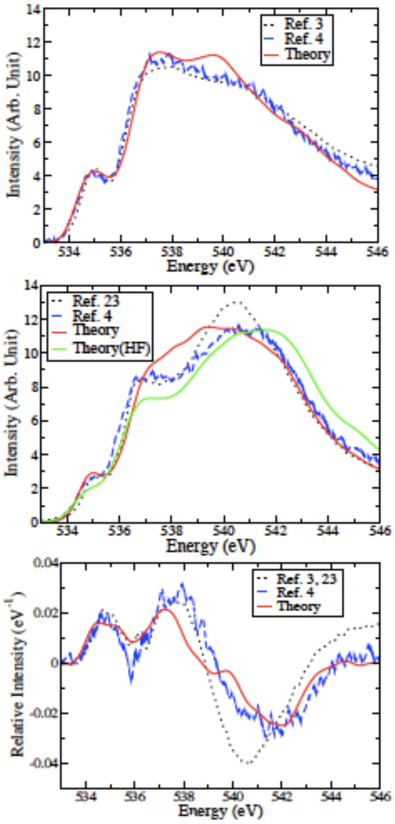

Fig. 2: comparison of calculated x-ray absorption spectra with experiments for water (top), ice (middle) and the difference between water and ice (bottom). Two sets of experimental data are included for each system (indicated as Ref. 3, 4, and 23, respectively). Hartree-Fock (HF) data on ice have also been included for comparison. HF corresponds to a GW calculation in which W is replaced by v, the bare Coulomb interaction. Water and ice configurations have been generated with PI-AIMD simulations based on DFT-GGA. Water is at room temperature in theory and experiments, ice is at T = 269K in the calculation, at T = 130K in Ref. 23 and at T = 40K in Ref. 4. Thermal effects are small compared to zero point motion and the differences between experiments in ice likely reflect differences in the samples and in the experiments (XAS in Ref. 23, XRS in Ref. 4). The difference spectrum is obtained from [I(water)-I(ice)]/S where I denotes spectral intensity and S is the integrated area of the spectra in the energy range of the figure.

Quantized nuclear motions affect the calculated spectra in Fig. 2 because zero point motion broadens the spectra via Franck-Condon factors that are included here by averaging over the distribution of Feynman paths. Moreover, in the case of water, quantum fluctuations modify the structure by facilitating H bond breaking. The spectral features (pre-edge, main- and post-edge) have excitonic character. The difference between water and ice in the main- and post-edge reflect IRO differences associated due to a non bonded molecular fraction brought within range of the first coordination shell in the liquid following partial collapse of the H bond network of crystalline ice [7].

Future Plans

The corrections to GGA water due to exact exchange, vdW interactions and quantized nuclei affect differently SRO and IRO but are all of similar magnitude and should be treated on the same footing. Thus an important goal of future research will be to perform a benchmark PI-AIMD simulation based on PBE0-TS. This will allow us to properly compute all pair correlations (g_{HH}, g_{OH} and g_{OO}) and to assess experimentally based estimates of triplet correlations (g_{OOO}). This study will give unprecedented insight on how basic molecular interactions, such as H bonding and vdW influence the local order (SRO, IRO) of water. Moreover we will assess if including two-body vdW interactions alone is sufficient or if inclusion of higher order terms [1] may lead to observable effects. The highly accurate molecular structures generated in this study will be used to further improve the XAS spectral calculations. In fact, while the overall greement between theory and experiment in Fig. 2 is unprecedented, residual discrepancies remain. In the case of water these are likely to come mainly from overstructuring still present in GGA PI-AIMD simulations. Improving the spectral calculation should also play a role, particularly in ice. The main approximation in the GW calculations of Fig.2 is in the adopted screening form, which underestimates the microscopic inhomogeneity of the medium. Full treatment of the inhomogeneity of the medium at the molecular scale is possible but computationally very challenging in systems that require large simulation cells and averages over many disordered realizations. Work in this direction is at an advanced stage of development.

Studying aqueous solutions will be a further step in this program. The modeling capability that we plan in this project will be extremely useful in studies of solvated ions, interfacial water and bio-molecular environments. In all these systems X-ray spectroscopy techniques are widely used at DOE facilities to extract microscopic information and the computational techniques that we are developing will be invaluable to gain insight on the origin of the spectral features that are observed in experiments and to associate these features to the details of the molecular structure.

List of Publications (2009-2012)

1. A. Tkatchenko, R. A. DiStasio Jr, R. Car, M. Scheffler, Accurate and Efficient Method for Many-Body van der Waals Interactions, *Phys. Rev. Letters* **108**, 236402 (2012)
2. D. Flammini, A. Pietropaolo, R. Senesi, C. Andreani, F. McBride, A. Hodgson, M.A. Adams, L. Lin, R. Car, Spherical momentum distribution of the protons in hexagonal ice from modeling of inelastic neutron scattering data, *J. Chem. Phys.* **136**, 024504 (2012)
3. B. Santra, J. Klimes, D. Alfe, A. Tkatchenko, B. Slater, A. Michaelides, R. Car, M. Scheffler, Hydrogen Bonds and van der Waals Forces in Ice at Ambient and High Pressures, *Phys. Rev. Letters* **107**, 185701 (2011)
4. L. Lin, J.A. Morrone, R. Car, Correlated Tunneling in Hydrogen Bonds, *J. Stat. Phys.* **145**, 365 (2011)
5. L. Lin, J.A. Morrone, R. Car, M. Parrinello, Momentum distribution, vibrational dynamics, and potential of mean force in ice, *Phys. Rev. B* **83**, 220302 (2011)
6. L. Lin, J.A. Morrone, R. Car, M. Parrinello, Displaced Path Integral Formulation for the Momentum Distribution of Quantum Particles, *Phys. Rev. Letters* **105**, 110602 (2010)
7. W. Chen, X.F. Wu, R. Car, X-ray Absorption Signatures of the Molecular Environment in Water and Ice, *Phys. Rev. Letters* **105**, 017802 (2010)
8. J. Morrone, L. Lin, R. Car, Tunneling and delocalization effects in hydrogen bonded systems: a study in position and momentum space, *J. Chem. Phys.* **130**, 204511 (2009)
9. X.F. Wu, A. Selloni, R. Car, Order-N implementation of exact exchange in extended insulating systems, *Phys. Rev. B* **79**, 085102 (2009)

THE PHYSICS OF GRAPHENE

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Project Scope

The research in this program involves theoretical investigations of electronic, optical and mechanical properties of graphene and its derivatives, such as bi-layer graphene, graphene heterostructures, strained graphene, as well as graphene on various surfaces. One line of research has been development of theoretical models that support graphene's large array of possible technological applications. For example one of our goals has been the understanding of surface plasmons and spin relaxation mechanisms in graphene, related to novel optoelectronics and spintronics applications. Our current research focus is on understanding the role of correlations in graphene under mechanical deformations, such as strain. The main goal is to describe the mutual interplay between strain and electron-electron interactions which could lead to the formation of novel electronic phases with strongly modified electronic, magnetic and optical properties. This direction of research will therefore lead to deeper understanding of interactions in graphene.

Recent Progress

Plasmonics in graphene

Plasmons are a direct consequence of electron-electron interactions. In graphene they are particularly interesting because, unlike what happens in three dimensional solids, their energy is highly dependent on the wavelength and hence they can have energy that varies from the infrared to the ultraviolet. Plasmons can be excited with light via the electron-photon interaction. Recently, graphene has been recognized as a versatile optical material for novel photonic and optoelectronic applications, such as ultrafast lasers, solar cells, optical modulators, photodetectors, light emitting devices and meta-materials. Graphene has strong coupling effect to light due to the unique electronic structure. Moreover, the linear dispersion of the Dirac electrons enables broadband applications. All of these photonic and optoelectronic applications rely on the interaction of propagating far-field photons with graphene. Surface plasmon-polariton waves exist in doped graphene. Surface plasmons in graphene exhibits a number of favorable properties: first of all, graphene plasmons are confined to volumes of the order of 10^6 times smaller than the diffraction limit, which facilitate strong light-matter interactions. Secondly, surface plasmons in graphene are tunable via electrical or chemical modification of the charge carrier density. Lastly, surface plasmon-lifetimes in graphene reach hundreds of optical cycles, which may circumvent one of the major bottlenecks facing noble-metal plasmonics. Our group has been providing theoretical guidance to one of the best plasmonics groups in the world lead by Prof. Dmitri Basov at UCSD.

Spintronics in graphene

Graphene is considered as a potential material for spintronics devices due to the weak spin-orbit (SO) interaction and long spin lifetimes. One of the most intriguing features of spintronics in graphene is that the observed spin relaxation time is significantly shorter than the values estimated theoretically. A number of recent experiments investigate which spin relaxation mechanism plays the major role both in single layer and in bilayer graphene. The Dyakonov-Perel and the Elliot-Yafet mechanisms have been discussed in the context of graphene. Experiments suggest that the main source of spin relaxation in single layer graphene is extrinsic, lending support to the Elliot-Yafet mechanism. Longer spin lifetimes have been reported in bilayer graphene than in single layer, when the SO coupling in the bilayer is expected to be somewhat stronger. We are currently developing the theoretical background to study spin relaxation in these systems which is built on top of our earlier successful theoretical proposal of the SO enhancement due to sp3 defects. We have made various predictions that are being tested in several labs around the world.

Strain engineering in graphene

Being one atom thick, graphene is a very soft material, and hence can be easily folded, twisted and stretched. For instance, we have shown theoretically that the edge scrolls in suspended graphene short-circuit the source-drain current paths in the quantum Hall regime inhibiting the observation of the Hall conductance quantization in such systems. Moreover, current growth techniques based on chemical vapor deposition (CVD) have shown that extended defects such as grain (GB) and domain boundaries (DB) are present in graphene samples, modifying their electronic and structural properties. Extended defects lead to internal strain and produce significant changes in the band structure. In this context, the nature of the electronic states introduced by such extended 1D defects in graphene is a topic that deserves close inspection. More specifically, whether GBs and DBs act as quasi-1D conducting channels immersed in the bulk of graphene is the question we have been studying. We also studied the issue of self-doping in graphene induced by the presence of such extended 1D defects, that occurs when a defect attracts charge carriers, resulting in charged defective lines surrounded by a doped graphene matrix.

Electron Correlations and Strain in Graphene

Long-range electron-electron interactions near the Dirac points can lead to profound effects, such as reshaping of the Dirac cones in suspended graphene as well as interaction-driven formation of “plasmarons” (i.e. quasiparticles bound to plasmons) in doped samples. The subject of electron correlations is currently at the forefront of the physics of graphene. For

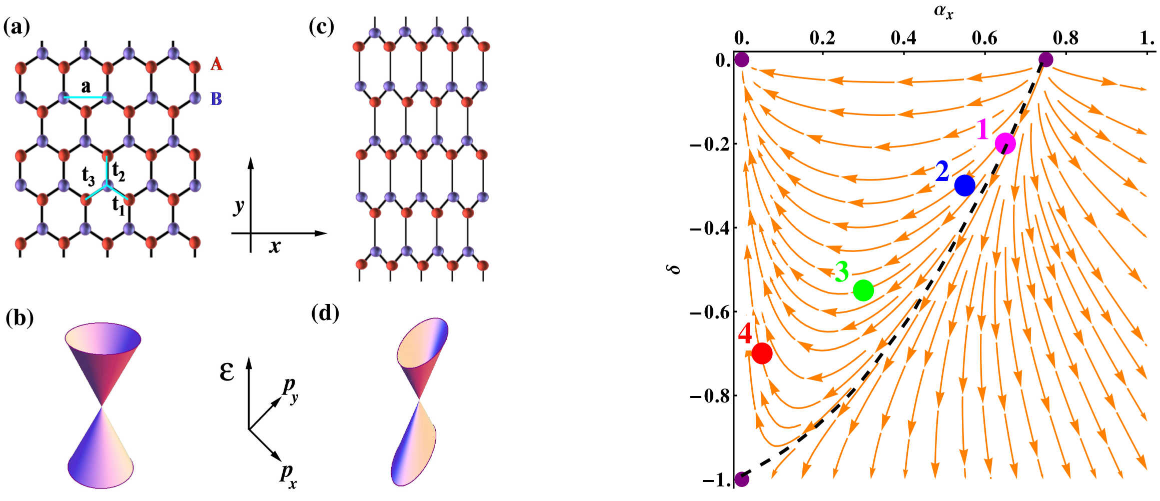

Figure 1: Left panel: Formation of Anisotropic Dirac Cones in Graphene under uniaxial strain (c)-(d). Right Panel: Mutual renormalization of the electron-electron interaction α and the Dirac fermion anisotropy $\delta = (v_y/v_x) - 1$. The value $\delta = -1$ corresponds to decoupled chains, while $\delta = 0$ is conventional (isotropic) graphene. A tendency towards interaction-driven quasi one-dimensional behavior is present below the critical (dashed) line. From: "Interacting Anisotropic Dirac Fermions in Strained Graphene and Related Systems," Anand Sharma, Valeri N. Kotov, and Antonio H. Castro Neto, arXiv:1206.5427 (2012).

example in graphene heterostructures the carbon atoms are not coupled directly by covalent bonds but by electron-electron interactions. One of the most amazing consequences of this kind of coupling is the so-called Coulomb drag. We have studied the Coulomb drag in such structures and have found that their properties are extremely sensitive to the distance between graphene layers. We have already made several theoretical predictions that await confirmation.

Most recently we have investigated correlation-driven phases due to the interplay of electron interactions and uniaxial strain (modeled as Dirac fermion anisotropy, i.e. different velocities $v_x \neq v_y$), and have found that a rich variety of electronic behavior is possible (Fig.1). In particular we have discovered unconventional interaction-driven quasi one-dimensional electronic phase (anisotropic excitonic insulator). This line of research could provide a new avenue for exploration of correlation effects in graphene, both theoretically and experimentally.

Future Plans

For the next year, we plan to continue our studies of strain effects in the electronic and magnetic properties of graphene. Focusing in particular on uniaxial strain, the following topics will be investigated:

- Renormalization of the Dirac cones due to the interplay of strain and electron-electron interactions, from weak to large strain. We will also analyze in more detail the nature of the novel correlated, strain-induced states, which we have found during our ongoing research.

• Effect of strain on the excitonic transition in graphene. Such a transition is from a semi-metal to an insulator, and has not yet been observed in conventional (isotropic) graphene. We will investigate how strain can facilitate the formation of the excitonic state.
• Studies of strain influence on the formation of magnetic states, both in the context of localized magnetism (Anderson impurity), and band magnetism of anisotropic (due to strain) Dirac fermions.
• Studies of charge re-distribution around external Coulomb impurities in strained graphene, and its effect on electronic transport.

Publications

(2011-2012)

"Gate-tuning of graphene plasmons revealed by infrared nano-imaging," by Z. Fei, A. S. Rodin, G. O. Andreev, W. Bao, A. S. McLeod, M. Wagner, L. M. Zhang, Z. Zhao, G. Dominguez, M. Thiemens, M. M. Fogler, A. H. Castro-Neto, C. N. Lau, F. Keilmann, D. N. Basov. Accepted in Nature.

"Infrared nanoscopy of Dirac plasmons at the graphene-SiO2 interface," by Zhe Fei, Gregory O. Andreev, Wenzhong Bao, Lingfeng M. Zhang, Alexander S. McLeod, Chen Wang, Magaret K. Stewart, Zeng Zhao, Gerardo Dominguez, Mark Thiemens, Michael M. Fogler, Michael J. Tauber, Antonio H. Castro-Neto, Chun Ning Lau, Fritz Keilmann, Dimitri N. Basov, Nano Lett. **11**, 470 (2011).

"Silicon Layer Intercalation of Centimeter-Scale, Epitaxially Grown Monolayer Graphene on Ru(0001)," by Jinhai Mao, Li Huang, Yi Pan, Min Gao, Junfeng He, Haitao Zhou, Haiming Guo, Yuan Tian, Qiang Zou, Lizhi Zhang, Haigang Zhang, Yeliang Wang, Shixuan Du, Xingjiang Zhou, A. H. Castro Neto, Hong-Jun Gao, Appl. Phys. Lett. **100**, 093101 (2012).

"Quenching of the quantum Hall effect in graphene with scrolled edges," by Alessandro Cresti, Michael M. Fogler, Francisco Guinea, A. H. Castro Neto, Stephan Roche. Journal-ref: Phys. Rev. Lett. **108**, 166602 (2012).

"Near-field spectroscopy of silicon dioxide thin films," by Lingfeng M. Zhang, Gregory O. Andreev, Zhe Fei, Alexander S. McLeod, Gerardo Dominguez, Mark Thiemens, Dimitri N. Basov, Antonio H. Castro Neto, Michael M. Fogler. Journal-ref: Phys. Rev. B **85**, 075419 (2012).

"Faraday effect in graphene enclosed in an optical cavity and the equation of motion method for the study of magneto-optical transport in solids," by A. Ferreira, J. Viana-Gomes, Yu. V. Bludov, Vitor M. Pereira, N. M. R. Peres, A. H. Castro Neto. Journal-ref: Phys. Rev. B **84**, 235410 (2011).

"Elliot-Yafet mechanism in graphene," by H. Ochoa, A. H. Castro Neto, F. Guinea, Phys. Rev. Lett. **108**, 206808 (2012).

"Coulomb Drag and High Resistivity Behavior in Double Layer Graphene," by N. M. R. Peres, J. M. B. Lopes dos Santos, A. H. Castro Neto. Journal-ref: EuroPhysics Letters **95**, 18001 (2011).

"Electron-Electron Interactions in Graphene: Current Status and Perspectives," by V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, and A. H. Castro Neto, Rev. Mod. Phys. **84**, 1067 (2012).

Quantum embedding and many-electron wavefunctions for strongly correlated solids

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This part of our DOE funded research program aims to develop controlled ab-initio methods to model realistic solids with strong electron correlations. Our quantum embedding project focuses on two techniques: density matrix entanglement embedding (DMET) and dynamical mean-field theory (DMFT). These formalisms provide a route to bulk properties from the solution of a local impurity model. We aim to go beyond current DFT-DMFT approximations, towards fully ab-initio theories free of double counting and empirical screening corrections. Our complementary wavefunction work targets the development of many-electron wavefunction methods directly in an ab-initio periodic boundary condition setting. We have recently been developing density matrix renormalization group, Jastrow-BCS, and coupled cluster techniques in this framework. At the meeting, I will describe recent progress and future plans in the above two areas. Some topics will include: the density matrix entanglement embedding theory and its applications to lattice and ab-initio Hamiltonians; improved solvers for dynamical mean-field theory; and periodic boundary condition ab-initio density matrix renormalization group calculations for three-dimensional solids.

I. QUANTUM EMBEDDING AND MANY-ELECTRON WAVEFUNCTION APPROACHES TO SOLIDS

A. Recent Progress

While the electronic properties of many solids are described well by periodic DFT, solids with strong correlations remain a major challenge for condensed matter electronic structure. For sufficiently small lattices or molecules, strong correlations can be handled by several techniques, including exact diagonalization, density matrix renormalization group, auxiliary field quantum Monte Carlo, and multi-reference configuration interaction to name a few. Such approaches, however, cannot easily be applied to infinite systems. Quantum embedding provides an attractive route to bridge the gap between typically local descriptions of strong correlation and the extraction of observables in bulk systems.

Over the last year we have devised a new rigorous quantum embedding formalism called *density matrix entanglement embedding* (DMET). DMET allows us to embed many-body wavefunction calculations in a correlated solid. Consider some small portion, say a unit-cell, of an infinite solid, which we term the impurity. The basic observation is that the remainder of the solid (the infinite environment) can be exactly replaced by a *finite* bath construction that reproduces the entanglement between the environment and the impurity. From the Schmidt decomposition, we can show that the entanglement of an impurity with M sites can be exactly reconstructed using *only M bath sites*, which is a tremendous simplification from the complexity of the infinite environment. In practice, such an exact bath construction requires the quantum state of the infinite system. In DMET we use an approximate bath construction that is exact in a mean-field sense and which

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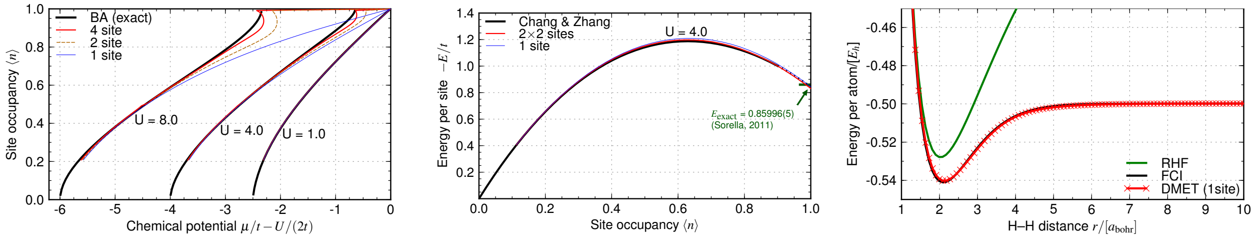

FIG. 1: . Left. DMET calculations of the 1D metal-insulator transition yield gaps in good agreement with the Bethe Ansatz. The results are of similar accuracy to similar sized cluster DMFT calculations but are many orders of magnitude less expensive. (Coloured lines: DMET, Black line: Bethe Ansatz). Center. DMET calculations of energies of the 2D doped Hubbard model, which compare very well to benchmark QMC (Chang and Zhang) results. Right. Initial combination of DMET with ab-initio Hamiltonians yields a dissociation curve for the H$_1$0 hydrogen lattice which is indistinguishable from the exact FCI.

is efficiently obtained. The physics of DMET, with local (impurity) degrees of freedom described exactly in the presence of Gaussian-like bath fluctuations, is similar to that of the dynamical mean-field theory (DMFT) approximation. However, DMET possesses several important computational advantages: the theory is completely frequency-independent, allowing for easy combination with a wide range of powerful pure-state impurity solvers such as the density matrix renormalization group or multireference configuration interaction, and the bath is of minimal size, greatly reducing the cost of calculation. Consequently, we find that DMET calculations are orders of magnitude faster than comparable DMFT calculations. In Fig. 1 we show the DMET energy for the 2D Hubbard model as compared to constrained-phase AFQMC and extrapolated QMC data: very good agreement is found and even using a modest 2×2-site embedded cluster, we find errors of only about 1% in the total energy. Fig. 1 we also show the $\partial n/\partial \mu$ compressibility curve for the 1D Hubbard model: compared to the Bethe Ansatz, Mott gaps are well reproduced, and the DMET description of the metal-insulator transition is comparable to the cluster DMFT description at a small fraction of the cost.

Over the last year, we have also been investgating several aspects of ab-initio DMFT. Using a Hartree-Fock description of the periodic solid, we carried out ab-initio DMFT calculations which are completely diagrammatically controlled, i.e. with no double counting error. We have also been exploring more efficient impurity solvers, with the view to ab-initio DMFT calculations where weakly correlated degrees of freedom are treated in a coupled manner with the strongly correlated impurity sites. We showed recently that simple configuration interaction wavefunctions yield highly accurate approximate solvers and can treat impurity bath problems with more than 30 orbitals with no discernible loss of accuracy when compared to exact diagonalization (see Fig. 2).

Our work on correlated wavefunction methods is complementary to the above efforts in quantum embedding. Here we aim to develop the capability to directly use correlated wavefunction methods in periodic systems. To extend powerful wavefunction methods, such as the density matrix renormalization group, to ab-initio descriptions of infinite systems, requires us to treat the infinite-range Coulomb matrix elements that occur in the periodic setting. Very initial results of this effort are in Fig. 2, where we show results from *fully periodic* coupled cluster and density matrix renormalization group calculations on a 2x2x2 Brillouin zone sampling of 3D LiH solid (compared to benchmark FCI data). While the results are very preliminary, they show that all the basic functionality is complete in our periodic implementation, and that fully correlated wavefunction calculations in 3D solids are feasible. In addition, we are also investigating new algorithms to efficiently handle the large number of orbitals within the typical correlation length of a three-dimensional solid. Using

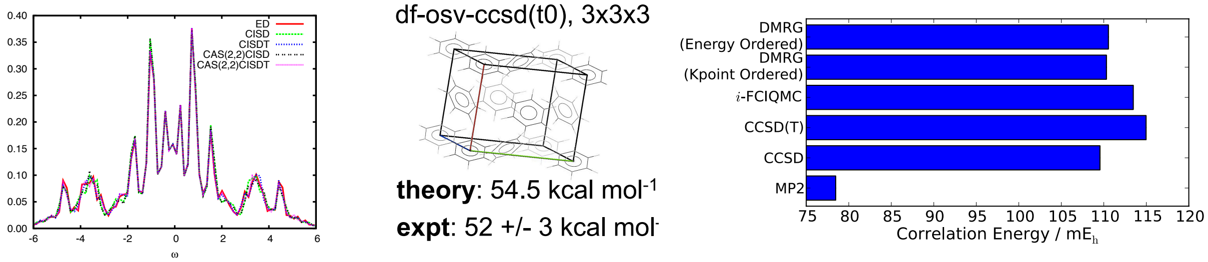

FIG. 2: Left. Comparison between ED and CI solvers for single-site DMFT spectral functions; the CI spectral functions are indistinguishable from ED, but the CI calculations are about 100 times faster. Centre. Using tensor factorizations of CC theory, we are able to carry out accurate calculations on molecular crystals. The computed binding energies have a smaller uncertainty than the experimental binding energies. Right. Initial applications of a periodic ab-initio density matrix renormalization group code to a 2x2x2 Brillouin zone sampling of the LiH crystal.

tensor factorization ideas we recently devised orbital-specific virtual (OSV) local coupled cluster methods that constitute the fastest local coupled cluster algorithms to date. We are in the process of applying OSV coupled cluster methods to molecular crystals; our early studies show that we are able to obtain theoretical binding energies with an uncertainty considerably better than the experimental estimate (Fig. 2).

B. Future plans

As stated above, the overarching aim in our work in quantum embedding and many-electron wavefunctions is to enable the fully ab-initio modeling of strongly correlated solids. In the next year, we will extend the basic DMET formalism to time-dependent quantities such as spectra. These basic developments will be applied and evaluated in further lattice Hamiltonian studies, including calculations of full phase diagrams and spectra. We will also embark on the combination of DMET with long-range and ab-initio Hamiltonians. Our early results appear highly promising. For example, in Fig. **??** we show an initial test of the ab-initio DMET embedding for the dissociation of a cyclic hydrogen lattice (which mimics a metal-insulator transition). As seen from the curve, the DMET dissociation curve is essentially indistinguishable from the exact curve. Over the next year, we will also extend our work on dynamical mean-field theory to treat long-range dynamical contributions within the quantum chemical perturbation theory/configuration interaction/coupled cluster hierarchy. Finally, we are also very excited to make further progress with our new periodic correlated wavefunction methodology, and we will initiate the study of 3D doped transition metal oxides using our periodic density matrix renormalization group implementation.

II. REFERENCES

- G. Knizia, G. K.-L. Chan, "Density matrix embedding: a simple alternative to dynamical mean-field theory", *Phys. Rev. Lett.*, submitted.
- D. Zgid, E. Gull, G. K.-L. Chan, "Truncated Configuration Interaction expansions as solvers for correlated quantum impurity models and dynamical mean field theory", *Phys. Rev. B*, submitted.

- Y. Kurashige, J. Yang, G. K.-L. Chan, F. R. Manby, “Optimization of orbital-specific virtuals in local Moller-Plesset perturbation theory”, *J. Chem. Phys.*, **136**, 124106 (2012)
- J. Yang, G. K.-L. Chan, F. R. Manby, M. Schuetz, H.-J. Werner, “The orbital-specific virtual local coupled cluster singles and doubles method: OSV-LCCSD”, *J. Chem. Phys.*, **136**, 144105 (2012)
- D. Zgid and G. K.-L. Chan, “Dynamical mean-field theory from a quantum chemical perspective”, *J. Chem. Phys.*, **134**, 094115 (2011)
- T. Yanai, Y. Kurashige, E. Neuscamman, and G. K.-L. Chan, “Joint density matrix renormalization group and canonical transformation theory for multireference electronic structure”, *J. Chem. Phys.*, **132**, 024105, (2010)
- E. Neuscamman, T. Yanai and G. K.-L. Chan, “Strongly contracted canonical transformation theory”, *J. Chem. Phys.*, **132**, 024106 (2010)
- T. Yanai, Y. Kurashige, D. Ghosh, G. K-L. Chan, “Accelerating convergence in iterative solutions of large active-space self-consistent field calculations”, Int. J. Quantum Chem. **109**, 2178 (2009)
- D. Zgid, D. Ghosh, E. Neuscamman, G. K-L. Chan, “A study of cumulant approximations to n-electron valence multireference perturbation theory”, *J. Chem. Phys.*, **130** 194107 (2009)
- J. J. Dorando, J. Hachmann, G. K-L. Chan, “Analytic theory of response in the density matrix renormalisation group”, *J. Chem. Phys.*, **130** 184111 (2009)
- E. Neuscamman, T. Yanai, G. K-L. Chan, “Quadratic canonical transformation theory and higher order density matrices”, *J. Chem. Phys.*, **130**, 124102 (2009)

Theory and simulation of defects in oxide materials

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Project Scope

The goal of our program is to examine an important class of materials: oxides with attention paid to the nature and role of defects in transition metal oxides. Transition metal oxides span a wide range of structural and electronic properties. These oxides crystallize in a wide range of structures and exhibit a wide range of interesting physical properties ranging from simple ferroelectricity to correlated electron effects such as magnetism and superconductivity. Oxide materials find numerous applications as passivating agents, dielectrics, actuators, switches, magnetic field sensors, photovoltaic materials, photocatalysts, and new types of electronic memory devices. In all these applications, defects play an important role. From basic thermodynamics, defects are unavoidable. Oxides of transition metals, in particular, are known to exhibit unusually high concentrations of defects owing to the variable valence or oxidation state of a metal with a partially filled d-shell. Elementary point defects include vacancies and interstitials, as well as dopant impurities, which may be either substitutional or interstitial. The electro-neutrality rule dictates more complex defects, *i.e.*, charge defects appear in balancing pairs such as Frenkel-type (vacancy plus same type interstitial) or Schottky type (pairs of vacancies) defects. Experimentally, the electronic properties of such defects can be determined by either optical or electric measurements, but the proper interpretation of both is far from trivial owing in part to sensitivity issues and in part to the complexity of the fundamental physics involved. Moreover, the experimental determination of the exact defect structure is extremely difficult, especially in the context of surfaces, interfaces or nanostructures.

As a consequence, theoretical modeling of the structure of the formation energy of defects is of great importance as a first step in any analysis. Once the defect structure is known, the electronic properties can be calculated and compared with those measured.

Recent progress

We outline some of our recent work in several different areas relevant to understand oxide materials, including advances in numerical approaches.

Oxide vacancies in dielectric materials: We have examined defects, oxygen vacancies, in an important high-k dielectric material: hafnia [2]. We calculated the quasiparticle defect states and charge transition levels (CTL's) of oxygen vacancies in monoclinic hafnia using density functional theory and the GW approximation. We found that the quality and reliability of CTL's can be assessed by calculating the same CTL via two different physical pathways. We showed that it is necessary to include important electrostatic corrections, which were previously neglected within the supercell density functional theory - GW approach. Contrary to previous reports, we determined that the oxygen vacancies in hafnia are large positive U centers, where U is the defect charging energy.

Dye sensitized solar cells; The development of new types of solar cells is driven by the need for clean and sustainable energy. In this respect dye-sensitized solar cells (DSC) are considered as a promising route for departing from the traditional solid state cells. The physical insight provided by computational modeling may help develop improved DSCs. To this end, it is important to obtain an accurate description of the electronic structure, including the fundamental gaps and level alignment at the dye-$\mathrm{TiO_2}$ interface. This requires a treatment beyond ground-state density functional theory. We presented a many-body perturbation theory study [8], within the $\mathrm{G_0W_0}$ approximation, of two of the crystalline phases of dye-sensitized $\mathrm{TiO_2}$ clusters, reported by Benedict and Coppens, [J. Am. Chem. Soc. 132, 2938 (2010)]. We obtained geometries in good agreement with the experiment by using density functional theory with the Tkatchenko-Scheffler van der Waals correction. We demonstrated that even when density functional gives a good description of the valence spectrum and a qualitatively correct picture of the electronic structure of the dye-$\mathrm{TiO_2}$ interface; $\mathrm{G_0W_0}$ calculations yield more valuable quantitative information regarding the fundamental gaps and level alignment. In addition, we systematically investigated the issues pertaining to$\mathrm{G_0W_0}$ calculations, namely: (i) convergence with respect to the number of basis functions, (ii) dependence on the mean-field starting point, and (iii) the validity of the assumption that the DFT wave function is a good approximation to the quasiparticle wave function. We showed how these issues are manifested for dye molecules and for dye-sensitized $\mathrm{TiO_2}$ clusters.

Oxide surfaces and heterointerfaces: We investigated electrostatic doping as a possible mechanism for achieving a 100% spin polarized two dimensional electron gas at the stoichiometric $\mathrm{LaAlO_3}$/EuO heterointerface [4]. We carried out a first-principles study of stoichiometric heterostructures composed of polar oxide $\mathrm{LaAlO_3}$ and the ferromagnetic semiconductor EuO. We found that electrostatic doping achieved by an electric field in the polar oxide leads to a fully spin-polarized two dimensional electron gas at the interface. The localized charge carrier density is on the order of 4×10^{13} $\mathrm{cm^{-2}}$ at the interface and decays exponentially within five to six EuO atomic layers ($\sim$10 Å). This mechanism contrasts with a previous calculation of the $\mathrm{LaAlO_3}$/EuO interface in which electron doping was introduced through a nonstoichiometric $\mathrm{LaAlO_3}$ layer. Our configuration allows a low level of doping in EuO that is comparable to the Gd-doped EuO as in recently reported experiments and tunable by adjusting the thickness of the $\mathrm{LaAlO_3}$ layers. We predict a change of the magnetic moment of Eu and increase of the Curie temperature in the doped layers of EuO.

We used density functional theory to investigate the influence of surface vacancies on the surface stability of a stoichiometric free-standing $\mathrm{LaAlO_3}$ (001) thin film [13]. Defect-free three and five unit cell thick $\mathrm{LaAlO_3}$ (001) thin films exhibited macroscopic electric fields of 0.28 V/Å and 0.22 V/Å, respectively. The built-in electric field was sufficiently strong for the five unit cell thick film to undergo a dielectric breakdown, within the local density approximation. We showed that the electric field can be effectively compensated by La vacancies on the LaO surface, O vacancies on the $\mathrm{AlO_2}$ surface, or both types of vacancy present at the same time. Comparing surface Gibbs free energies we found that several surface vacancy structures are thermodynamically stable. Recently, $\mathrm{SrTiO_3}$ (STO) and $\mathrm{LaAlO_3}$ (LAO) have attracted considerable attention due to the two dimensional electron gas observed at the interface between these two wide gap insulators. The origin of this two dimensional electron gas has been a source of considerable debate. Oxygen vacancies form an n-type defect in both STO and LAO and the origin of charge in LAO/STO heterostructures is sometimes attributed to the presence of these defects [13]. The electronic structure and nature of vacancy induced defect states in these oxides are important.

Numerical algorithms: Another aspect of our work involved the development of high performance algorithms for solving the Kohn-Sham equation, which arises in density functional theory.

Obtaining a solution of the Kohn-Sham equation is a standard procedure to determine the electronic structure of atoms, molecules, and condensed matter systems. The solution of this nonlinear eigenproblem is used to predict the spatial and energetic distribution of electronic states. However, obtaining a solution for large systems is computationally intensive because the problem scales super-linearly with the number of atoms. We demonstrated a "divide and conquer" method that partitions the necessary eigenvalue spectrum into slices and computes each partial spectrum on an independent group of processors in parallel [6,7]. We focused on the elements of the spectrum slicing method that are essential to its correctness and robustness such as the choice of the filter polynomial, the stopping criterion for a vector iteration, and the detection of duplicate eigenpairs computed in adjacent spectral slices. We resolved several issues in developing an optimized implementation, *e.g.*, the addition of extra layer of parallelism and the ability to examine systems with hundreds of thousands of atoms.

The generation of unoccupied orbitals within density functional theory for use in GW calculations of quasiparticle energies becomes prohibitive for large systems. We showed that, without any loss of accuracy, the unoccupied orbitals may be replaced by a set of simple approximate physical orbitals made from appropriately prepared plane waves and localized basis orbitals, which represent the continuum and resonant states of the system, respectively [14]. Our approach allows for accurate quasiparticle calculations using only a very small number of unoccupied density functional orbitals, often resulting in an order of magnitude gain in speed.

Planned activities

Doping titania: The conduction band energies of TiO_2 are properly matched to the redox properties of water, making it an excellent system for hydrogen production by water-splitting. The main challenges for this application are to engineer the band alignments of the TiO_2-based photocatalyst system to utilize visible light instead of ultraviolet and to decrease the recombination rate of photo-excited electron-hole pairs. TiO_2 has been doped with several transition metal ions to reduce its band gap by introducing defect levels in it. These defects are expected to introduce localized states, which promote sub-band-gap absorption in the material. However, experimental studies on transition metal dopants have shown both increase and decrease in photoreactivity of TiO_2 depending on the sample preparation method. The increase in photoreactivity is due to enhanced absorption, while its decrease has been attributed to the recombination of carriers at the defect center. It has been proposed that co-doping transition metal ions with appropriate anions can alleviate the problem of decrease of photoreactivity by charge compensation. We plan to perform calculations using V and Cr ions as substitutional defects and determine CTL's, formation energies, and optical properties. Further, we also plan to assess the effect of co-doping V with N and Cr with C. This is important because in addition to charge compensation, co-doping can potentially change the electronic structure of the system and have unintended consequences on optical properties.

Oxide heterojunctions: The ability to control the length scale, strain, and orbital order in oxides offers a uniquely rich toolbox for designing materials. Because the oxide layers are very thin, the physics is often controlled by the interface. The electronic properties of oxide interfaces are governed by a subtle interplay of many competing mechanisms such as polar catastrophe, Jahn-Teller coupling, electron correlation, defects, and phase stability issues. The sheer number of materials systems is overwhelming: $SrTiO_3$ (STO), $SrRuO_3$ (SRO), $BaTiO_3$ (BTO), $LaAlO_3$ (LAO), $LaTiO_3$ (LTO), $CaMnO_3$ (CMO), $CaRuO_3$ (CRO), and $YMnO_3$ (YMO), to name a few. The properties range from high-k dielectrics to superconducting; ferromagnetic to antiferromagnetic to piezoelectric, ferroelectric and even multiferroic. It is not clear which, if any, of these systems will find applications in future devices. However, they undoubtedly hold tremendous promise. The possibility for building all-oxide electron devices has been suggested following the discovery of the high mobility two dimensional electron gas at the LAO/STO interface. An important development in the field of oxide heterostructures is monolithic integration with Si using MBE. This opened new avenues for band gap engineering, and combining electronic properties of $3d$ electrons in the oxide with those of sp^3 electrons in the semiconductor. We will focus on the perovskite oxides ABO_3, where the d manifold of the transition metal ion can be manipulated both in terms of its occupation and its interactions with the local environment.

Publications from 2009-present.

1. H. Kwak and J.R. Chelikowsky: "Size-dependent Spin-polarization of Carbon-doped ZnO Nanocrystals," Applied Phys. Lett. **95**, 263108 (2009).
2. M. Jain, J. R. Chelikowsky, and S. G. Louie: "Quasiparticle Excitations and Charge Transition Levels of Oxygen Vacancies in Hafnia," Phys. Rev. Lett. **107**, 216803 (2011).
3. M. Jain, J. R. Chelikowsky, and S. G. Louie: "Reliability of hybrid functionals for predicting band gaps," Phys. Rev. Lett. **107**, 216806 (2011).
4. J.K. Lee, N. Sai, and A.A. Demkov: "Spin-polarized 2DEG through electrostatic doping in $LaAlO_3$ EuO heterostructures," Phys. Rev. B **82**, 235305 (2010).
5. N. Sai, K. Leung and J.R. Chelikowsky: "Hybrid density functional study of oligothiophene/ZnO interface for photovoltaics," Phys. Rev. B **83**, 121309 (2011).
6. G. Schofield, J.R. Chelikowsky and Y. Saad: "Using Chebyshev-Filtered Subspace Iteration and Windowing Methods to Solve the Kohn-Sham Problem," *Practical Aspects of Computational Chemistry I: An Overview of the Last Two Decades and Current Trends*, J. Leszczynski and M.K. Shulka, editors, (Springer, Berlin), Chapter 6, p. 167 (2012).
7. G. Schofield, J.R. Chelikowsky and Y. Saad: "A Spectrum Slicing Method for the Kohn-Sham Problem," Comp. Phys. Comm. **183** 497 (2012).
8. N. Marom, J. E. Moussa, Xi. Ren, A. Tkatchenko, and J.R. Chelikowsky: "G0W0 Calculations of Dye-Sensitized TiO_2 Clusters," Phys. Rev. B **84**, 245115 (2011)
9. Y. Saad, J.R. Chelikowsky and S. Shontz: "Numerical Methods for Electronic Structure Calculations of Materials," SIAM Review **52**, 3 (2010).
10. A. Posadas, M. Berg, H. Seo, D.J. Smith, H. Celio, A.P. Kirk, D. Zhernokletov, R.M. Wallace, A. de Lozanne, and A.A. Demkov: "Strain-induced ferromagnetism in correlated oxide $LaCoO_3$ epitaxially grown on Si (100)," Appl. Phys. Lett. **98**, 055104 (2011).
11. A. Posadas, R. Dargis, M. Choi, A. Slepko, J.J. Kim, D.J. Smith, and A.A. Demkov: "Formation of single-orientation epitaxial islands of TiSi2 on Si (001) using Sr passivation," J. Vac. Sci. Technol. B **23**, 1071, (2011).
12. A. Posadas, M. Berg, H. Seo, D.J. Smith, H. Celio, A.P. Kirk, D. Zhernokletov, R.M. Wallace, A. de Lozanne, and A.A. Demkov: "Strain-induced ferromagnetism in $LaCoO_3$: Theory and growth on Si (100)," Microelectronics Engineering, **88**, 1444 (2011).
13. H. Seo and A.A. Demkov: "First-principles study of polar $LaAlO_3$ (001) surface stabilization by point defects," Physical Review B **84**, 045440 (2011).
14. G. Samsonidze, M. Jain, J. Deslippe, M.L. Cohen, and S.G. Louie, "Simple Approximate Physical Orbitals for GW Quasiparticle Calculations," Phys. Rev. Lett. **107**, 186404 (2011).
15. J. Deslippe, G. Samsonidze, M. Jain, M. L. Cohen and S. G. Louie, "Coulomb-hole summations and energies for GW calculations with limited number of empty orbitals: a modified static remainder approach," Phys. Rev. B., in press (2012).
16. J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, Marvin L. Cohena, S. G. Louie, "BerkeleyGW: A Massively Parallel Computer Package for the Calculation of the Quasiparticle and Optical Properties of Materials and Nanostructures," Comp. Phys. Commun. **183**, 1269 (2011).
17. N. Marom, M. Kim and J. R. Chelikowsky: "Structure Selection Based on High Vertical Electron Affinity for TiO_2 Clusters," Phys. Rev. Lett. **108**, 106801 (2012).

Theory of Functionalized Nanostructures

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Project Scope

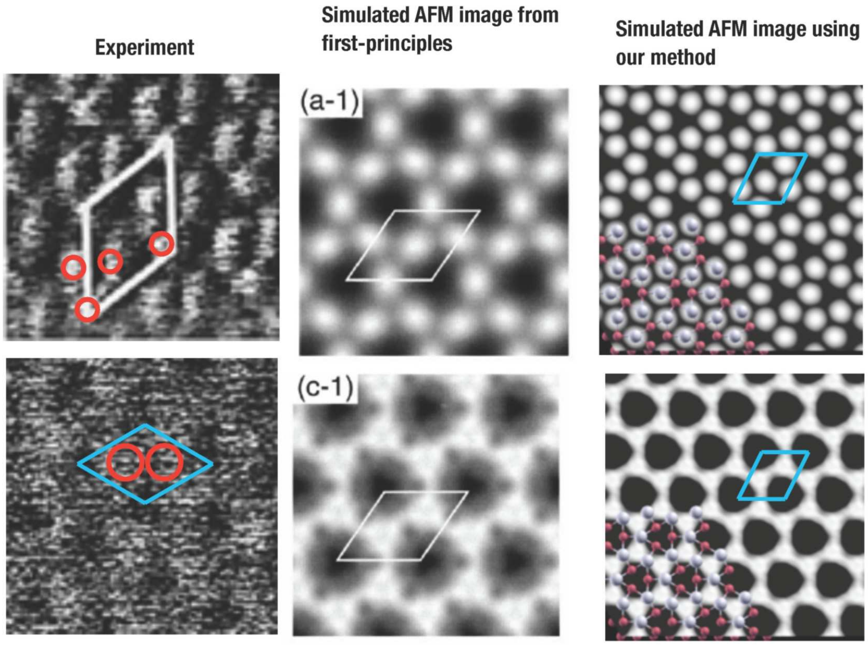
The theme of this research program is to develop and implement theoretical methods for predicting and understanding the properties of functionalized matter at the nanoscale. Within this regime, phenomena occur that are characteristic of neither the atomic limit, nor the macroscopic limit. Such phenomena can have direct consequence for understanding materials appropriate for applications in electronic, optical and spintronic devices. To capitalize properly on predicting such phenomena in this transition (nano) regime, a deeper understanding of the electronic, optical and magnetic properties of matter will be required. Our research program builds on our previous work within this area of study, and explores promising areas of materials and computational research. We focus on the following areas: (a) The electronic and structural properties of dopants relevant for the functionalization of nanostructures (nanocrystals, nanowires, and nanofilms), including both magnetic and non-magnetic dopants. (b) The origin and mechanisms involved in the self-purification process of nanostructures, specifically the energetics and diffusion of defects at both the macroscopic- and nano- scales. (c) The evolution of bulk-like properties from the nano to macro scale, with particular emphasis on the role of dimensionality and quantum confinement. Our proposed areas of research will enhance our understanding materials and the role of quantum confinement and dimensionality at the nanoscale.

Recent progress

We will illustrate our progress by outlining a number of different topics below. Each of these topics corresponds to a published paper as indicated. Unless otherwise stated, we used a real space pseudopotential method to solve the Kohn-Sham problem.

Efficient first-principles simulation of non-contact atomic force microscopy for structural analysis [4]: Atomic force microscopy (AFM) was developed to overcome a basic drawback of scanning tunneling microscopy (STM). STM can only image the surface of conducting or semiconducting materials. AFM has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples. However, one notable drawback of AFM compared to STM concerns the existence of a simple theoretical method for the interpretation of AFM images. Our work addressed this issue. We developed a method to simulate AFM images by employing quantum mechanical approaches to find the force of the substrate on the tip. The presence of the substrate perturbs the vibrational modes of the AFM probe, which determines the AFM image. Our method is simple, requires only a knowledge of the electrostatic potential of the substrate, and can be used to rapidly screen structural models. Most importantly our work does not require a detailed atomistic structure of the AFM probe. Current applications include imaging semiconductor nanocrystals and fragments of DNA and other large biological molecules. An example of an AFM image (see Figure below) using a first principles simulation is shown below for Ag overlaid on a silicon substrate

Controlling Li diffusion in semiconductor nanostructures by size and dimensionality [5]: The ability to control the diffusion of dopants or impurities is a controlling factor in the functionalization of materials used in devices both at the macro- and nanoscales. At the nanoscale, manipulating diffusion of dopants is complicated by a number of factors such as the role of quantum confinement and the



large surface to volume ratio. In this work, we examined Li in Si nanostructures. Atoms with low atomic mass such as Li can be used as a carrier for energy storage with high specific energy capacity. Specifically, Li-ion batteries with specific energy capacity as high as 4200 mAh/g using Si nanowires as anodes have been achieved. We determined how the factors of size and dimensionality can be used to achieve an optimal diffusion of Li atoms in Si nanostructures.

n-type doping via avoiding the stabilization of DX centers in InP quantum dots [9]: We demonstrated that it is preferable to dope III-V semiconductor nanocrystals by n-type anion substitution as opposed to cation substitution. Specifically, we showed the dopability of zinc-blende nanocrystals to be more efficient when the dopants are placed at the anion site as quantified by formation energies and the stabilization of DX-like defect centers. Our results were based on calculations for InP quantum dots doped with Si (cation site) and Se (anion site).

Self-purification in Si nanocrystals [10]: We examined the energetics of dopants in Si nanocrystals to understand the phenomena of "self-purification," *i.e.*, a process by which extrinsic defects in the interior of a nanocrystal are expelled to the surface. Specifically, we calculated the changes in the total energy of a dopant atom in a Si nanocrystal with respect to position. We considered typical dopant atoms such as P, B, and Li. We found that these dopants exhibit different variations in total energies as they move from the center toward the surface of a nanocrystal. These differences can be explained by the change in electronic binding energy and the interaction of the dopant with the surface, *i.e.*, the interaction of a dopant-induced strain with the nanocrystal surface energy. Li dopants are always more stable in the interior of the quantum dot, whereas B and Si are only stable for larger dots.

First-principles study of confinement effects on the Rahman spectra of Si Nanocrystals [11]: We investigated the Raman spectra of Si nanocrystals as a function of nanocrystal diameter using pseudopotential density functional theory and the Placzek approximation. Our calculations reproduce the red-shift and broadening of the optical Raman peak with decreasing nanocrystal size, and calculated peak frequencies showed good agreement with experimental values. We also found that a surface induced softening of vibrational modes is largely responsible for the Raman red-shift, with relaxation of momentum conservation playing only a minor role.

Multidimensional nanoscale materials from fused quantum dots [15]: The synthesis of fused quantum dots offers new possibilities for the design of nanoscale devices. We considered semiconductor InP quantum dots, fused along zinc-blende crystal directions, to construct nanomaterials systematically in one, two, and three dimensions. We solved for and explained the electronic structure of such nanomaterials. We also discussed the potential use of these nanostructures for electronic applications such as current splitters, field-effect transistors, and logic gates.

First-Principles Calculations of Lattice-Strained Core-Shell Nanocrystals [16]: We examined the properties of CdS-ZnS and ZnS-CdS core-shell nanocrystals over a range of shell thicknesses. The effect of structural relaxation was shown to be important as it leads to significant changes in the band gap and frontier orbital localizations. We predicted that strains at the core-shell interface are only affected by addition of the first few shell layers, with subsequent layers producing small changes in the strain configuration. This strain saturation gives rise to a "thin" shell regime in which both confinement and strain effects contribute to the evolution of the band gap and a "thick" shell regime in which band-gap variations from bulk values are strongly dependent on confinement effects but approximately constant with respect to strain.

Charged dopants in semiconductor nanowires with partially periodic boundary conditions [17]: We developed a one-dimensional, periodic real-space formalism for examining the electronic structure of charged nano wires from first principles. The formalism removes spurious electrostatic interactions between charged unit cells by appropriately specifying a boundary condition for the Kohn-Sham equation. The resultant total energy of the charged system remains finite, and a Madelung-type correction is unnecessary. We demonstrated our scheme by examining the ionization energy of P-doped Si $< 110 >$ nanowires. We found that there is an effective repulsion between charged P dopants along the nanowire owing to the repulsive interaction of the induced surface charge between adjacent periodic cells. This repulsive interaction decays exponentially with unit cell size instead of a power law behavior assumed in typical charged calculations.

Planned activities

Our work over the coming year will be centered on the following areas, which by and large will continue our current research activities. We will focus our efforts on the following areas.

- The electronic and structural properties of nanowires. In particular, we plan to examine the *mechanical* properties of Ge nanowires. The mechanical properties of wires show notable differences from bulk materials, *e.g.*, nanowires are often more malleable.
- Raman spectra of Si nanocrystals included in silica. We have examined the role of quantum confinement on Raman lines of isolated Si nanocrystals, but these results appear to be quite different.
- Graphene dot embedded in hexagonal BN sheets. We are interested in how quantum confinement modify the "zero gap" of graphene.
- The role of static electric fields on vibrational modes of molecules and clusters, *i.e.*, the Stark shift in vibrational modes. If we can establish a correspondence between electric fields and vibrational modes, it made be possible to determine the internal electric field in a photovoltaic material by measuring the vibrational modes.
- Imaging defects and dopants at the nanoscale. We will build on recent work simulating atomic force microscopy to learn about the structural and electronic properties of defects at or near the surface of a crystal.

Publications from 2009-present.

1. J.R. Chelikowsky: "Algorithms for Predicting the Physical Properties of Nanocrystals and Large Clusters," *Computational Nanoscience*, *Computational Nanoscience,* RSC Theoretical and Computational Chemistry Series No. 4, editor: Elena Bichoutskaia, (Royal Society of Chemistry, London, 2011), p. 1.
2. T.-L. Chan, A. T. Zayak, G. M. Dalpian, and J. R. Chelikowsky: "Role of Confinement on Diffusion Barriers in Semiconductor Nanocrystals," *Phys. Rev. Lett.* **102**, 025901 (2009).
3. J.R. Chelikowsky, A. T. Zayak, T.-L. Chan, M. L. Tiago, Y. Zhou and Y. Saad: "Algorithms for the Electronic and Vibrational Properties of Nanocrystals," *J. Phys. Cond. Matter* **21**, 064207 (2009).
4. T.-L. Chan, C. Z. Wang, K. M. Ho, and J.R. Chelikowsky: "Efficient first-principles simulation of non-contact atomic force microscopy for structural analysis," *Phys. Rev. Lett.* **102**, 176101(2009).
5. T.-L. Chan and J.R. Chelikowsky: "Controlling lithium diffusion in semiconductor nanostructures by size and dimensionality," *Nano Letters* **10**, 821 (2010).
6. J.-H. Eom, T.-L. Chan and J.R. Chelikowsky: "Vacancies and B doping in Si nanocrystals," *Solid State Commun.* **150**, 130 (2010).
7. M. Lopez del Puerto, M. Jain, and J.R. Chelikowsky: "Time-dependent density functional theory calculation of the Stokes shift in hydrogenated silicon clusters," *Phys. Rev. B* **81**, 035309 (2010).
8. H. Kwak and J.R. Chelikowsky: "Size-dependent Spin-polarization of Carbon-doped ZnO Nanocrystals," *Applied Phys. Lett.* **95**, 263108 (2009).
9. L. V. Besteiro, L. Tortajada, M. L. Tiago, L.J. Gallego, J. R. Chelikowsky, and M. M. G. Alemany: "n-type doping via avoiding the stabilization of DX centers in InP quantum dots," *Phys. Rev. B* **81**, 121307 (2010).
10. T.-L. Chan, H. Kwak, J.-H. Eom, S. Zhang, and J. R. Chelikowsky: "Self-purification in Si nanocrystals: An energetics study," *Phys. Rev. B* **82**, 115421 (2010).
11. K.H. Khoo, A.T. Zayak, H. Kwak and J.R. Chelikowsky: "First-principles study of confinement effects on the Rahman spectra of Si Nanocrystals," *Phys. Rev. Lett.* **105**, 115504 (2010).
12. T.-L. Chan, J. R. Chelikowsky and S. B. Zhang: "An effective one-particle theory for formation energies in doping Si nanostructures," *Appl. Phys. Lett.* **98**, 133116 (2011).
13. J. Han, T.-L. Chan and J. R. Chelikowsky: "Quantum confinement, core level shifts, and dopant segregation in P-doped Si$\langle 110 \rangle$ nanowires," *Phys. Rev. B* **82**, 153413 (2010).
14. J.R. Chelikowsky, T.-L. Chan, M.M.G Alemany and G. Dalpian: "Computational studies of doped nanostructures," *Rep. Prog. Phys.* **74**, 046501 (2011).
15. L. Tortajada, L. V. Besteiro, M. L. Tiago, L. J. Gallego, J. R. Chelikowsky, and M. M. G. Alemany: "Multidimensional nanoscale materials from fused quantum dots," *Phys. Rev. B* **84**, 205326 (2011).
16. K. H. Khoo, J. T. Arantes, J. R. Chelikowsky, and G. M. Dalpian: "First-Principles Calculations of Lattice-Strained Core-Shell Nanocrystals," *Phys. Rev. B* **84**, 075311 (2011).
17. T.-L. Chan, S. Zhang and J.R. Chelikowsky: "Charged dopants in semiconductor nanowires with partially periodic boundary conditions," *Phys. Rev. B* **83**, 245440 (2011).

Computational approach to complex interfaces and junctions

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The scope of this project spans fundamental physical processes at interfaces and across nano-molecular-junctions, with emphasis on electronic transport, via large-scale computation and simulation. Theoretical treatment for electronic degrees of freedom is mainly at the level of density functional theory with generalized gradient approximations. Various theories, methods and techniques including scattering theory, non-equilibrium green functions, the density matrix method, Boltzmann transport theory, classical molecular dynamics, and van der Waals corrections etc. are used to calculate physical and chemical quantities needed for addressing problems and issues. We focus on problems in complex interfaces and junctions, including a) electron transport through metal-azobenzene-molecule-metal junctions, where the molecule can transform between trans and cis configurations in response to light excitation; b) bonding, atom diffusion, and magnetization in systems containing the tris(8-hydroxyquinolino) aluminum (Alq_3) molecule between two magnetic leads, for its role as an insulator spacer in magnetic tunneling junctions; and c) electron dynamics coupled with structural relaxation and phonon-electron interaction after photo-excitation in carbon nanotubes and graphene that are functionalized by adsorbed organic molecule. One common theme unifying these systems is that interfacial structure has critical effects on properties, and our investigations based on first-principles can provide not only interpretation but also guidance for experiments on these seemingly vastly different systems. Finally, we include a major effort to develop a new method and algorithms. Based on scattering theory, our method combines a layer approach and a planewave basis in conjunction with pseudo-potentials. The method is optimal for studying electron transport across molecular- and nano-junctions

Recent Progress

Azobenzene molecular junctions

We investigated from first principles the change in transport properties of a two-dimensional azobenzene monolayer, sandwiched between two Au electrodes, that undergoes molecular switching (Fig.1) [1]. We focused on transport differences between a chemisorbed and a physisorbed top monolayer-electrode contact. The conductance of the monolayer junction with a chemisorbed top contact is higher in the *trans* configuration, in agreement with previous theoretical results for one-dimensional, single molecule junctions. However, with a physisorbed top contact, the ”ON” state, with larger conductance, is associated with the *cis* configuration due to a reduced effective tunneling pathway, which successfully explains recent experimental measurements on azobenzene monolayer junctions. A simple model was developed to explain electron transmission across subsystems in the molecular junction, that is, $T = T_{bc} \cdot T_{mol}^{pl} \cdot T_{mol}^{p2} \cdot T_{tc}$, where T_{bc} and T_{tc} are transmission coefficients of the two contacts and the two middle factors are effective transmission coefficients of the two molecular segments. We also studied effects on the calculated transmission functions of monolayer packing density, molecule tilt angle, and contact geometry. In particular, we find that a tip-like contact with chemisorption significantly affects the electric current through the *cis* monolayer, leading to highly asymmetric current-voltage characteristics as well as large negative differential resistance behavior.

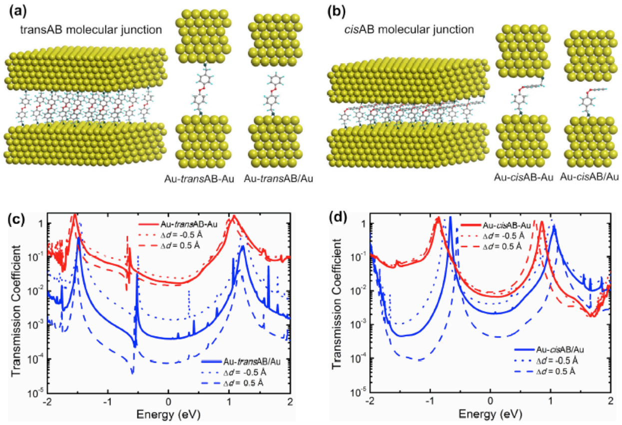

Fig. 1: Equilibrium geometries (a-b) and zero-bias electron transmission functions (c-d) of *trans* and *cis* monolayer junctions with two types of top contact. In panels (c) and (d) the y-axis is on a logarithmic scale, and the Fermi level is shifted to 0. The quantity Δd represents the change in the electrode-electrode separation for a junction with its geometry slightly away from the equilibrium structure.

Adsorption of Alq$_3$ molecules on cobalt surfaces

We studied the adsorption of tris(8-hydroxyquinoline) aluminum (Alq$_3$) molecules on cobalt surfaces using density functional theory with the generalized gradient approximation [2]. The van der Waals interaction between Alq$_3$ molecules and cobalt surfaces was included by the dispersion correction. Magnetization of Alq$_3$ molecules, adsorption energies, and bonding energies were obtained for smooth and defective surfaces and for various molecule-surface configurations. Electronic structures were analyzed for states that are relatively stable. We found that both the permanent electric dipole of Alq$_3$ molecules and charge redistribution near the interface contribute to the interface dipole, and the interface dipole due to charge redistribution is important to determine the work function of a Co/Alq$_3$ surface. Our calculated energy-level alignment at interfaces is consistent with experimental observations.

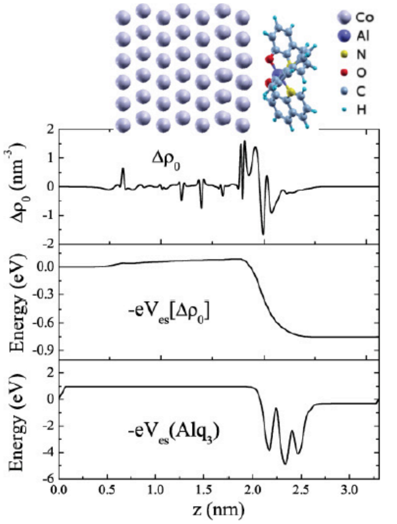

Fig.2 The *x*-*y*-plane-averaged charge redistribution (top) when facial Alq$_3$ molecules are adsorbed on a smooth cobalt surface, the resulting electrostatic energy (middle), and the electrostatic energy of the facial Alq$_3$ molecule layer (bottom). A side view of the configuration is illustrated by the topmost picture.

Method and code development

After completing an algorithm that combines the idea of scattering theory that underlies the layer Korringa-Kohn-Rostoker (KKR) electronic structure code [3] and pseudopotentials in conjunction with a planewave expansion, we started code development for electronic transport and complex band calculations. The basic equation for each slice is written as, $\Psi_{out} = \underset{\sim}{S}\Psi_{in} + \Phi_o$, where $\underset{\sim}{S}$ is the scattering matrix when the local potential is present alone, and Φ_o is the special solution including the non-local potential. Our code interfaces with the Quantum Espresso package and will also utilize subroutines from the layer KKR code. Since the beginning of the new funding period, 12/1/2011, we have finished coding and testing the module of scattering due to the local part of the pseudopotential. This development is

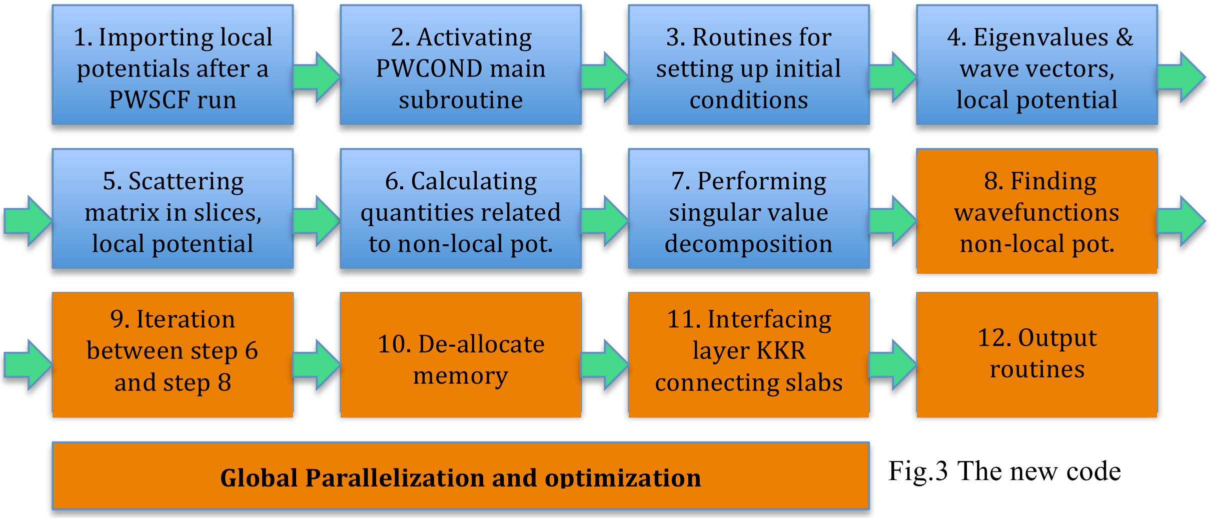

Fig.3 The new code

one significant step beyond our effort [4] that generalizes the current implementation of planewave-based transport theory in PWCOND. The calculated transmission coefficients can be used as inputs in the Boltzmann equations to compute account for resistance of grain boundaries for metal junctions. [4] Fig.3 is a simplified flow chart of our new code. The blue blocks indicate the finished subroutines, and the orange ones are parts we plan to work on in near future.

Plan for Now through 2014

In the remaining time of this funding period we plan to code calculations involving the non-local part of psudopotentials in a sequence of 2D slices in which the potential is to be constant. The orange blocks in Fig.3 are subroutines yet to be written. This part is very different from the layer KKR approach, because the non-local nature of the potential makes slices inseparable. Singular value decomposition is therefore used to reduce the computational intensity of the eigenvalue calculations. Our code is designed that when the scattering region can be physically divided into regions between which there is no overlap of core potentials, layer KKR techniques will be used to connect the regions (or slabs, see block 10).

We plan to continue investigations of electronic and transport properties of azobenezene molecules under various physical conditions and environments. We will continue to investigate the role of contact geometry in systems depicted in Fig.1, and the difference in transport behavior between 1D and 2D contacts. One other problem concerning azobenzene molecules is the electron-hopping rate between two quantum dots (Fig.4). In the quantum dot arrays, electron transport is mainly achieved by the hopping mechanism, as illustrated in our prior studies using a molecule much simpler than azobenzene [5]. In the next two years, we plan to investigate the hopping rate as a function of the size of quantum dots.

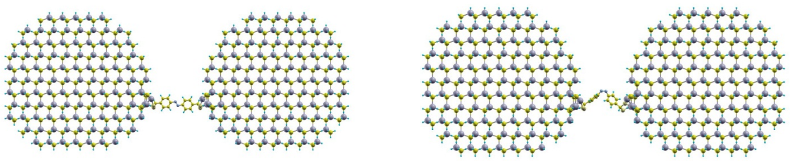

Fig. 4 Two 1916-atom CdSe particles connect by an azobenzene: left, trans; right, cis.

The second molecular system is a complex containing a pyrene, a CH_2 chain and two NO_2 groups that is anchored on semiconducting carbon nano-tubes (CNTs). Upon optical excitation, we will investigate phonon-assisted charge transfer from CNTs to the two molecular NO_2. Using reduced density matrix formulae, we plan to investigate electron relaxation dynamics and electron and hole relaxation times. To do so, it is necessary to obtain the interface binding between the molecular complex and CNTs for which the van der Waals functional is important, and needs to be validated by comparing with GGA+empirical vdW and experiments.

The third group of molecular systems belongs to the single molecule nano-magnet family, which consists of a $[MnO]_n$ core organic ligands. The spin states of these molecules have been studied extensively. Our interest is on the molecular magnetocapacitance, a completely new concept we introduced recently [6]. We plan to study the charging energy of $[MnO]_n$ (n=3,12, etc) as functions of spin states, from which the magnetocapacitance can be defined, i.e. $MC = \frac{C_{HS} - C_{LS}}{C_{LS}}$, where HS and LS represents high and low spin states, respectively. The difference in capacitance between the two state results in an "on" and "off" switching in conductance when these molecules are used in single-molecule junctions. We plan to search for molecules with large MC and with a small magnetic field required to convert low spin ground state to high spin state.

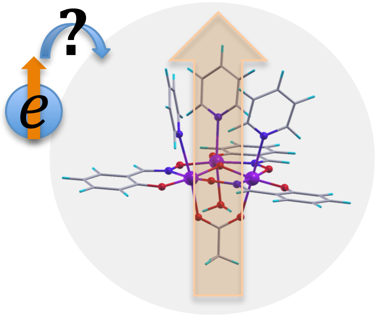

Fig.5 The charging energy of $[Mn]_3$ varies depending on spin

1. Wang, Y. and H.-P. Cheng, *Electronic and transport properties of azobenzene monolayer junctions as molecular switches.* Physical Review B, 2012, accepted.
2. Wang, Y.-P., X.-F. Han, Y.-N. Wu, and H.-P. Cheng, *Adsorption of tris(8-hydroxyquinoline)aluminum molecules on cobalt surfaces.* Physical Review B, 2012. **85**(14): p. 144430.
3. MacLaren, J.M., S. Crampin, D.D. Vvedensky, R.C. Albers, and J.B. Pendry, *Layer Korringa-Kohn-Rostoker electronic-structure code for bulk and interface geometries.* Comput. Phys. Comm., 1990. **60**(3): p. 365.
4. Srivastava, M.K., Y. Wang, X.Y. Zhang, D.M.C. Nicholson, and H.-P. Cheng, *Plane wave transport method for low symmetry lattices and its application.* Physical Review B, 2012, submitted.
5. Chu, I.-H., M. Radulaski, N. Vukmirovic, H.-P. Cheng, and L.-W. Wang, *Charge Transport in a Quantum Dot Supercrystal.* Journal of Physical Chemistry C, 2011. **115**(43): p. 21409-21415.
6. Wu, Y.-N., X.Y. Zhang, and H.-P. Cheng, *Molecular magnetocapacitance.* http://arxiv.org/abs/1205.0855, 2012.

First-Principles Investigation of Complex Materials Properties

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Project Scope

This project concentrates on studying complex materials properties using first-principles electronic-structure methods. The computational tools that we will employ include density functional theory (DFT) within the local-density or generalized gradient approximation (LDA or GGA), the pseudopotential method with a plane-wave basis, quantum Monte Carlo methods for systems with considerable electron correlation, density-functional perturbation theory for the vibrational properties, and nonequilibrium Green's function methods for electron transport. Our goal is to unambiguously explain the phenomena observed in the experiment and to reliably predict new materials properties. Recently, we have focused on low-dimensional electronic systems that exhibit interesting physics not present in typical bulk systems. In particular, we have concentrated on studying the interesting properties of graphene and semiconductor nanowires. Graphene has been recognized as a unique system containing two-dimensional fermions with linear dispersions near the Fermi level. The recent success in fabricating graphitic samples consisting of only a few layers of carbon sheets has revealed intriguing properties of this system. We have initiated a computational effort in the current funding period and have identified several important projects to be covered in the next year.

Recent Progress

(a) Charge transport through graphene junctions with wetting metal leads

Graphene is believed to be an excellent candidate material for next-generation electronic devices. However, one needs to take into account the nontrivial effect of metal contacts in order to precisely control the charge injection and extraction processes. We have performed state-of-the-art charge transport calculations for graphene junctions with Ti contacts using Green's functions and density functional theory. The potential profile across the junction follows a simple exponential or power-law behavior at different sections. The calculated energy-dependent conductance exhibits strong fluctuations due to contact scattering. We have reported a quantitative estimate of the reduced transparency of these junctions and have analyzed its fluctuations statistically. We have shown that these fluctuations cannot be attributed exclusively to Fabry-Perot oscillations, but that they must be due to energy- and transverse k-point-specific contact scattering. The statistical distribution of transmission eigenvalues matches to numerical precision that of a diffusive wire. We conclude that transport through the studied junction is pseudo-diffusive to our statistical accuracy. Accordingly, the shot noise through the studied junctions has a Fano factor close to 1/3, in agreement with experiment. The results represent a vast improvement over the previous theoretical modeling of transport through graphene junctions, indicating the relevance of the electronic structure at the metal/graphene interfaces for graphene devices.

(b) Fractal Landau-Level Spectra in Twisted Bilayer Graphene

The Hofstadter butterfly spectrum for Landau levels in a two-dimensional periodic lattice is a rare example exhibiting fractal properties in a truly quantum system. However, the observation of this physical phenomenon in a conventional material will require a magnetic field strength several orders of magnitude larger than what can be produced in a modern laboratory. It turns out that, for a specific range of rotational angles, twisted bilayer graphene serves as a special system with a fractal energy spectrum under laboratory accessible magnetic field strengths. This unique feature arises from an intriguing electronic structure induced by the interlayer coupling. Using a recursive tight-binding method, we systematically map out the spectra of these Landau levels as a function of the rotational angle. Our results give a complete description of LLs in twisted bilayer graphene for both commensurate and incommensurate rotational angles and provide quantitative predictions of magnetic field strengths for observing the fractal spectra in these graphene systems.

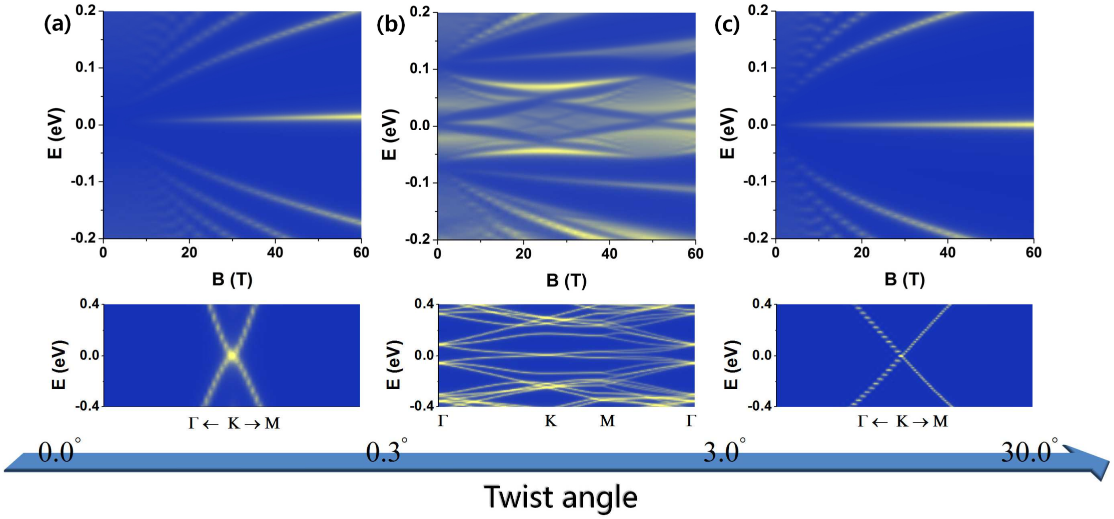

Figure 1. Landau-level spectra for twisted bilayer graphene at three commensurate angles representing three ranges of the twist angle θ.

(c) Enhanced optical conductivity induced by surface states in ABC-stacked few-layer graphene

We have investigated the evolution of the surface states in ABC-stacked few-layer graphene and their effects on the optical conductivity. These surface states are localized on one single sublattice in the outermost layers, and the amplitudes decay exponentially into the inner layers. The surface bands are quite flat around K in the Brillouin zone, and the flat region increases as the layer number increases. The formation of these surface states is well elucidated by a tight-binding model. Compared with AB-stacked few-layer graphene, the surface states in ABC-stacked few-layer graphene have significant effects on the optical absorption spectra. The infrared optical conductivity is calculated within the single-particle excitation picture. These surface states introduce pronounced absorption peaks at around 0.3 eV in the optical conductivity spectra of ABC-stacked few-layer graphene when the polarization is parallel to the sheets, in good agreement with recent experimental measurement. As the layer number increases, the absorption amplitudes are greatly enhanced due to the strong localization of the surface states, and the absorption peak red-shifts as the layer number increases, providing a feasible way to identify the number of layers for ABC-stacked few-layer graphene using optical conductivity measurements.

Interestingly, the absorption due to the surface states is sensitive to the polarization direction. The enhanced absorption can only be found for the polarization parallel to the graphene sheets.

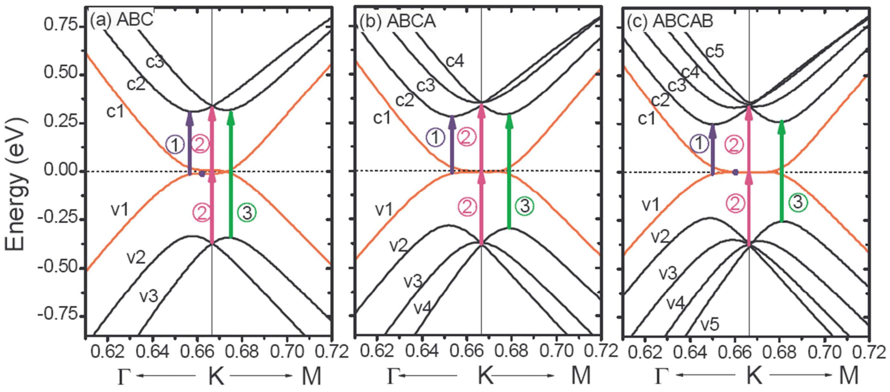

Figure 1. Band dispersions for (a) ABC, (b) ABCA, and (c) ABCAB few-layer graphene in the vicinity of the Fermi level. The surface states are the flat bands near the Fermi level. The valence and conduction bands are labeled. The main allowed optical transitions between different sets of valence and conduction bands are indicated by arrows. For clarity, transition 1 between v2 and c1 is not marked.

Future Plans

Wave-Packet Dynamics in Twisted Bilayer Graphene

It has been shown recently that high-quality epitaxial graphene (EPG) can be grown on the SiC substrate that exhibits interesting physical properties. In particular, the multilayer graphene films grown on the C-face show rotational disorder. It is expected that the twisted layers exhibit unique new physics that is distinct from that of either single layer graphene or graphite. In this work, the time-dependent wave-packet propagation in twisted bilayer graphene (TBG) will be studied based on a tight-binding model with parameters derived from density functional theory. Our study is designed to reveal the intriguing dynamical behavior of electrons in TBG, which is related to the specific interlayer coupling. By varying the twist angle and the initial wave packet, we can effectively control the propagation of electrons in TBG.

Magnetism in Graphene Derivatives

Traditional magnetic materials are based on transition metals such as Fe, Co and Ni, where the magnetic ordering originates from the partially filled d bands. Metal-free carbon structures exhibiting magnetic ordering represent a new class of materials. The central problem is to understand the origin of magnetism in a system containing only s- and p-electrons and traditionally thought to show diamagnetic behavior only. Lieb's theorem provides the base for theoretical studies of graphene magnetism, which states that for a bipartite system with N_A and N_B atoms, the number η of midgap states is given by the imbalance of A and B atoms in the system, $\eta = |N_A - N_B|$; If these midgap states are half-filled, the total spin of the ground state is, according to Hund's rule, given by $S = |N_A - N_B|/2$. Lieb's theorem was proved rigorously within the Hubbard model and has been applied successfully to count the ground-state magnetic moments of graphene vacancy defects and graphene fragments with a simple edge. It is, however, physically unclear why the number of midgap states and the imbalance of atomic A and B sites are relevant. In additions, while the ground state magnetic moments of graphene derivatives have always been found to agree with Lieb's theorem, it has also been known to undercount the midgap states of some fragments with a complex geometry such as the Clar's goblets. A counting rule based on the number of the dangling π-bonds will be developed for determining the midgap states and ground state magnetic moments consistently. Examples will be given to demonstrate their presence and the physical consequences of their interactions.

Publications (2009-2012)

1. "Electron-Phonon Interactions for Optical Phonon Modes in Few-Layer Graphene," J.-A. Yan, W. Y. Ruan, and M. Y. Chou, Phys. Rev. B 79, 115443 (2009).
2. "First-Principles Investigation of Sodium and Lithium Alloyed Alanates," Z. Ma and M. Y. Chou, J. Alloys Compd. 479, 679 (2009).
3. "Phase Relations Associated with One-Dimensional Shell Effects in Thin Metal Films," T. Miller, M. Y. Chou, and T.-C. Chiang, Phys. Rev. Lett. 102, 236803 (2009).
4. "Path to Wigner Localization in Circular Quantum Dots," L. Zeng, W. Geist, W.Y. Ruan, C.J. Umrigar, and M.Y. Chou, Phys. Rev. B 79, 235334 (2009).
5. "Structural and Electronic Properties of Oxidized Graphene," Jia-An Yan, Lede Xian, and M. Y. Chou, Phys. Rev. Lett. 103, 086802 (2009).
6. "Effects of Metallic Contacts on Electron Transport through Graphene," S. Barraza-Lopez, M. Vanevic, M. Kindermann, and M. Y. Chou, Phys. Rev. Lett. 104, 076807 (2010).
7. "Low-Lying Spectra of Massless Dirac Electrons in Magnetic Dots and Rings," C. M. Lee, R. C. H. Lee, W. Y. Ruan, and M. Y. Chou, Appl. Phys. Lett. 96, 212101 (2010).
8. "Quantum Size Effects on the Work Function of Metallic Thin-Film Nanostructures," J. Kim, S. Qin, W. Yao, Q. Niu, M. Y. Chou, and C.-K. Shih, Proc. Natl. Acad. Sci. 107, 12761 (2010).
9. "Energy Spectra of a Single-Electron Magnetic Dot Using Massless Dirac-Weyl Equation," C. M. Lee, R. C. H. Lee, W. Y. Ruan, and M. Y. Chou, J. Phys.: Condens. Matter 22, 355501 (2010).
10. "Theoretical Investigation of Intermediate Phases between Li_2NH and $LiNH_2$," Feng Zhang, Yan Wang, and M. Y. Chou, Phys. Rev. B 82, 094112 (2010).
11. "Oxidation Functional Groups on Graphene: Structural and Electronic Properties," J.-A. Yan and M. Y. Chou, Phys. Rev. B 82, 125403 (2010).
12. "Stability of the Hydrogen-storage Compound $Li_6Mg(NH)_4$ from First Principles," by Feng Zhang, Yan Wang, and M. Y. Chou, Phys. Rev. B 83, 012101 (2011).
13. "Theoretical Study of the Vibrational Properties of $NaAlH_4$ with AlH_3 Vacancies," Feng Zhang, Yan Wang, and M. Y. Chou, Faraday Discussion 151, 243 (2011).
14. "Catalytic Effect of near-Surface Alloying on Hydrogen Interaction on the Aluminum Surface," Y. Wang, F. Zhang, P. Lin, R. Stumpf, and M. Y. Chou, Phys. Rev. B 83, 195419 (2011).
15. "Lattice Vibrational Modes and their Frequency Shifts in Semiconductor Nanowires," L. Yang and M. Y. Chou, Nano Lett. 11, 2618 (2011).
16. "Enhanced Optical Conductivity Induced by Surface States in ABC-stacked Few-Layer Graphene," J. Yan, W. Ruan, and M. Y. Chou, Phys. Rev. B 83, 245418 (2011).
17. "Effect of Electrostatic Fields and Charge Doping on the Linear Bands in Twisted Graphene Bilayers," L. Xian, S. Barraza-Lopez, and M. Y. Chou, Phys. Rev. B 84, 075425 (2011).
18. "Phase Diagram of Graphene Nanoribbons and Band-Gap Bifurcation of Dirac Fermions under Quantum Confinement," Y. Y. Sun, W. Y. Ruan, X. Gao, J. Bang, Y. H. Kim, K. Lee, D. West, X. Liu, T.-L. Chan, M. Y. Chou, and S. B. Zhang, Phys. Rev. B 85, 195464 (2012).
19. "Charge Transport through Graphene Junctions with Wetting Metal Leads," S. Barraza-Lopez, M. Kindermann, and M. Y. Chou, Nano Lett. 12, 3424 (2012).
20. "Fractal Landau-Level Spectra in Twisted Bilayer Graphene," Z. F. Wang, F. Liu, and M. Y. Chou, Nano Lett. 12, 3833 (2012).
21. "Optical Phonon Anomaly in Bilayer Graphene with Ultrahigh Carrier Densities," J.-A. Yan, K. Varga, and M. Y. Chou, Phys. Rev. B (in press).

DYNAMICS OF THE MAGNETIC FLUX IN SUPERCONDUCTORS

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I. PROJECT SCOPE

Recently pursued research topics include dynamics of the magnetic flux induced by the motion of dislocations in a type-II superconductor subjected to mechanical stress, instanton-glass model of a superconductor-insulator transition in disordered thin films, spin-Hall effect in anisotropic crystals, classical and quantum theory of electromagnetic coupling between superconducting weak link and a nanomagnet, and a theory of macroscopic quantum tunneling of the magnetic flux in the intermediate state of a type-I superconductor. Current work and research planned for the nearest future include extension of the superinsulator model that takes into account quantized vortices, studies of the magnetization reversal in a nanomagnet inside a Josephson junction, rotational dynamics of a two-state system and generic decoherence of a flux qubit due to conservation laws, computation of the tunneling rate for a superconductor - normal metal interface in type-I superconductors, computation of the lifetime of skyrmions in cuprates and other layered materials, and exploration of a skyrmion-molecule model of electron pairing in high-temperature superconductors. The DOE sponsored research is integrated with education through involvement of graduate and undergraduate students.

II. RECENT PROGRESS

Superinsulator as an Instanton Glass

We have studied correlations of the order parameter in a two-dimensional array of strongly coupled superconducting grains in the presence of weak Gaussian noise [1]. The prevailing view has been that the ground state of a granular superconductor depends on the ratio of the Josephson coupling energy and the charging energy. If this ratio is large, the Cooper pairs move freely between the grains and the system is a superconductor. If the ratio is small, then moving an excess charge into the grain costs too much energy and the Cooper pairs are localized. We have shown that the phase correlations decay exponentially, in both space and imaginary time, regardless of the above ratio and of the amplitude of the noise, pointing towards the insulating state at temperatures below the finite localization energy. This effect is pertinent to 2+1 dimensions and does not appear in a 3d superconductor.

Dependence of the Spin Hall Effect on Crystal Symmetry

This study has been a continuation of the earlier work of the PI on spin Hall effect. Most of the existing theoretical models use Boltzmann-type kinetic equation to describe spin and charge transport under certain assumptions about spin-orbit interaction, nature of scatterers, band structure, and boundary effects. The PI suggested a simple theory based upon Aharonov-Casher effect.

Parameter-free expression for the spin Hall conductivity was obtained for cubic crystals that agreed with experiments. A number of experiments on spin Hall effect were performed in noncubic crystals. In a follow-up paper [2] we derived the fictitious spin-dependent magnetic field for anisotropic crystals. It produces the same effect on the orbital motion of electrons as the real magnetic field does in the conventional Hall effect, but with the Hall currents having opposite directions for electrons with opposite spin polarizations. This effect has been computed explicitly for crystals of tetragonal symmetry and experiment has been suggested that can test our predictions.

Interaction of a Weak Superconducting Link with a Nanomagnet

In Ref. [3] we studied interaction between a nanomagnet and a superconducting weak link. The magnetic field of the nanomagnet alters the Josephson current flowing through the link, while the magnetic flux generated by the Josephson junction acts on the magnetic moment of the nanomagnet. We derived and solved numerically the dynamical equations describing a coupled nanomagnet - weak link system in classical and quantum limits. Three problems have been investigated: Shapiro-type steps generated by the magnet in the I-V curve of the link, the reversal of the magnetic moment by a time-dependent bias voltage in the link, and Rabi oscillations of the quantum spin induced by a constant bias voltage. A remarkable observation is that despite the weakness of the field generated by the tunneling current of the link, for a certain time dependence of the bias voltage it can effectively pump spin excitations into the magnet, leading to the reversal of its magnetic moment. Study of the quantum problem has demonstrated that a spin qubit can be successfully manipulated by the voltage on the Josephson junction.

Quantum Tunneling of Interfaces in Type-I Superconductors

Quantum tunneling of flux lines in type-II superconductors has been subject of intensive research in the past. In Ref. 4 we demonstrated that similar effects exist in type-I superconductors. The model of dissipative macroscopic quantum tunneling of normal-superconducting interface in type-I superconductor was developed and the temperature of the crossover from thermal activation to quantum tunneling was estimated. The PI has initiated experimental work that confirmed theoretical predictions through measurements of non-thermal low-temperature magnetic relaxation of lead samples. In a follow up work [5] mathematical model has been developed, that describes current-driven quantum depinning of the interface from a grain boundary or from artificially manufactured pinning layer. Crossover between thermal activation and quantum tunneling has been studied and the crossover temperature has been computed. Our results, together with recent observation of non-thermal low-temperature magnetic relaxation in lead, suggest possibility of a controlled measurement of quantum depinning of the interface in a type-I superconductor.

Conservation of Angular Momentum and Decoherence of a Flux Qubit

Rotational dynamics of a two-state system has been studied in application to decoherence of a superconducting flux qubit [6, 7]. Entanglement of quantum states of the qubit with quantum states of a macroscopic body, dictated by the conservation of angular momentum, has been investigated within an exactly solvable rigid-body model and for the elastic model that takes into account internal elastic torques. We show that while the quantum state of a flux qubit is, in general, a mixture of a large number of rotational states, slow decoherence is permitted if the system is sufficiently large. Practical implications of this research include dependence of decoherence

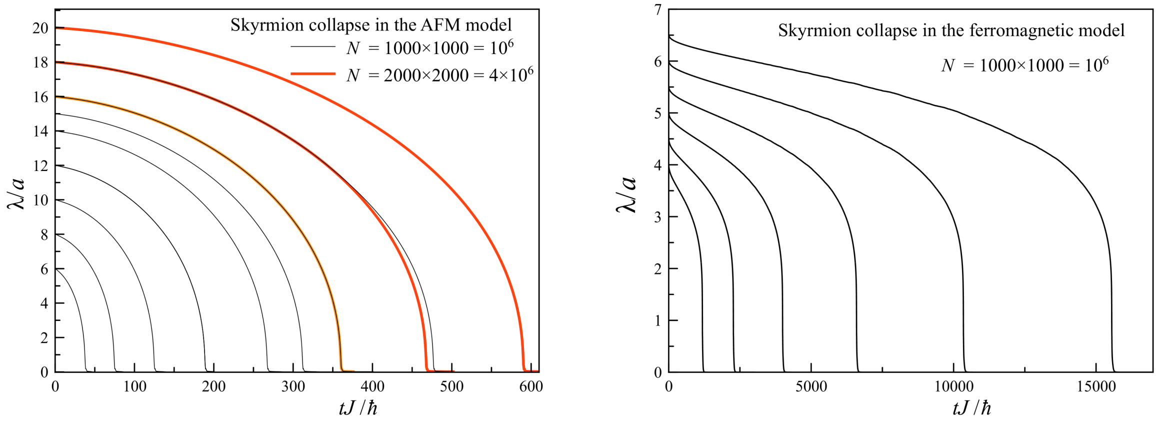

FIG. 1. *Left*: Skyrmion collapse in an antiferromagnet for different initial skyrmion sizes. The collapse time scales as $t_c \propto \lambda_0^{2.15}$. *Right*: Skyrmion collapse in a ferromagnet. The collapse time scales as $t_c \propto \lambda_0^5$.

on rotational states of nanomechanical devices incorporating SQUIDs, decoherence from strain relaxation in solids, enhanced decoherence due to superradiant emission of acoustic waves by an assembly of flux qubits, and others.

Lifetime of Skyrmions in Cuprates and Other Layered Materials

Many undoped parent compounds of high-temperature superconductors, such as cuprates and pnictides, have weakly coupled antiferromagnetic layers that possess topological spin excitations such as skyrmions. We have studied collapse of a skyrmion due to the discreteness of a crystal lattice analytically and by numerical solution of equations of motion for up to 2000×2000 classical spins on a square lattice coupled via Heisenberg exchange interaction J. Excellent agreement between analytical and numerical results has been achieved. The lifetime of the skyrmion scales with its initial size, λ_0, as $(\lambda_0/a)^5$ in ferromagnets and as $(\lambda_0/a)^{2.15}$ in antiferromagnets, with a being the lattice parameter, see Fig. 1. This makes antiferromagnetic skyrmions significantly shorter lived than ferromagnetic skyrmions.

III. FUTURE PLANS

Instanton Glass in the Magnetic Field

So far we have studied the superinsulator state of a disordered film in the absence of the external magnetic field. The magnetic field is known to suppress Josephson tunneling. A more subtle effect of the field consists of the introduction of vortices into the film. It is easy to modify our instanton equations to include N quantized vortices. Computation of the path integral for the correlation function of the superconducting order parameter with account of vortices will be one of the directions of our research. We are currently performing large scale computer simulations of the random phase model in 2+1 dimensions. It resembles the random-anisotropy XY model that has been studied in the past by renormalization group methods, with conflicting results obtained by various groups. The increased computer capabilities now permit numerical studies of the weak disorder regime, which has not been done before. Preliminary results show important contribution of the topological defects to the correlation functions.

Josephson Junction with a Nanomagnet

In a follow up on our study of the manipulation of a nanomagnet by voltage across the Josephson junction, we are investigating the optimal regime for the reversal of the magnetic moment by a time-dependent voltage. This problem is being addressed by us with the use of both, numerical and analytical methods. We have already demonstrated that the analytical problem reduces to a variance of the Landau-Zener problem and are now working on the exact analytical solution for the magnetization reversal in the absence of damping. The problem with damping will be addressed numerically. Preliminary results show that moderate damping does not prevent the magnetic moment from the full reversal. The goal is to obtain the phase diagram that would show the areas of the reversal plotted as function of the rate at which the voltage is changing, the amplitude of the RF field at the location of the nanomagnet, and the damping parameter.

Electron-Skyrmion States in Parent Compounds of Layered Superconductors

The existence of competing magnetic and superconducting phases in layered high-temperature superconductors has made many people to speculate about the role of spin fluctuations in pairing electrons. Skyrmions have been studied in this context by a number of researchers. We have recently contributed to these studies by computing the lifetime of skyrmions in 2d ferro- and antiferromagnetic lattices. Very short lifetimes of antiferromagnetic skyrmions have been obtained in the absence of interactions other than the exchange interaction between nearest-neighbor spins in the lattice. The next step is to see whether doping can form stable electron-skyrmion (hole-skyrmion) structures that may be relevant to the pseudogap and superconducting phases. Modification of the skyrmion texture by the electron spin and by the interlayer coupling will be studied. We also plan to investigate the renormalization of the coupling between skyrmion pairs due to RKKY interaction in the background of charge carriers.

IV. PUBLICATIONS THAT RESULTED FROM THE DOE SPONSORED RESEARCH (2009 - 2012)

[1] E. M. Chudnovsky, Instanton glass generated by noise in a Josephson-junction array, Physical Review Letters **103**, 137001 (2009).

[2] E. M. Chudnovsky, Intrinsic spin Hall effect in noncubic crystals, Physical Review B **80**, 153105 (2009).

[3] L. Cai and E. M. Chudnovsky, Interaction of a nanomagnet with a weak superconducting link, Physical Review B **82**, 104429 (2010).

[4] E. M. Chudnovsky, S. Velez, A. Garcia-Santiago, J. M. Hernandez, and J. Tejada, Quantum tunneling of the interfaces between normal-metal and superconducting regions of a type-I Pb superconductor, Physical Review B **83**, 064507 (2011).

[5] R. Zarzuela, E. M. Chudnovsky, and J. Tejada, Dissipative macroscopic quantum tunneling in type-I superconductors, Physical Review B **84**, 184525 (2011).

[6] M. F. O'Keeffe, E. M. Chudnovsky, and D. A. Garanin, Quantum tunneling of the magnetic moment in a free particle, Journal of Magnetism and Magnetic Materials **324**, 2871 (2012).

[7] E. M. Chudnovsky, D. A. Garanin, and M. F. O'Keeffe, Conservation of angular momentum in a flux qubit, Journal of Superconductivity and Novel Magnetism **25**, 1007 (2012).

[8] Liufei Cai, E. M. Chudnovsky, and D. A. Garanin, Collapse of skyrmions in two-dimensional ferromagnets and antiferromagnets, Physical Review B **86**, 024429 (2012).

Theory of layered organic and inorganic materials with charge-spin frustration

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Project Scope

This project focuses on understanding the properties of correlated electrons in two dimensional (2D) frustrated systems. We propose a bottom-up approach to the theory of superconductivity (SC) in organic charge-transfer solids (CTS) and related materials. We note that the antiferromagnetic-to-superconductor transition found within resonating valence-bond (RVB) theories of the $\frac{1}{2}$-filled band Hubbard model on a triangular lattice is an artifact of approximations [2]. Since transitions to SC in the CTS occur from antiferromagnets as well as from correlated charge-ordered semiconductors, these different types of semiconductors must be linked. We discuss a pressure-induced lattice frustration-driven transition from antiferromagnetism (AFM) to a paired-electron crystal (PEC), within the dimerized $\frac{1}{4}$-filled band with strongly interacting electrons [6,9]. We propose that further frustration drives a PEC-to-SC transition. The electron-pairs within our model are the mobile pseudo-molecules in Schafroth's theory of SC. We further propose that this theory can be applied to the layered cobaltates, spinels, as well as the hydrocarbon superconductors K_3phenanthrene, K_3picene, and K_3dibenzopentacene, which we argue have effectively $\frac{1}{4}$-filled bands.

Recent Progress

Absence of superconductivity in the frustrated $\frac{1}{2}$-filled band Hubbard model [2]

Many authors have proposed RVB and spin-fluctuation mediated theories of pairing within the $\rho = 1$ triangular lattice Hubbard model (ρ is the carrier density per site). In particular, because of their dimerized structure with one electron or hole per dimer, the $\rho = 1$ anisotropic model has long been proposed to describe the electronic properties of the κ-(BEDT-TTF)$_2$X family of superconductors. We have calculated superconducting correlations for large triangular lattices using the *Path Integral Renormalization Group* (PIRG) technique [2]. The large lattice calculations demonstrate unambiguously that (i) superconducting pair-pair correlations decrease monotonically with increasing Hubbard repulsion U for inter-pair distances greater than nearest neighbor, and (ii) the distance dependence of the correlations is the same as that within the noninteracting electrons model. We conclude that SC is not obtained within the $\rho = 1$ frustrated Hubbard model, and this model cannot describe SC in the CTS superconductors.

Layered cobaltates [3,5,7]

The organic CTS superconductors have often been compared to the cuprates because of their two dimensionality and the existence of AFM adjacent to SC. We have recently pointed out that in fact the organics are even more similar to another class of strongly-correlated superconductor, the layered cobaltates. Both the organics and the cobaltates are 2D and have frustrated lattices. We have recently shown that the same mechanism can explain the systematic variation of electronic properties with carrier density in both the cobaltates *and* quasi-one dimensional CTS [7].

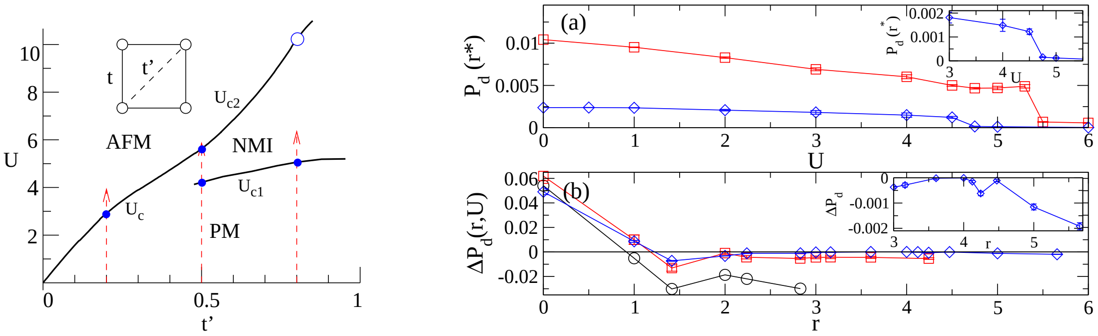

Figure 1: *Left: phase diagram of the* $\frac{1}{2}$*-filled Hubbard model on the anisotropic triangular lattice. Right: (a) Long-range* $d_{x^2-y^2}$ *pair-pair correlation at zero temperature as a function of Hubbard* U *for* $t'/t = 0.5$ *(b)* ΔP*, the enhancement of the pairing over the noninteracting model, as a function of distance for* $U/t = 4.5$*. In (a) and (b), circles, squares, and diamonds are for 4×4, 6×6, and 8×8 lattices, respectively. In all cases we find that* $P(r)$ *decreases monotonically with increasing* U*.*

The unusual doping dependence of the electronic properties of the layered cobaltates $\mathrm{Na}_x\mathrm{CoO}_2$, $\mathrm{Li}_x\mathrm{CoO}_2$, and the "misfit" $[\mathrm{Bi}_2\mathrm{A}_2\mathrm{O}_4][\mathrm{CoO}_2]_m$, has attracted wide attention and was considered a theoretical challenge. These materials have a susceptibility that is characterized as Pauli paramagnetic for small x but Curie-Weiss for large x. We have given a natural explanation of this carrier concentration dependence within an extended Hubbard Hamiltonian with significant V/U (V is the nearest-neighbor Coulomb interaction). As a measure of correlations, we calculate the normalized probability of double occupancy, $g(\rho)$ in the ground state, $g(\rho) = \langle n_{i,\uparrow} n_{i,\downarrow} \rangle / \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle$. The holes are assumed to occupy nondegenerate a_{1g} orbitals on the Co-ions, based on photoemission spectroscopy. Smaller (larger) g corresponds to stronger (weaker) e-e correlations and enhanced (unenhanced) magnetic susceptibility. We performed exact calculations for six different finite clusters with realistic $U/t = 10$ and $0 \leq V/t \leq 3$. In all cases g is nearly x-dependent for $V/t = 0$; for $V/t \neq 0$ the ρ-dependence is exactly as expected from experiments. The calculated crossover between small g (strong correlations) and large g (weak correlations) is near $\rho \approx 0.30 - 0.35$ and not 0.5, which is precisely the density range where recent experiments find a crossover in magnetic properties.

$\mathrm{Na}_x\mathrm{CoO}_2$ is superconducting when hydrated, $\mathrm{Na}_x\mathrm{CoO}_2 \cdot y\mathrm{H}_2\mathrm{O}$, for $x \sim 0.35$. The original assumption that the Na-concentration determines the hole density also in the hydrated material has been found to be not true; some water molecules enter as $\mathrm{H}_3\mathrm{O}^+$, and the actual ρ in the superconductor is much smaller than the 0.65 that would be guessed from the Na-concentration. There have been several reports that SC occurs over a very narrow range of hole density, and that maximum T_c occurs at or very close to Co-ion valency 3.5^+, corresponding to $\rho = 0.5$, the density where SC is found in the organic CTS.

Future Plans

Search for the paired-electron liquid

We have shown that in the 2D correlated band with $\rho = 0.5$, a correlated insulating state, the Paired Electron Crystal (PEC) can occur [4,6,9]. The PEC gains stability in the presence of electron-electron interactions and lattice frustration, and can be viewed as the $\rho = 0.5$ equivalent

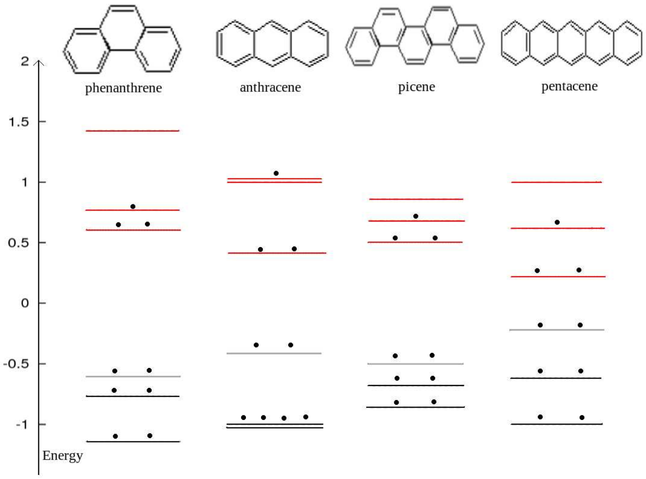

Figure 2: *Bonding (black) and antibonding (red) molecular orbitals of the neutral molecules, and electron occupancies of the trinegative molecular ions, within nearest neighbor tight-binding theory. Energies are in units of the hopping integral* $|t|$. *The LUMO and LUMO+1 orbitals are unusually close in phenanthrene and picene, compared to anthracene and pentacene. In coronene (not shown) the LUMOs are doubly degenerate.*

of the $\rho = 1$ valence bond solid (VBS). In the PEC, pairs of electrons are separated by "vacant" sites, so the PEC state necessarily contains coexisting charge, bond, and spin order. We further propose that localized PEC pairs can gain mobility, resulting in a "paired electron liquid" which is a realization of Schafroth's theory of SC, which described a condensate of real-space pairs [3,6].

Except for our emphasis on $\rho = \frac{1}{2}$, our proposed model has strong parallels with other proposals for theories of correlated-electron SC. Within most, if not all, these theories, the evolution to the superconducting state occurs via a spin-singlet insulator at the boundary of a metal-insulator transition. This is for example true for all RVB theories of SC, irrespective of whether the singlet state appears as a function of doping of the $\rho = 1$ square lattice, or due to increased bandwidth and frustration within the $\rho = 1$ triangular lattice. The key differences between our theory and many of the existing proposals are that, (a) the occurrence of the spin-singlet insulating PEC state in our case is not a conjecture, it has been already proved [6,9]; (b) these singlets have the same character as that of the charged Bosons within Schafroth's theory of SC; and (c) there appear to be several classes of materials in which SC appears to occur at strictly $\rho = \frac{1}{2}$, without doping [3]. At the very least, our proposed research in this subsection will give a definitive answer to the question whether or not the similarities between the different classes of materials we have indicated are merely coincidental or whether they are connected by a deep fundamental relationship.

Metal-intercalated hydrocarbon superconductors

A_3phenanthrene, A_3picene, A_3coronene, and A_3dibenzopentacene (A = K, Rb) are attracting attention as unconventional superconductors. In addition to the high T_c in A_3dibenzopentacene (33 K), these systems exhibit other perplexing features: (i) while the doping concentration can vary over a wide range, SC is limited to anionic compounds with charge -3 on the hydrocarbons, and (ii) SC is absent in the charged acenes (anthracene and pentacene), which are obtained through "linear" fusions of the benzene rings. $A_x$pentacene is metallic but not superconducting. It is very likely that the limitation of SC to a specific stoichiometry (reminiscent of superconducting A_3C_{60}) and a specific molecular structure are both hints to a correct theoretical mechanism of the phenomenon.

Although electron-molecular vibration (e-mv) couplings in the doped acenes and phenacenes are strong, multiple observations suggest that the mechanism of SC is primarily electronic, with e-mv interactions playing however a significant role, as in the CTS. Early calculations giving strong e-mv coupling suggested that monoanions should be superconducting. The calculated couplings decrease with increasing size of the hydrocarbon molecule, predicting a higher T_c in A_3phenanthrene than in A_3picene, contradicting experiments. Secondly, pressure *increases* T_c in both A_3phenanthrene and A_3picene. This is opposite to what is seen in BCS superconductors where pressure decreases T_c due to decreasing density of states. Finally, any electron-phonon mediated mechanism will fail to explain the absence of SC in acenes. Our goal is to derive a microscopic molecular site-based description of the A_3phenazine and A_3coronene focusing on the charged anions only. We believe that with exactly 3 extra electrons per phenacene (but not acene) molecule, the solid can be described as a doubly-degenerate $\rho = \frac{1}{2}$ system. If true, this will indicate a common theme between intercalated hydrocarbons and CTS.

Publications 2009-2012

1. R. T. Clay, J. P. Song, S. Dayal, S. Mazumdar, "Ground State and Finite Temperature Behavior of 1/4-Filled Band Zigzag Ladders," *J. Phys. Soc. Jpn.* **81**, 074707 (2012).
2. S. Dayal, R. T. Clay, S. Mazumdar, "Absence of long-range superconducting correlations in the frustrated half-filled-band Hubbard model", *Phys. Rev. B* **85**, 165141 (2012).
3. S. Mazumdar, R. T. Clay, "Is there a common theme behind the correlated-electron superconductivity in organic charge-transfer solids, cobaltates, spinels, and fullerides?", *Phys. Status. Solidi B* **249**, 995 (2012).
4. R. T. Clay, S. Dayal, H. Li, S. Mazumdar, "Beyond the quantum spin liquid concept in frustrated two dimensional organic superconductors", *Phys. Status. Solidi B* **249**, 991 (2012).
5. S. Mazumdar, R. T. Clay, H. Li, "Similarities in electronic properties of organic charge-transfer solids and layered cobaltates," *Physica B* **407**, 1722 (2012).
6. S. Dayal, R. T. Clay, H. Li, S. Mazumdar, "Paired Electron Crystal: Order from Frustration in the Quarter-Filled Band," *Phys. Rev. B* **83**, 245106 (2011).
7. H. Li, R. T. Clay, S. Mazumdar, "Theory of Carrier Concentration-Dependent Electronic Behavior in Layered Cobaltates," *Phys. Rev. Lett.* **106**, 216401 (2011).
8. R. T. Clay, H. Li, S. Sarkar, S. Mazumdar, T. Saha-Dasgupta, "Cooperative orbital ordering and Peierls instability in the checkerboard lattice with doubly degenerate orbitals," *Phys. Rev. B* **82**, 035108 (2010).
9. H. Li, R. T. Clay, S. Mazumdar, "The Paired-Electron Crystal in the Two-Dimensional Frustrated Quarter-Filled Band," *J. Phys. Cond. Matt.* **22** 272201 (2010).
10. R. T. Clay, H. Li, S. Mazumdar, "Bipolaron density-wave driven by antiferromagnetic correlations and frustration in organic superconductors," *Physica B* **405** 253 (2010).
11. R. T. Clay, S. Mazumdar, H. Li, "Local singlets, frustration, and unconventional superconductivity in the organic charge-transfer solids," *Physica B*, **404**, 487 (2009).
12. S. Mazumdar, R. T. Clay, H. Li, "From valence bond solid to unconventional superconductivity in the organic charge-transfer solids," *Synth. Metals*, **159**, 2419 (2009).

SPIN AND ORBITAL PHYSICS IN NOVEL CORRELATED MATERIALS

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Project Scope

Recent experiments highlight new kinds of superconductors, magnets, metals and insulators, in which the spin and orbital physics, coupled relativistically and through structural chemistry and geometry, provide a new setting for novel electronic behavior. This proposal describes research on the role of coupled orbital, spin and geometrically frustrated degrees as drivers of new kinds of correlated electron behavior. The science behind these phenomena has an important role to play in establishing new concepts to underpin design and discovery of materials to transform our future. The education of the postdoctoral and graduate students carried out as part of this research plays an important part in helping to raise a new generation of leaders in research and development.

A. Topological Kondo Insulators

We are investigating, in collaboration with experimental and computational physicists, the proposal that strongly spin-orbit coupled 4f states drive topological behavior in the family of Kondo insulators. These insulating heavy electron materials have recently attracted renewed interest both through their possible application as efficient thermo-electric materials and the proposal, that a subset of these materials may exhibit topological insulating behavior[1]. While the high resistivity of Kondo insulators and the simplicity of their cubic structure[2] would make them competitive new entries into the family of topological insulators, the strong correlation of the f-bands makes these systems currently inaccessible to conventional band-structure calculations.

The ongoing research is developing a tight-binding theory of cubic Kondo insulators, built around an analytical model, to be later extended with band-theory input. This model will be used to identify strong candidate topological Kondo insulators and to study the tunneling into the hybridized surface Dirac cones of a topological heavy electron insulator. Our future work will

- Develop a scheme for selectively introducing a large spin-orbit coupling into the f-bands within band theory, while preserving a realistic description of the conduction sea. We will use the code “Wannier-90” to extract a tight-binding and a corresponding plane-wave decomposition of the spd bands in real Kondo insulators. We shall use this technique to provide a tentative prediction of which of the known Kondo insulators are topological.

- Develop a theory of scanning tunneling microscopy into the two-band surface states of a Kondo insulator. This will involve taking into account the direct tunneling into the conduction band and the co-tunneling into the f-band that produces STM Fano resonances.

- Calculate the bound-state spectrum and conductance of a dislocation line within a topological Kondo insulator, with the view to future experimental studies of the conductivity in dislocation-damaged Kondo insulators.

B. A tetrahedral approach to the Iron-based Superconductors

The discovery of iron-based superconductors in 2008 has attracted immense interest, adding a new family of high temperature d-electron superconductors to complement the cuprate family of superconductors[3]. Experimental studies suggest a range of electron correlation effects and a strong correlation between the superconducting transition temperature and the tetrahedral symmetry of the Fe-As unitse[4, 5]. In recent work with postdoc Tzen Ong[6], we have examined the physics of an individual iron-based tetrahedron , showing that the interplay of Hunds coupling with the spin and orbital fluctuations that develop near perfect tetragonality drive novel non-Fermi liquid impurity physics. We found that Hund's coupling selectively suppresses the spin Kondo temperature, while leaving the orbital Kondo temperature unaffected. The high temperature quenching of the orbital fluctuations leads to a "shapeless" magnetic moment in which magnetic scattering takes place in the e_{2g} channels, while preserving the orbital index, giving rise to an overscreened spin Kondo model, with critical pair fluctuations[7] that may pay a role in the iron-based superconductivity.

The ongoing research will:

- carry out a Wilson renormalization group calculation on the tetrahedral mixed valence model proposed by Ong and Coleman[6], aiming to verify the predicted Hund's driven separation of orbital and spin Kondo scales, examining the dynamical spin susceptibility to compare with future neutron scattering and dilution experiments.

- Develop and study a series of BCS models in which local anisotropic pairing interaction is aligned with the staggered iron tetrahedron structure. Initial work suggests that a model with staggered d_{xy} pairing, aligned with the iron tetrahedra gives a fully gapped Fermi surface.

- Develop a model of composite pairing within the staggered iron-tetrahedra. This work will build on our previous experience with models of composite pairing for heavy electron systems. Composite pairs formed between $d_{x^2-y^2}$ and d_{z^2} orbitals (in the staggered As basis) have the potential to drive staggered d_{xy} and hence $s^{+/-}$ pairing.

- Develop a a model for the pair breaking generated by scattering off Co subsituted iron tetrahedra, both within a conventional $s^{+/-}$ BCS model, and within a model of composite pairing, with the view to comparison with recent Co-substitution STM experiments.

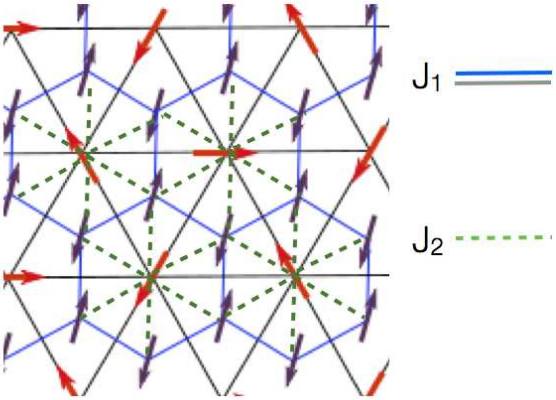

FIG. 1: Interpenetrating triangular and honeycomb lattices. Bonds in the triangular or honeycomb lattices are antiferromagnetic (afm) with strength J_1. Bonds between the two lattices have afm strength J_2.

C. Frustrated Magnetism and the emergent Clock Model.

Motivated by a renewed interest in the emergent discrete physics of frustrated Heisenberg antiferromagnets[8, 9], we are currently studying a family of Heisenberg models with that develop an emergent n-fold order parameter described by the n-state Clock-model. Simple arguments suggesting the possibility of an emergent Berezinskii-Kosterlitz-Thouless transition, will be evalauated and explored in detail[10]. 20 years ago, Chandra, Coleman and Larkin discovered a way in which frustrated magnets can defeat the Mermin Wagner theorem through the development of nematic Ising order[11], driven by order-from-disorder[12]. In the J_1-J_2 classical Heisenberg model, the individual spins have a finite correlation, but the nematic order parameter

$$\vec{S}_1(i) \cdot \vec{S}_2(i) = \pm S^2$$

behaves as an emergent Ising variable that develops Ising order at a *finite temperature* due to the effects of order-from-disorder. The fascinating lesson from this result, is that composite combinations of spin, such as this Ising order parameter, can develop infinite range interactions, even though the underlying spin physics involves a *finite* correlation length. This raises the possibility that order from disorder induce more complex forms of discrete order in the two-dimensional Heisenberg model? For example, can we find discrete Z_3 or Z_n emergent clock models in appropriately frustrated Heisenberg models. Jose et al have shown that for the n-state clock models with $n \geq 5$, a Berezinskii Kosterlitz Thouless phase develops in these systems at finite temperatures.

Motivated by the spinel magnets, the ongoing research is carrying out a study of the interpenetrating honeycomb-triangular lattice shown in Fig. (1). When the two lattices are coupled via a weak J_2, frustration causes them to decouple in the ideal classical ground-states, however, once the effect of temperature on fluctuations isincluded, order-from-disorder will find entropic and energetic advantage by aligning the honeycomb antiferromagnetic order to become coplanar with the triangular lattice spin order. This gives rise to an emergent clock model variable, in which

$$\vec{S}_{\hexagon}(i).\vec{S}_{\triangle}(i) = S^2 \cos\left[\frac{2\pi}{6} r\right], \qquad\qquad (r = 1, 6)$$

where $S_{\hexagon}$ and $S_{\triangle}$ denote neighboring spins on the two lattices within a single unit cell. Whereas emergent Ising order develops via a single Ising phase transition, classical six-state order is expected to develop via two separate Berezinski-Kosterlitz-Thouless transition. We have recently computed the renormalization flows of J_1-J_2 hexagonal-triangular model, tentatively confirming the presence of a finite temperature BKT transition. Ongoing work will

- Carry out Monte Carlo studies of this model to confirm the proposed phase diagram. By measuring spin current fluctuations, we will follow the Heisenberg and spin wave stiffnesses as a function of distance scale.

- Working with colleague Sang Cheong, attempt to identify quasi-two dimensional candidate spinel structures that may exhibit some of the above clock-model physics over intermediate temperature ranges.

[1] Maxim Dzero, Kai Sun,Victor Galitski and Piers Coleman, *Topological Kondo Insulators*, *Phys. Rev. Lett.* **104**, 106408,(2010).

[2] J. C. Cooley, M. C. Aronson, Z. Fisk, and P. C. Canfield, Physical Review Letters 74, 1629 (1995).

[3] P. J. Hirschfeld and M. M. Korshunov and I. I. Mazin, *"Gap symmetry and structure of Fe-based superconductors"*, Reports on Progress in Physics, **74**,124508-124551(44) (2011).

[4] P. Dai, *et. al.* Nature Mat. **7**, 953 (2008).

[5] K. Yamada, *et. al.* J. Phys. Soc. Jpn **77**, 083704 (2008).

[6] T. Tzen Ong and Piers Coleman, *"Local Quantum Criticality of an Iron-Pnictide Tetrahedron"*, Phys. Rev. Lett. 108, 107201 (2012).

[7] V.J. Emery, and S.A. Kivelson Phys. Rev. B **46**, 10812 (1992); V.J. Emery, and S.A. Kivelson, Phys. Rev. Lett. **71**, 3701 (1993).

[8] R. Coldea et al, *"Quantum Criticality in an Ising Chain: Experimental Evidence for Emergent E8 Symmetry"*, Science 327, 177 (2010).

[9] S. H. Lee, C. L. Broholm, W. Ratcliff, G. Gasparovic, Q. Huan, T. H. Kim and S. W. Cheong, *"Emergent excitations in a geometrically frustrated magnet"* , Nature **418**, 856 (2002).

[10] P. Orth, P. Chandra, P. Coleman and J. Schmalian, arXiv 1206.5740 (2012).

[11] P. Chandra, P. Coleman, and A. I. Larkin, *"Ising Phase Transition in Frustrated Heisenberg Models"*, Phys. Rev. Lett. 64, 88 (1990).

[12] C. L. Henley, Phys. Rev. Lett., *"Ordering due to disorder in a frustrated vector antiferromagnet"*, **62**, 2056 (1989).

THEORETICAL STUDIES OF COMPLEX COLLECTIVE PHENOMENA

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PROJECT SCOPE

The research in this program focuses on the theoretical study of the emergence of complex collective electronic states in several families of materials. The possible competition, or cooperation, of these complex states in special regimes of temperatures, carrier densities, and external fields is studied by our team. The specific materials that are investigated include colossal magnetoresistance manganites, iron- and copper-based high temperature superconductors, cobaltites, molecule-based magnets, multiferroics, and also a variety of artificially-created superlattices and interfaces involving oxide perovskites. These compounds are characterized by having several simultaneously active spin, charge, and orbital degrees of freedom, forming states where the many competing tendencies are delicately balanced. At present, our work deals with three specific objectives: (1) the study of new collective states that may appear in artificial heterostructures, with associated exotic transport properties; (2) the study of competing interactions in frustrated magnets and associated multiferroic tendencies; (3) the study of the iron-based superconductors in the intermediate Hubbard repulsion regime and also via spin fermion models, and the search for novel states with spin/orbital order. Our team takes advantage of the ORNL research environment via several collaborations with other local experimental and theoretical teams, and with researchers at the ORNL neutron and computational user facilities.

RECENT PROGRESS

(1) Iron-based High Temperature Superconductors. The superconducting pnictides and chalcogenides are of considerable importance because they may offer clues on the pairing process of high-T_c superconductors in general. Our team has recently used the Hartree-Fock (HF) technique and the Lanczos method on small clusters to study the two-dimensional multiorbital Hubbard model for electrons hopping between iron atoms. The hopping terms are from band-structure calculations or from fits of angle-resolved photoemission (ARPES) experiments. The HF method showed the presence of a metallic magnetic state with (π,0) wavevector in an intermediate range of Hubbard U and Hund J_H couplings, compatible with several experiments [1.1].

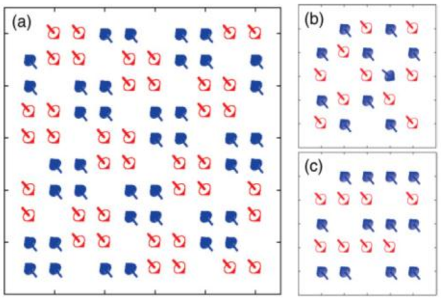

Fig. 1: (a) $K_{0.8}Fe_{1.6}Se_2$ magnetic state found in HF studies. (b,c) are close competitors [1.2].

Recent developments in this field include the discovery of an exotic insulator in $K_{0.8}Fe_{1.6}Se_2$ with $\sqrt{5}$x$\sqrt{5}$ Fe vacancies, as shown in Fig. 1(a). Neutron-scattering measurements suggest an associated magnetic state as shown in Fig. 1(a) as well. We have used the HF procedure to analyze the Hubbard model with $\sqrt{5}x\sqrt{5}$ Fe vacancies [1.2]. At intermediate values of U and J_H/U~0.25, the state in Fig. 1(a) indeed becomes stable, as in neutron results. Moreover, the states in Figs. 1(b) and (c) have competing energies. The regime of couplings is similar to the one identified by comparing theory with neutron, transport, and ARPES results for the pnictides [1.3].

Another of our recent studies focused on the exact solution of the electron-doped two-orbital *xz*-*yz* Hubbard model on a small cluster, adding extra Heisenberg terms to enhance the $(\pi,0)$ spin-order strength, thus inducing pairing even in small systems [1.4]. The main result was that an A_{1g} state (*s*-wave) is the most favored pairing channel in a robust range of U and J_H. Competitors with B_{1g} and B_{2g} symmetries are stabilized by modifications in the electronic bandwidths [1.4].

More recently, a review for Nat. Physics has been written where evidence is provided that Fermi surface nesting is not applicable in many of the iron-based superconducting materials [1.5].

(2) Magnetic Structures and Spin Dynamics of Multiferroic Materials. Oxides displaying non-collinear spin states are of much importance because they provide an opportunity to study the interplay between magnetism and ferroelectricity. Our recent work on $CuFeO_2$ showed that the AFM coupling between nearest-neighbor S=5/2 iron ions within each hexagonal plane produces geometric frustration and a rich phase diagram. With increasing magnetic fields, several additional transitions occur before magnetic saturation [2.1].

Collaborating with neutron-scattering experts from ORNL, our team recently studied several multiferroic materials. In particular, whereas the elastic spectrum of doped $CuFeO_2$ contains only two peaks, the inelastic spectrum [Figs. 2(a,b)] contains a wealth of information that provides a “dynamical fingerprint” of the multiferroic ground state. The inelastic spectrum of 3.5% Ga-doped $CuFeO_2$ exhibits both primary and secondary Goldstone modes, the latter produced by lattice distortions [2.2]. Comparing the predicted [Fig. 2(c)] [2.3] and measured inelastic spectrum, we have shown that the spin spiral state is characterized by alternating small and large turn angles [2.4].

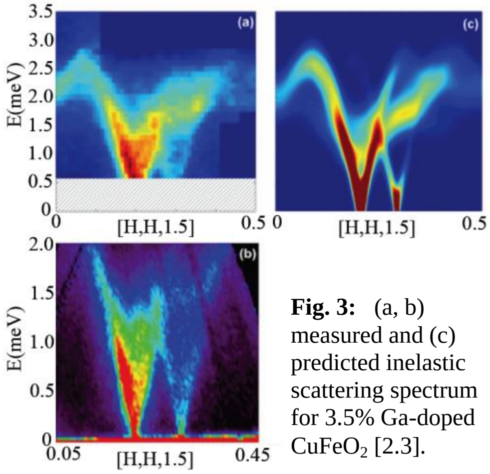

Fig. 3: (a, b) measured and (c) predicted inelastic scattering spectrum for 3.5% Ga-doped $CuFeO_2$ [2.3].

Complementary work on molecule-based magnets affords the opportunity to study competing interactions that can be readily tuned by magnetic fields, pressure, or the choice of organic cation. One of the most interesting molecule-based magnets, diruthenium tetracarboxylate ($Cr(Ru_2)_3$ for short) contains two interpenetrating cubic sublattices that are weakly AFM-coupled. While materials that develop three-dimensional (3D) magnetic order due to the weak coupling between one-dimensional or two-dimensional sublattices are fairly common, $Cr(Ru_2)_3$ is the only known material where each of the weakly-interacting sublattices is already 3D ordered. Because the AFM exchange between neighboring Cr and Ru_2 complexes within each sublattice is much stronger than the weak AFM dipolar coupling between sublattices, each sublattice behaves as a giant rigid moment. Predictions for this metamagnetic transition based on a model containing Zeeman and Heisenberg interactions [2.5] are in agreement with experiments.

(3) Electronic Properties of Strongly Correlated Heterostructures. Perovskite manganites $La_{1-x}Sr_xMnO_3$ (LSMO) are of great importance because of their FM metallic behavior, relatively high Curie temperatures T_C, and large magnetic polarizations. Controlling the magnetic interaction at interfaces involving manganites could produce a technological breakthrough for electronic devices that use the tunneling magnetoresistance or exchange-bias effect. Thus, a Goodenough-Kanamori-type description of the interfacial magnetic interactions is desired. In recent efforts, these rules were developed for interfaces involving a manganite [3.1]. Considering the interaction derived from the $3z^2{-}r^2$ orbitals, which have the largest hybridization across the interface, the sign of the interaction is fixed by the molecular orbitals formed at the interface.

The scheme developed in [3.1] became the basis for recent interpretations of many experimental results [3.2; 3.3]. Interfacial magnetism explains several anomalous features of manganite-cuprate-manganite trilayer systems. For example, the SC critical temperature T_c of $YBa_2Cu_3O_7$ (YBCO) is more strongly suppressed when combined in superlattices with FM $La_{1\text{-}x}Ca_xMnO_3$ (LCMO) than with a nonmagnetic cuprate. Further, a robust inverse spin-switch effect (ISSE) was reported in LCMO/YBCO/LCMO trilayers. In contrast to the conventional exclusion between SC and magnetism, SC is favored by the parallel alignment of the LCMO FM moments layers in a magnetic field. Our research showed that the key ingredient for understanding this anomalous behavior is the interfacial AFM coupling [3.4]. This coupling induces a negative spin polarization inside the YBCO region and influences SC more strongly than merely injecting spin-polarized quasiparticles without the coupling [Fig. 3].

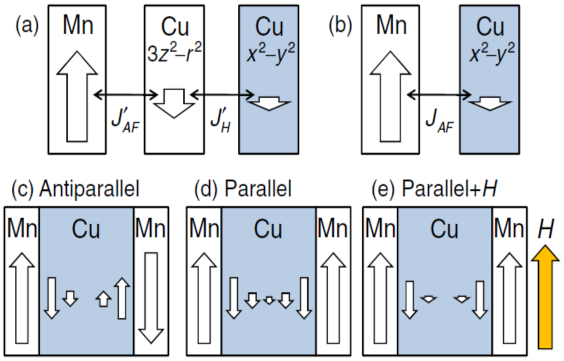

Fig. 3: Magnetic interaction between neighboring Cu and Mn layers. (a) Realistic model including two Cu e_g orbitals, (b) simplified model focusing only on the x^2-y^2 orbital. Magnetic states of manganite-cuprate-manganite trilayers: (c) Antiparallel spin configuration and (d) parallel configuration without an applied magnetic field H. (e) Parallel spin configuration with H.

In addition, models were used to study oxide heterostructures with ferroelectric (FE) components [3.5]. A generic DE system (LSMO) was employed as the conducting channel attached to a FE gate. Charge accumulation/depletion near the interface, achieved by switching the FE polarization orientation, drives interfacial metal-insulator transitions that induce robust magnetoelectric responses, as in previous density-functional theory calculations.

FUTURE PLANS

(1) The spin fermion model recently proposed for the iron superconductors will be studied using computational techniques similar to those widely applied before to study the manganites. In particular, we are searching for orbitally ordered states and also we are studying transport properties to compare against experiments that suggested the presence of nematic states. A review is also in preparation (by invitation for Rev. Mod. Phys.) about the iron selenides with alkaline layers separating the Fe_2Se_2 layers. It will be argued that these materials are in a regime where the Fermi surface nesting mechanisms to generate magnetism does not apply. Mott insulators could be the parent states of the superconductivity found in these compounds.

(2) The study of frustrated magnets continues in our team. Quantum fluctuations will be incorporated in the analysis of several multiferroics, and lattice distortions will also be included to address secondary Goldstone modes. Phase diagrams varying magnetic fields are also being studied for a variety of materials, including $CuFeO_2$. Very rich phase diagrams have been obtained for these compounds, with a variety of collinear and noncollinear phases being predicted. Also, competing energies in molecule-based magnets are being analyzed. This includes

collaborations with neutron scattering experts at ORNL to test the predicted ground states of some of these materials.

(3) In the area of oxide interfaces, our current research is about the influence of strain in thin films of cobaltites, to be studied with dynamical mean field theory and DFT methods. Using models Hamiltonians, we are also studying the interface of manganites with several oxides, such as nickelates and cuprates. Transport properties are also being analyzed in this context. Interfaces grown along the [111] direction are being pursued as realizations of the Quantum Hall Effect. Also non-equilibrium phenomena in the Hubbard model context is being studied with time-dependent DMRG methods, in collaboration with theorists at the nanocenter of ORNL.

PUBLICATIONS (just a small fraction of the total):

[1.1] Yu, R., Trinh, K., Moreo, A., Daghofer, M., Riera, J., Haas, S., Dagotto, E., *Phys. Rev. B* **79**, 104510 (2009).

[1.2] Luo, Q.-L.; Nicholson, A.; Riera, J.; Yao, D.-X.; Moreo, A.; Dagotto, E.; *Phys. Rev. B* **84**, 140506(R) (2011).

[1.3] Luo, Q.-L.; Martins, G.; Yao, D.-X.; Daghofer, M.; Yu, R.; Moreo, A.; Dagotto, E.; *Phys. Rev. B* **82**, 104508 (2010).

[1.4] Nicholson, A.; Ge, W.-H.; Zhang, X.; Riera, J.; Daghofer, M.; Oles, A.M.; Martins, G.B.; Moreo, A.; Dagotto, E.; *Phys. Rev. Lett.* **106**, 217002 (2011).

[1.5] P. Dai, J. Hu, and E. Dagotto, to appear in Nat. Physics.

[2.1] Fishman, R.S., *Phys. Rev. Lett.* **106**, 037206 (2011).

[2.2] Fishman, R.S., Okamoto, S., *Phys. Rev. B* **81**, 020402(R) (2010).

[2.3] Haraldsen, J.T., Ye, F., Fishman, R.S., Fernandez-Baca, J.A., Yamaguchi, Y., Kimura, K., Kimura, T., *Phys. Rev. B* **82**, 020404(R) (2010).

[2.4] Haraldsen, J.T. and Fishman, R.S., *Phys. Rev. B* **82**, 144441 (2010).

[2.5] Fishman, R.S., Shum, W.W., Miller, J.S.; *Phys. Rev. B* **81**, 172407 (2010).

[3.1] Okamoto, S., *Phys. Rev. B* **82**, 024427 (2010).

[3.2] Yu, P., Lee, J.-S., Okamoto, S., Rossell, M. D., Huijben, M.,Yang, C.-H., He, Q., Zhang, J. X., Yang, S.Y., Lee, M. J., Ramasse, Q. M., Erni, R., Chu, Y.-H., Arena, D. A., Kao, C.-C., Martin, L.W., Ramesh, R.; *Phys. Rev. Lett.* **105**, 027201 (2010).

[3.3] Garcia-Barriocanal, J., Cezar, J. C., Bruno, F. Y., Thakur, P., Brookes, N. B., Utfeld, C., Rivera-Calzada, A., Giblin, S. R., Taylor, J. W., Duffy, J. A., Dugdale, S. B., Nakamura, T., Kodama, K., Leon, C., Okamoto, S., Santamaria, J.; *Nat. Commun.* **1**:82 doi: 10.1038/ncomms1080 (2010).

[3.4] Salafranca, J., Okamoto, S., *Phys. Rev. Lett.* **105**, 256804 (2010).

[3.5] Dong, S.; Zhang, X.; Yu, R.; Liu, J.-M.; Dagotto, E.; *Phys. Rev. B* **84**, 155117 (2011).

First-Principles Calculation of Vibrational Mode Lifetimes in Complex Materials

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Project Scope

We will implement a new method for calculating vibrational mode lifetimes in complex materials based on first-principles electronic structure calculations, and to apply the method to several complex materials. The approach is to implement a recently developed scheme for calculating mode lifetimes. The new approach is based on techniques in non-equilibrium thermodynamics, using principally the Liouvillian operator to obtain dynamics, and is combined with the recursion method to study the properties of the resolvent. The result is an expression for the lifetime of a normal mode that is based on Monte Carlo evaluation of operators related to the mode occupation. This technique should represent a substantial improvement over existing techniques.

Planned Activities: 2012-2013

Our activities for the first year will include:

(1.) Study dissipation in simple, low-dimensional models that exhibit chaotic behavior in some regimes. This combined numerical and analytical study will help to test the new approach in simple but non-trivial systems.

(2.) Study mode lifetimes in simple extended systems with rattlers. This extends the work that was done previously using a simple non-linear vibrating lattice model.

(3.) Implement the new method in LAMMPS, to allow the calculations to be done with empirical potentials already implemented there.

Publications

(This is a new award, so there have been as yet no publications under this grant.)

Time-dependent current-density-functional theory of charge, energy and spin transport and dynamics in nanoscale systems

GRANT #DE-FG02-05ER46204

Principal Investigator: Massimiliano Di Ventra
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Project scope

The goals and objectives of this research program are the study of non-equilibrium phenomena associated with charge, energy and spin transport in nanoscale systems and atomic gases. A large part of this program aims at developing time-dependent density functional methods that are particularly suited for the above studies. In particular, we have extended time-dependent (current) DFT to open quantum systems, a theory we have named Stochastic TDCDFT, and applied it to simulate electrical and thermal transport. We are now in the process of developing a new DFT formulation that explicitly handles thermal currents. Part of this work is done in collaboration with Prof. Giovanni Vignale at the University of Missouri, Columbia. For instance, we have worked together on the calculation of the viscosity in nanostructures due to the geometrical constriction experienced by electrons scattering across it. This is an exciting new area of research that is leading to a better understanding of the transport properties of nanoscale systems, and has inspired us to include energy currents in the basic formulation of time-dependent DFT.

Recent progress

1. Viscous corrections to electrical currents

It is well known that the viscosity of a homogeneous electron liquid diverges in the limits of zero frequency and zero temperature. A nanojunction breaks translational invariance and necessarily cuts off this divergence. However, the estimate of the ensuing viscosity is far from trivial. Together with Prof. Vignale we have proposed an approach based on a Kramers-Kronig dispersion relation, which connects the zero-frequency viscosity $\eta(0)$ to the high-frequency shear modulus μ_∞ of the electron liquid via $\eta(0) = \mu_\infty\tau$, with τ the junction-specific momentum relaxation time. We have first checked that this approach gives reasonable results for the Fermi gas by comparing it to the hydrodynamic solution obtained by Abrikosov and Khalatnikov. The agreement of the viscosity as obtained by this simple approach with the much more involved calculation by Abrikosov and Khalatnikov is impressive (see Fig. 1).

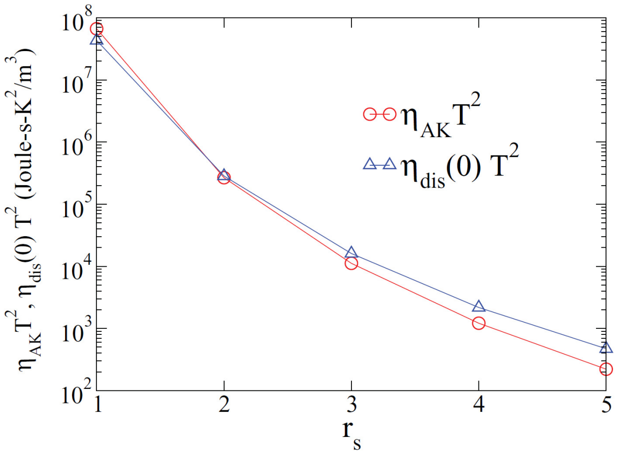

Fig. 1. The comparison between the viscosity calculated by Abrikosov and Khalatnikov, η_{AK}, and the viscosity calculated using the proposed dispersion relation for different values of the density r_s. The connecting lines are a guide to the eye.

Confident of the strengths of this method we have then set to compute the viscosity in the case of a scattering potential. We have used a model potential that has allowed us to compute the viscosity analytically as a function of the single-particle transmission probability. We have then used this viscosity to calculate the corrections to the single-particle (Lanadauer) current for this scattering problem. In agreement with what was previously reported this "dynamical" resistance is relatively small at large transmissions due to the small variation of the density across the junction. However, it increases substantially at very low transmissions with values that can greatly exceed, for the particular model potential chosen, the dynamical resistances estimated previously (see Fig. 2). We feel we have now undoubtedly shown that there are dynamical corrections to the Landauer formula which are related to the viscous nature of the electron liquid.

2. Fundamentals of transport in nanoscale systems and atomic gases

We have used the micro-canonical picture of transport – a framework ideally suited to describe the dynamics of closed quantum systems such as ultra-cold atom experiments - which the PI (Di Ventra) has suggested in 2004 to show that the exact dynamics of non-interacting fermions and bosons exhibit very different transport properties when the system is initially in the ground state and set out of equilibrium by removing the particles from half of the lattice. We find that fermions rapidly develop a finite quasi steady-state current reminiscent of electronic transport in nanoscale systems. This result is robust – it occurs with or without a harmonic confining potential and at zero or finite temperature. The bosonic current instead exhibits strong oscillatory behavior that decays

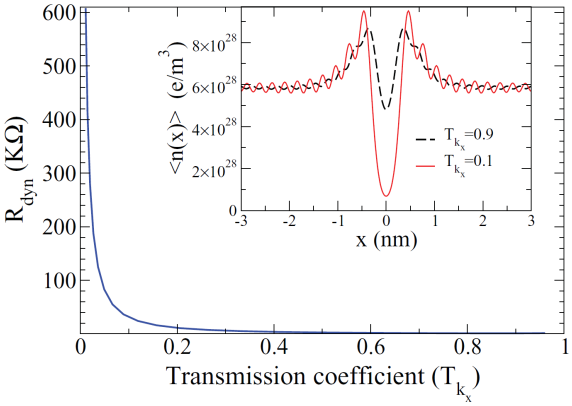

Fig. 2. Dynamical viscous resistance as a function of transmission coefficient. The inset shows the averaged density across the nanojunction for the longitudinal transmission coefficient 0.1 and 0.9.

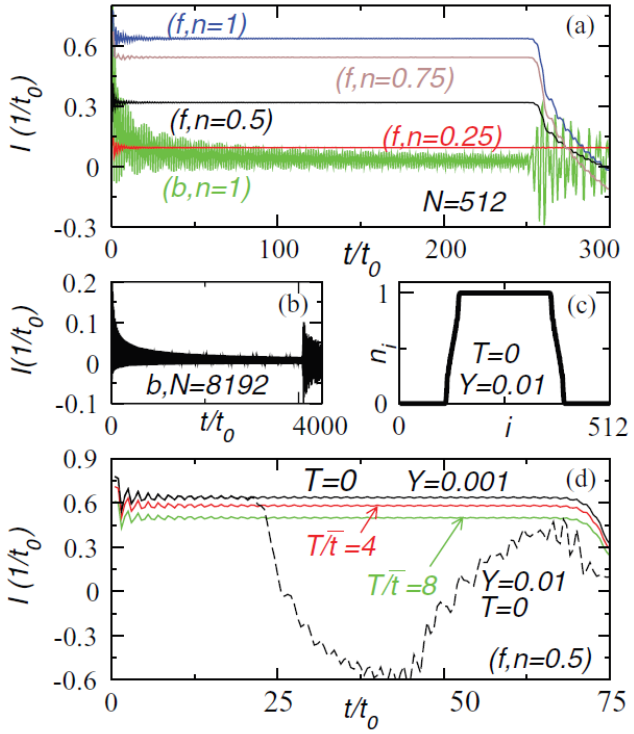

Fig. 3. (a) Currents in a uniform lattice for fermions (top) and bosons (bottom) with initial fiilling n = 1 at T = 0 after the atoms on the right are removed. The fermionic currents for initial fillings n = 0.75, 0.5, 0.25 are also shown (labeled next to each curve). (b) The bosonic current for initial filling n = 1. (c) The density profile for fermions at T = 0. (d) Fermionic currents in a lattice with a harmonic potential.

into a steady-state of zero current only in the thermodynamic limit (Fig. 3). These predictions can be readily verified experimentally and show that the existence and the formation of a finite steady state current in fermionic systems is unrelated to the presence of interactions, a fact which is not fully appreciated by the community.

In addition, unlike typical condensed-matter systems, ultra-cold atoms loaded into optical lattices allow separate control of both the particle number and system size. As a consequence, there are two distinct ”thermodynamic” limits that can be defined for these systems: i) ”infinite-volume limit” at constant finite density, and ii) ”empty-lattice limit” at constant particle number. To probe the difference between these two limits and their crossover, we have considered a partially occupied lattice and study the transport of non-interacting fermions and fermions interacting at the mean-field level into the unoccupied region. We find that in the infinite-volume limit, a finite steady-state current emerges. On the other hand, in the empty-lattice limit there is no finite steady-state current. By changing the initial filling, we find a smooth crossover between the two limits. Again, these predictions may be verified using available experimental tools and demonstrate a fundamental difference between isolated small systems such as ultra-cold atoms and conventional condensed-matter systems.

Planned activities

As planned we would like to compare the assumptions and predictions of the Landauer formalism, semiclassical full-counting statistics (FCS), and microcanonical formalism of transport. Particularly we will focus on their applicability to ultra-cold atoms in engineered optical potentials where experiments can be performed that control both local and global interactions. For two lattices connected by a junction, we plan to determine the fully quantum-mechanical current and particle number fluctuations from the microcanonical formalism and the corresponding values predicted by the Landauer formalism and FCS assuming a binomial distribution. We would also like to investigate the fundamental question of whether the assumption of two reservoirs with Fermi-Dirac distributions in the Landauer formalism is necessary for a steady-state current to develop.

In keeping with the planned activities of our proposal, we will develop a practical approach to electron conduction using Stochastic TD-CDFT, namely the extension of TD-CDFT for open quantum systems developed by the PI. We plan to implement this approach on an in-house code and apply it both to the study of the formation of steady states and universal conductance fluctuations.

With Prof. Vignale we plan to explore a new formulation of TDCDFT which will include for the first time a space- and time-dependent temperature. This formulation will allow us to study, within the DFT framework, heat transport, local heating, and thermoelectric phenomena. In view of the growing interest in thermoelectricity, we anticipate that this formulation, if successfully completed, will be one of the most important outcomes of our efforts to date.

Publications

1) D. Roy, G. Vignale and M. Di Ventra, "Viscous corrections to the resistance of nanojunctions: A dispersion relation approach", Phys. Rev. B **83**, 075428 (2011).
2) Chih-Chun Chien, Michael Zwolak, and Massimiliano Di Ventra, "Bosonic and fermionic transport phenomena of ultra-cold atoms in 1D optical lattices", submitted to Phys. Rev. A **85**, 041601 (2012), Rapid Communications.
3) Chih-Chun Chien, and Massimiliano Di Ventra, "Dynamical crossover between the infinite-volume and empty-lattice limits of ultra-cold fermions in 1D optical lattices", Europhysics Lett. (*in press*).
4) Chih-Chun Chien, Michael Zwolak, and Massimiliano Di Ventra, "Interaction-induced transport and conducting-nonconducting transition of ultra-cold atoms in 1D optical lattices", arXiv:1203.5094

Quantum dynamics and control of individual spins in diamond

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Project scope:

The research in this program is focused on development and analysis of the quantum control approaches for the individual electronic and nuclear spins in solids, and ensembles of such spins. Understanding and controlling matter at the level of individual quantum particles is an exciting scientific endeavor, and is one of the Grand Challenges identified by the DOE Office of Science. The ability to preserve and manipulate quantum coherence of the spins opens many new opportunities for the research supported by the DOE: besides fundamental interest, the studies on quantum spin control are important for applications ranging from nanosciences to advanced electric and magnetic field sensing and quantum information processing. Since the possibility to access and probe individual spins in solids is very new, there is a pressing need to develop adequate theoretical approaches and experimental tools for such studies. Our successful works, presented here have become possible due to high degree of synergy between different FWPs, and close collaborative work with external experimental groups.

Recent progress

Protecting quantum coherence of a single spin in diamond and application to magnetic sensing

For a number of years, our work has been focused on developing and using novel theoretical techniques for investigating and controlling the quantum spin dynamics of individual electronic and nuclear spins in solids, which are coupled to their environment [1]. With these tools, we are able to design efficient approaches for controlling quantum spins, including realistic imperfections, and reliably assess the protocols' performance.

The analytical and numerical approaches which we have developed, and the corresponding software implementing them, has been particularly useful for understanding the dynamics and control of the electronic spins of the individual nitrogen-vacancy (NV) impurity centers in diamond [2]. These centers have attracted much attention recently due to their unusual properties, such as the possibility to probe the electronic spin state of a single center (perform quantum measurement of the electronic spin), the ability to prepare the NV center's spin in a well-defined quantum state, and the possibility to manipulate the NV spin by magnetic fields and by optical illumination.

Our theoretical investigation of the quantum dynamics of the single NV spin under realistic experimental conditions has guided our joint theory/experiment work, and has enabled first demonstration of the dynamical decoupling of a single solid-state spin from its environment [3]. The work has been performed together with the experimental team of Prof. R. Hanson and the Delft University of Technology (the Netherlands). By applying a specially designed sequence of up to 136 magnetic field pulses, we were able to extend the coherence time of the NV spin by a factor of 26. The experiments have also clearly confirmed other theoretical predictions. The coherence time T_c was increasing as $N_p^{2/3}$ with the number N_p of the applied pulses for all measured sequences, with N varied from 2 to 136, and the coherence decay had a universal form $\exp(-t^3/T_c^3)$ for all studied values of N_p (see Fig. 1).

The ability to use the quantum control tools for extending the coherence time of the single NV spin is an important advantage, which can seriously help improving the high-sensitivity magnetometry. Together with the group of Prof. R. Hanson, we have demonstrated that, using the NV spin as a magnetic probe for measurement of the oscillating magnetic field [4]. Moreover, besides controlling only the NV spin, it is possible to use the same ideas to control both the NV spin and its environment [5]. In this way, we were able to investigate the internal dynamics of the environment. Moreover, the control of the environment makes possible extending the bare dephasing time of the electronic spin of the NV center, which is important for measurement of arbitrary time-dependent magnetic fields with NV spins.

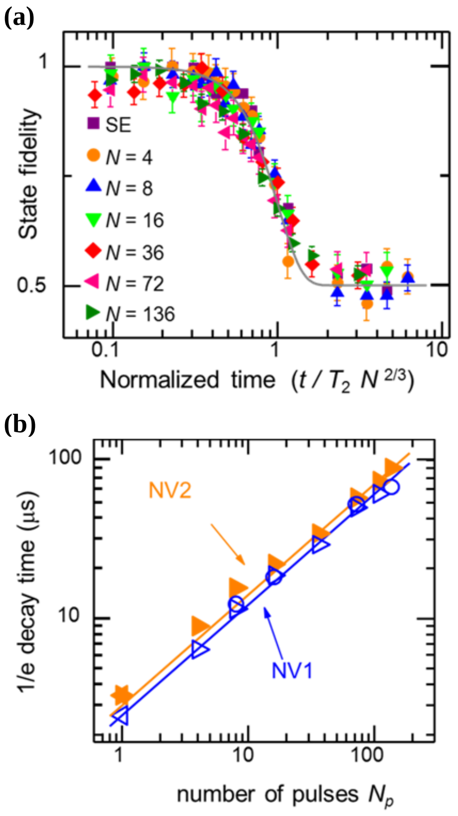

Fig. 1. Reprinted excerpts from Ref. 3, G. de Lange et al., *Science* **330**, 60 (2010). Dynamical decoupling of a single electronic spin of a NV center in diamond. (a) Universal form of the coherence decay. (b) Increasing coherence time as a function of the number of decoupling pulses.

Decoherence-protected entangling operation and nanoscale magnetic tomography with single-spin sensitivity

Along with extending the coherence time of a single electronic spin of a NV center, it is important to be able to implement decoherence-protected operations on two spins. The second spin can be a nuclear spin belonging to the ^{14}N nitrogen atom of the NV center, or the nuclear spin of a ^{13}C atom in the diamond lattice. A fundamental problem arises on this path: the dynamical decoupling can insulate the electronic spin of a NV center from the environment, but it also insulates the two spins from each other, thus disrupting the coupling between them and precludes formation of the quantum-correlated (entangled) two-spin state.

However, our theoretical studies have shown that, by applying the decoupling pulses in exact resonance with the motion of the nuclear spin, it is possible to protect the electronic spin from decoherence, and at the same time preserve the coupling between the electronic and the nuclear spins [6]. This finding has opened the way to first implementation of the decoherence-protected quantum entangling operation on two solid-state spins [6], performed in collaboration with the experimental groups of Prof. D. D. Awschalom (UC Santa Barbara) and Prof. R. Hanson (Delft, the Netherlands). One of the results of this work is that we were able to implement for the first time a full-fledged quantum algorithm on two individual solid-state spins.

Moreover, this work enabled us to perform tomography of the environment of the NV center, with nanometer resolution and the sensitivity to a single nuclear spin. By varying the timing of the decoupling pulses, we encounter special situations, when the pulses are applied in resonance with the motion of some of the 13C nuclear spins. These spins become entangled with the NV electronic spin, and the observed signal sharply drops. Thus, by varying the timing of the pulses, we can explore, one by one, the nuclear spins which form the environment of a given NV center, and map out their positions [7].

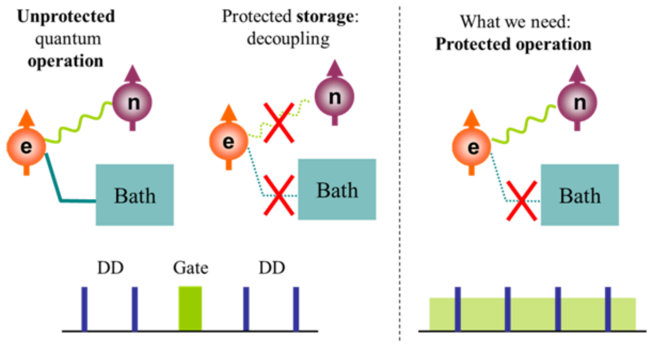

Fig. 2. Reprinted excerpts from Ref. 6, T. van der Sar et al., *Nature* **484**, 82 (2012). Decoherence-protected entangling quantum operation on two spins (electronic and nuclear) belonging to a single NV center. Dynamical decoupling in general disrupts the coupling between the two spins and precludes formation of the entangled state (on the left). Our protocol allows protection of the electron spin from decoherence, and at the same time preserves the coupling between the electronic and the nuclear spin (on the right).

Future plans

We plan to pursue further the studies of the quantum dynamics of the spins of individual NV centers in diamond. A host of unsolved problems related to the fundamental dynamics of the NV spin, its relation to the electronic structure of the NV center, and the phonon excitations in diamond, are to be studied in order to understand in detail the quantum spin properties of the NV centers. Our first attempt in this direction has efficiently utilized the joint expertise existing within different groups at Ames Laboratory [8], but much more research effort is needed to gain better knowledge of the NV spin properties in its orbital ground and excited states.

We will also continue working on the protocols for quantum control of single spins in various solid-state structures, focusing mostly on the NV centers in diamond, but also using our expertise to better understand other semiconductor systems, such as quantum dots, and impurity centers in silicon. In order to achieve that, we will work on improved numerical approaches to modeling the non-equilibrium quantum dynamics in many-spin systems. Such problems are very difficult to model efficiently, but a number of promising approaches, based on the mean-field theories and their extensions, may help modeling larger systems with better accuracy. We expect that our research in this direction, along with fundamental advances, will lead to novel approaches for nanoscale magnetic and electric field sensing with high spatial resolution and high sensitivity, as has been demonstrated in our previous works [4,7], and these tools will be valuable for nanosciences, and nanomagnetism in particular.

Moreover, we plan to use our expertise in modeling the quantum many-spin dynamics and in theoretical development of the tools for the quantum spin control in order to study the nuclear magnetic resonance (NMR) experiments. The solid-state NMR is an important tool for various research efforts related to the DOE mission, and a special FWP is devoted to the solid-state NMR studies within Ames Laboratory. Due to a natural synergy between our work and the solid-state NMR, we expect that our analytical and numerical tools will be useful, and will greatly benefit both research directions.

References

[1] V. V. Dobrovitski and H. A. De Raedt, ”Efficient scheme for numerical simulations of the spin-bath decoherence”, *Phys. Rev. E* **67**, 056702 (2003);
W. Zhang, N. Konstantinidis, K. A. Al-Hassanieh, and V. V. Dobrovitski, ”Modelling decoherence in quantum spin systems” (Topical Review), *J. Phys.: Cond. Matter* **19**, 083202 (2007).
[2] R. Hanson, V. V. Dobrovitski, A. E. Feiguin, O. Gywat, D. D. Awschalom, ”Coherent dynamics of a single spin interacting with an adjustable spin bath”, *Science* **320**, 352 (2008)
[3] G. de Lange, Z. H. Wang, D. Riste, V. V. Dobrovitski, and R. Hanson, ”Universal dynamical decoupling of a single solid-state spin from a spin bath”, *Science* **330**, 60 (2010).
[4] G. de Lange, D. Riste, V. V. Dobrovitski, and R. Hanson, ”Single-spin magnetometry with multipulse sensing sequences”, *Phys. Rev. Lett.* **106**, 080802 (2011).
[5] G. de Lange, T. van der Sar, M. Blok, Zhi-Hui Wang, V. V. Dobrovitski, and R. Hanson, ”Controlling the quantum dynamics of a mesoscopic spin bath in diamond”, *Scientific Reports* **2**, 382 (2012).
[6] T. van der Sar, Z. H. Wang, M. S. Blok, H. Bernien, T. H. Taminiau, D. Toyli, D. Lidar, D. D. Awschalom, R. Hanson, and V. V. Dobrovitski, ”Decoherence-protected quantum gates for a hybrid solid-state spin register”, *Nature (London)* **484**, 82 (2012).
[7] T. H. Taminiau, J. J. T. Wagenaar, T. van der Sar, F. Jelezko, V. V. Dobrovitski, R. Hanson, ”Detection and control of individual nuclear spins using a weakly coupled electron spin”, *Phys. Rev. Lett.* (in print).
[8] J. H. Zhang, C. Z. Wang, Z. Z. Zhu, and V. V. Dobrovitski, ”Vibrational modes and lattice distortion of a nitrogen-vacancy center in diamond from first-principles calculations”, *Phys. Rev. B* **84**, 035211 (2011).

ELECTRONIC STRUCTURE AND NOVEL PROPERTIES IN COMPLEX OXIDES AND HETERO-INTERFACES

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Project scope

In this program, we explore various kinds of interfaces such as transition metal interfaces, metal-semiconductor interfaces and so forth. These interfaces possess rich physics including superconductivity, topological insulators, and electric-field driven magnetism. Theoretical/computational developments in electronic structure studies will provide an excellent tool for identifying striking phenomena as well as for guiding the exploratory synthesis of novel materials. This program now focuses on the elucidation of several striking, diverse and challenging phenomenon observed in perovskite hetero-interfaces, semiconductor hetero-bonded interfaces. More specifically, we focus on (i) interface electronic structure and the excitonic mechanism of superconductivity, (ii) electric field induced magnetism at surfaces and interfaces, (iii) topological insulators, (iv) LaAlO3/SrTiO3 hetero-interfaces and its possible interface superconductivity, and (v) structure and magnetic order in bilayer manganites.

Recent Progress

Topological Insulators

In spite of the clear surface state Dirac cone features in the pristine Bi_2Se_3 slab, its Dirac point is quite close to the bulk states and both Dirac point and bulk states appear at the same energy level, which can be a source of scattering. By appropriate substitutions at the surface, the changes in the surface potential affect the level of the surface state and finally we can acquire the ideal Dirac cone which is placed inside the bulk band gap of Bi_2Se_3.

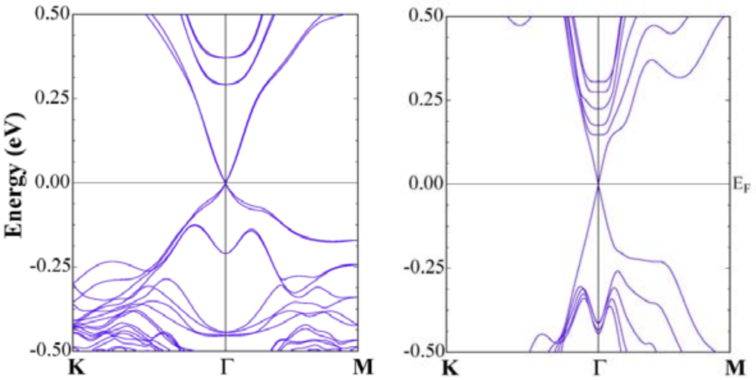

FIG.1 Quasi-particle dispersions of Bi2Se3 slab with (a) 50% and (b) 100% O substitutions.

When we substitute O for the surface Se atom at the end of the Bi_2Se_3 film, the topologically protected surface state connecting the inverted bulk conduction and valence bands moves upward, showing an ideal and isolated Dirac cone with a point-like Fermi surface at Γ. Figs.1(a) and (b) are the electronic band structures with 50% and 100% O substitutions of the surface Se atoms, respectively. Comparing the two different surface coverage of oxygen atoms, the position of the Dirac point relative to the bulk valence bands moves upward as the coverage ratio increases. From these results, we can get a hint to tune the position of the Dirac point continuously by controlling the amount of O substitutions.

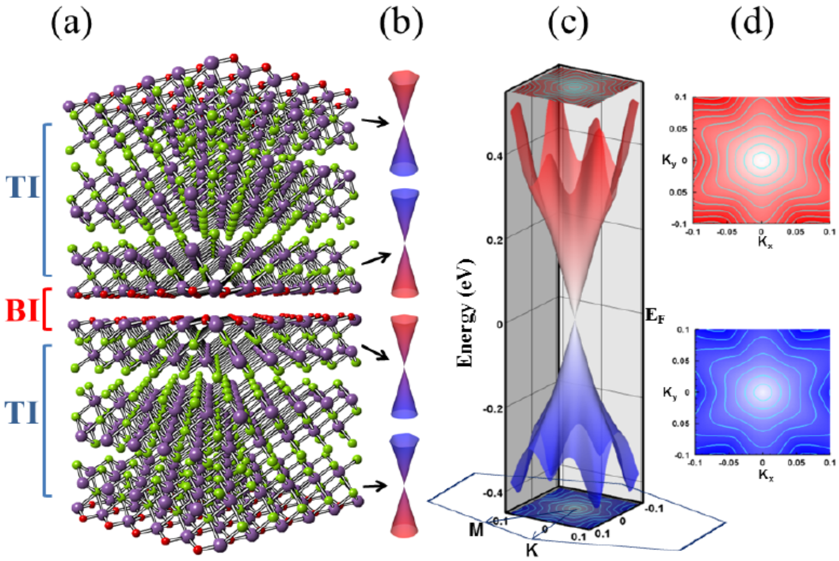

FIG.2 (a) Superlattices of alternating band (BI) and topological (TI) insulators. (b) Dirac cones representing each interface state between the layers of band and topological insulators in (a). (c) 3D plot of the interface state of (a), and (d) its contour plot above and below the Kramers point.

The extension of a single surface to multiple interfaces, i.e., a periodic array of alternating band and topological insulators or *topologica/band insulator (TI/BI) superlattices*, has not been attempted yet, although multiple interfacial Dirac cones in bulk led to new technological opportunities for practical applications such as thermoelectric and spintronic devices [4].
The Bi_2Se_3 crystal has a rhombohedral unit cell or a layered structure stacked along the c-axis of the hexagonal lattice, as shown as Fig. 3(a). One quintuple-layer slab has one formula unit in which the anion Se atom has two different sites. The Se atom at the center has covalent bonds with six Bi atoms, and the other Se site has three covalent bonds with Bi, but has van der Waals interactions with three Se atoms in the other quintuple-layer slab. To construct TI/BI superlattices, we use the hexagonal supercell structures whose (0001) interfaces correspond to a two-dimensional hexagonal Brillouin zone, as in the film geometry.

Electric field-induced magnetism phenomena at surfaces and intefaces

The role of an electric field at a transition metal and MgO interface has been studied such as on magnetocrystalline anisotropy (MCA).[6,10] For the Fe/MgO interface, monolayer Fe gives rise to a perpendicular MCA, and the electric field introduces some modification. Interestingly, the MCA of $Fe_{0.75}Co_{0.25}$/MgO is gigantically modified. In this study, the existence of an FeO layer at the interface is mostly responsible for the resultant physics. Furthermore, possible switching by the electric field between out-of-plane and in-plane MCA at the Fe/MgO interface was also investigated.

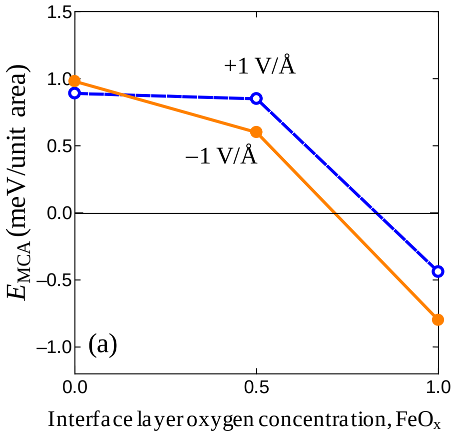

Fig.3 Dependence of E_{MCA} on the oxygen concentration x in the interfacial FeO_x layer for the Au-capped Fe/MgO interfaces, for external electric fields of 1 VÅ (open circles) and -1 V/Å (closed circles).

Multiplets in a ligand field within density functional theory

The treatment of multiplets in a ligand field within density functional theory has been also explored.[1] Multiplet structures of transition metals in a ligand field can be dealt with multi-dimensional Slater determinants, which however is computationally too demanding. We proposed alternative approach in determining multiplet structure within a density functional calculation by imposing a density-matrix constraint on d-orbital occupation number consistent with local site and state symmetries. We applied this method for the case of an isolated Fe phthalocyanine (FePc) molecule with overall D_{4h} symmetry. Among possible three stationary states, ^3E_g, $^3A_{2g}$, and $^3B_{2g}$ symmetries of the Fe^{+2} ion, $^3A_{2g}$ turns out to be the lowest energy configuration. By contrast, a columnar stacking of FePc molecules (a-FePc) is found to change the ground state to ^3E_g due to hybridization between adjacent molecules.

Interface electronic structure and possible high-Tc superconductivity in a hetero-bonded metal-semiconductor superlattice

To explore the excitonic mechanism of superconductivity, it is indispensable to know the screened Coulomb interaction. In other words, the dielectric function, $\varepsilon_{G,G'}(q,\omega)=\delta_{G,G'}-4\pi V(q+G')\chi_{G,G'}(q,\omega)$, where V(q+G) is the bare Coulomb potential. So far, the formulation of the susceptibility, $\chi_{G,G'}(q,w)$, has been done with matrix elements fully taken into account. To proceed, the validity of the summation to evaluate $\chi_{G,G'}(q,w)$, at first a constant matrix approximation has been invoked for the Sc case, where nesting along the (001) direction was identified in the 70’s. Our test result also shows nesting along the (001) direction which agrees with previous work.

In addition to the exploration for excitonic mechanism, we also studied the recently discovered pnictide superconductor, SrPtAs, which is first hexagonal without the Fe atom. In this material, due to large spin-orbit coupling at Pt, the admixture of spin singlet and triplet occurs. Despite the presence of the global inversion center as shown in Fig.4, locally broken inversion symmetry at the PtAs layer gives characteristics of non-centrosymmetric superconductivity. This is by far the first example of a non-centrosymmetric superconductor with global inversion center.

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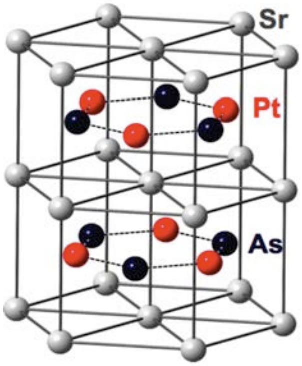

Fig. 4 Crystal structure of SrPtAs

Planned activities: 2011-2012

Superconductivity

Recent progress in code development of $\chi(q,\omega)$ will provide a concrete result on the excitonic mechanism of superconductivity; it is now in the final stage of debugging and testing the validity of the code implementation. In addition, the microscopic model of the excitonic mechanism is pursued to extend the ABB model based on formulation of Eliashberg theory, which may enable us to estimate the transition temperature by first-principles. In parallel to exploration the for excitonic mechanism, manuscript on the first hexagonal pnictide superconducting material without Fe, namely SrPtAs will be finished, where the detailed calculation of local spin structure and phonon dispersion of SrPtAs are discussed.

Topological insulator

We plan to investigate the role of a magnetic impurity such as Fe in topologically protected surface states. The topologically protected state may be destroyed by the introduction of a magnetic impurity due to broken time-reversal symmetry, which also induces the anomalous Hall effect (AHE). This AHE is known to be directly associated with the non-trivial Berry's phase, which we plan to calculate by first-principles. Also, in addition to well-explored Bi_2Se_3 and similar, there have been intensive research in exploration for new class of topological insulator – such as half-Heusler alloy, cubic system and so forth. We push ourselves in the same context to investigate systems such as cubic-halides in perovskite structure.

Electric field driven magnetism at interfaces and surfaces:

The electric field induced spin-dependent surface/interface phenomena will be pursued further. More specifically, work function and spin-dependent transport in an electric field will be tackled with our film FLAPW method. For spin-dependent transport with an electric field, Landauer theory will be utilized. Calculations will focus first on transition-metal surfaces such as Fe, Co, and Ni with several surface orientations. Our ultimate goal is to treat half-metallic surface systems such Fe_2O_3 and Cr_2O_3, which would maximize the spin degree of freedom. These offer a new and exciting opportunity for controlling the magnetism by the application of an electric field.

Publications

1. “Constraint density functional calculations for multiplets in a ligand-field applied to Fe-phthalocyanine” Kohji Nakamura, Yukie Kitaoka, Tory Akiyama, Tomonori Ito, M. Weinert, and A.J. Freeman; Phys. Rev. B **85**, 235129 (2012).

2. “Role of strong spin-orbit coupling in the superconductivity of the hexagonal pnictide SrPtAs” S.J. Youn, M.H. Fischer, S.H.Rhim, M. Sigrist, and D.F. Agterberg; Phys. Rev. B **85**, R220505 (2012).

3. “CsSnI3: Semiconductor or Metal? High Electrical Conductivity and Strong Near-Infrared Photoluminescence from a Single Material. High Hole Mobility and Phase-Transitions”, Chung In, Jung-Hwan Song, Jino Im, JohnAndroulakis, Christos D. Malliakas, Hao Li, Arthur J. Freeman, John T. Kenney, and Mercouri G.Kanatzidis, J. Am. Chem. Soc. **134**, 8579 (2012).

4. “Multiple Dirac fermions from a topological insulator and graphene superlattice” , Hosub Jin, Jino Im, Jung-Hwan Song, and A. J. Freeman, Phys. Rev. B **85**, 045307 (2012).

5. “Topological and magnetic phase transisions in Bi2Se3 thin films with magnetic impurities”, Hosub Jin, Jino Im, and A.J. Freeman, Phys. Rev. B **84**, 134408 (2011).

6. “Electric Field-induced Modification of Magnetocrystalline Anisotropy in Transition-metal Films and at metal-insulator interfaces” Kohji Nakamura, Toru Akiyama, Tomonori Ito, M. Weinert, and A.J. Freeman, J. Magnetics **16**, 161 (2011).

7. “Dirac cone engineering in Bi2Se3 thin films” Hosub Jin, Jung-Hwan Song, and A.J. Freeman, Phys. Rev. B **83**, 125319 (2011).

8. “Candidates for topological insulators: Pb-based chalcogenide series”, Hosub Jin, Jung-Hwan Song, and A.J. Freeman, Phys. Rev. B **83**, 041202 (2011).

9. “Interfacial Dirac cones from alternating Topological Invariant superlattice structure of Bi2Se3”, Jung-Hwan Song, Hosub Jin, and A.J. Freeman, Phys. Rev. Lett. **105**, 096403 (2010).

10. “Role of an interfacial FeO layer in the electric-field-driven switching of magnetocrystalline anisotropy at the Fe/MgO interface” Kohji Nakamura, Toru Akiyama, Tomonori Ito, M. Weinert, and A. J. Freeman, Phys. Rev. B **81**, 220409 (2010).

11. “Surface-stabilized nonferromagnetic ordering of a layered ferromagnetic manganite” V. B. Nascimento, J.W. Freeland, R. Saniz, R. G. Moore, D. Mazur, H. Liu, M. H. Pan, J. Rundgren, K. E. Gray, R. A. Rosenberg, H. Zheng, J. F. Mitchell, A. J. Freeman, K. Veltruska, and E. W. Plummer, Phys. Rev. Lett. **103**, 227201 (2009).

12. “Orbital Mixing and Nesting in the bilayer Manganites La(2-2x)Sr(1+2x)Mn2O7”, R. Saniz, M.R. Norman, and A.J. Freeman, Phys. Rev. Lett. **101**, 236402 (2008).

Time-resolved photoemission, transmissivity, X-ray absorption spectroscopy and resonant inelastic X-ray scattering in strongly correlated materials

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Project scope

The emphasis of this work is to develop new algorithms and solve and analyze the solutions for a range of different pump/probe types of experiments taking place in the ultrafast regime. Examples include time-resolved photoemission spectroscopy where experiments have recently examined charge density wave systems and seen a transient filling in of the gap with a nonvanishing order parameter. Another example is high harmonic generation in the solid state from applying a pump that generates Bloch oscillations, whose Fourier components are odd multiples of the fundamental frequency of the pump pulse. Our work will strive to understand and explain these experiments as well as examine newer experiments like time-resolved X-ray absorption spectroscopy or time-resolved Compton scattering. Our main emphasis is on exact solutions which can be found for noninteracting models, or with techniques like dynamical mean-field theory, generalized to nonequilibrium situations. We are part of a CMCSN team on pump/probe spectroscopies (also supported by DOE) and collaborate with the Devereaux group at SLAC and Stanford as well as with international researchers in the Ukraine and India.

Recent Progress

Nonequilibrium “melting” of a charge density wave

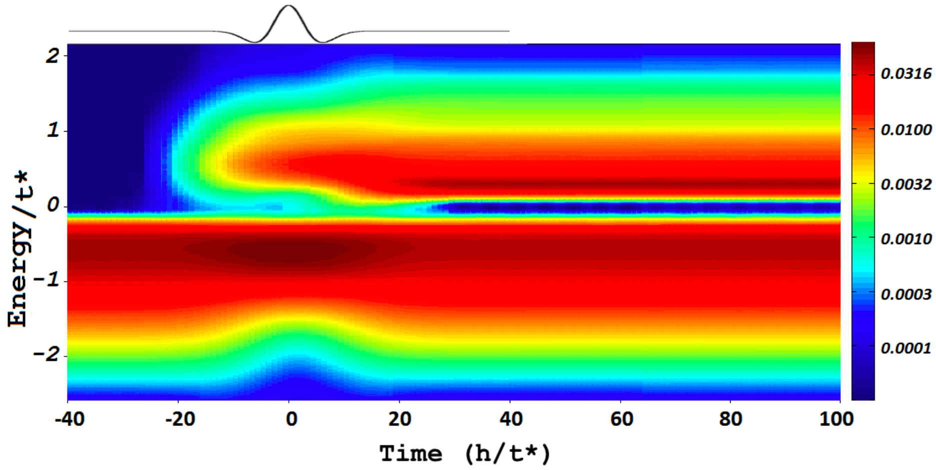

Figure 1: *False-color image of the transient closing of a charge-density-wave gap (light green and cyan for times between -15 and 30) when pumped by an electric field (shown schematically above the image). The gap closes and reforms while the order parameter (not shown) remains large. One time step is on the order of 4 fs. Note also how the higher band is filled and remains filled for long times due to the heating of the system from the pump pulse.*

We have found a simple noninteracting model that can be solved exactly for the nonequilibrium behavior of a charge density wave that is pumped by a large amplitude ultrafast pulse. The model is just that of noninteracting electrons in a lattice with a basis where the site energy is 0 on one sublattice and U on the other. This model can be solved exactly in nonequilibrium by working in momentum space and determining evolution operators of the two coupled momenta **k** and **k**+**Q** via a Trotter formula for 2×2 matrices $(\mathbf{Q} = (\pi, \pi, \ldots))$. The solution is exact for all spatial dimensions, although we illustrate our results on a d-dimensional hypercubic lattice in the limit as $d \to \infty$.

The solution for the transient density of states is shown as a false color image in Fig. 1. One can see for intermediate times, both when the pulse starts and for some time after it ends, the gap becomes filled in and then reforms. This is exactly the scenario seen in experiments, except there the transient region lasts longer due to an energy exchange between the electronic system and the phonons which takes a longer period of time to damp out.The order parameter is reduced by about 20% during this time, but never goes to zero, even when the gap vanishes, so the nonequilibrium “melting” is qualitatively different from the equilibrium phase transition where the order either occurs simultaneously with the gap formation or after the gap formation (as the temperature is lowered). This work is under review at *Nature Physics*.

High harmonic generation from Bloch oscillations

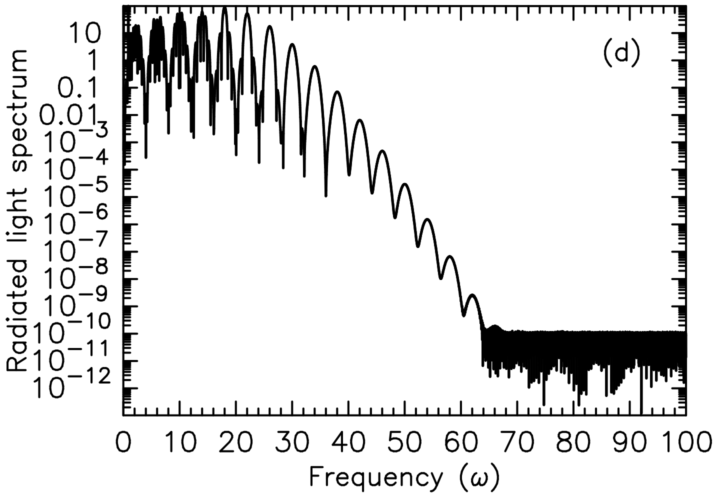

Figure 2: *Semilog plot of HHG from a nearest-neighbor tight-binding hypercubic lattice in any dimension. The peaks occur at odd harmonics of the fundamental frequency of the pump pulse before they hit a noise floor at high frequencies. At low frequencies, the peaks develop additional subpeak structure that is not well understood.*

When a system is hit with a large pulse, it causes a current to flow that oscillates rapidly. Because the wavevector cannot evolve outside the Brillouin zone, but is Bragg scattered back in, the oscillations will have many high order harmonics in them. By assuming that the acceleration of the electrons leads to photon emission, one can construct the radiation spectra from the Fourier transform of the current versus time. We have examined the simplest systems in this problem, including high harmonic generation (HHG) in metals (see Fig. 2), in photodoped silicon, and photodoped ZnO. We also have investigated effects due to impurity scattering and phonon scattering. We find in many cases, the response is similar regardless of the details of the bandstructure or the crystal orientation that the light shines on. The results also look similar to those seen in HHG from atoms. We have one paper to appear in *Physica Scripta* and one under review at *New Journal of Physics*.

X-ray photoemission spectroscopy and X-ray absorption spectroscopy

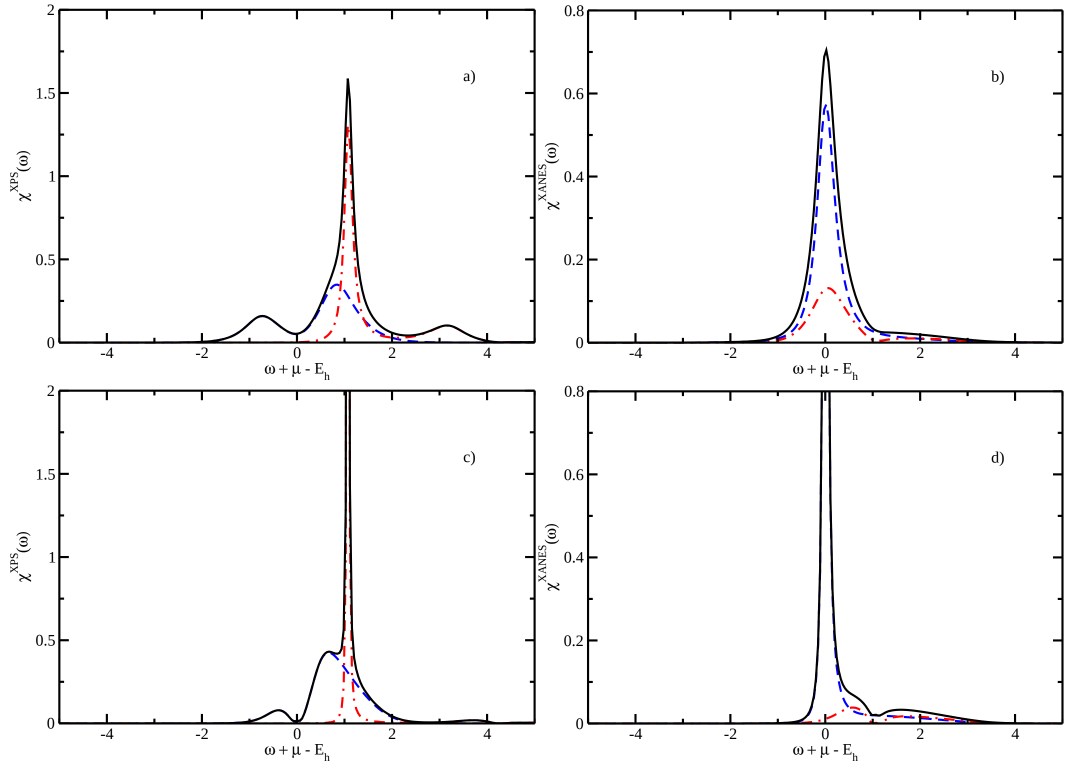

Figure 3: *Core-hole XPS (left) and XAS (right) for a Mott insulator at high (top) and low (bottom) temperature. Note the similarity between the two spectroscopies and the development of large peaks as the temperature is lowered. The main difference is the additional low-energy features in the core-hole propagator (XPS) signal.*

We have been studying both core-level X-ray photoemission spectroscopy (XPS), where an X-ray shines on a material with enough energy to eject a core electron out from the material and be detected by a detector, and X-ray absorption spectroscopy (XAS), where the X-ray energy is tuned to excite a core electron up to unoccupied states in the conduction band of the material. The two spectroscopies in Fig. 3 are closely related, with the former being given by the core-hole propagator and the latter by a mixed core-hole/conduction-electron correlation function. Both spectra can be calculated exactly in the Falicov-Kimball model with dynamical mean-field theory and both processes illustrate the orthogonality catastrophe in their response. This work has been submitted to *Condensed Matter Physics*.

Future work for 2012-2013

We have a number of different projects we will be working on during the next year. We will continue the charge-density-wave work by examining the exact solution of the nonequilibrium Falicov-Kimball model in the ordered phase. This solution can be done with dynamical mean-field theory at the expense of working with a spatially inhomogeneous system. Matrix sizes that need to be inverted double, and the computations must be done at lower initial temperatures, which will increase the computational time by about an order of magnitude relative to normal phase calculations. We will examine the TR-PES in this system to see what the systematic behavior is as the order parameter is reduced, which creates significant additional scattering in the system. We also will examine HHG in the simpler charge-density-wave model we described above. This result is particularly interesting because we can directly model both the photoexcitation and the Bloch oscillations in the system as a function of time. We find interesting oscillatory behavior for the energy absorbed by the charge-density wave during HHG as a function of the gap size.

We plan to extend the XPS and XAS work from equilibrium into the time domain to see what new effects might be present there. This problem can also be solved exactly within dynamical mean-field theory for the Falicov-Kimball model. We hope that we can find interesting new effects in the XAS spectra that will interest experimental groups in looking into this behavior.

Finally, we plan on examining the effect of electron-phonon coupling by treating phonons within a perturbative approach, similar to Migdal-Elisahberg theory, but in nonequilibrium. We will examine relaxation phenomena, the time-dependent momentum distribution (as measured by Compton scattering), and charge-density-wave systems that are formed via the electron-phonon interaction.

Publications supported by DOE 2009-2012

[1] O. P. Matveev, A. M. Shvaika, and J. K. Freericks,*Nonresonant Raman and inelastic X-ray scattering in the charge-density-wave phase of the spinless Falicov-Kimball model*, Phys. Rev. B **79**, 115130 (2009). 10.1103/PhysRevB.79.115130 .

[2] O. P. Matveev, A. M. Shvaika, and J. K. Freericks, *Total electronic Raman scattering in the charge-density-wave phase of the spinless Falicov-Kimball model*, J. Phys. Stud. (Ukraine) **13**, 4703 (2009).

[3] B. Moritz, T. P. Devereaux, and J. K. Freericks, *Time-resolved photoemission of strongly correlated electrons driven out of equilibrium*, Phys. Rev. B **81**, 165112 (2010). 10.1103/PhysRevB.81.165112; Virtual Journal of Ultrafast Science, Vol. **9**, Iss. 5 (2010).

[4] O. P. Matveev, A. M. Shvaika, and J. K. Freericks, *Resonant Raman scattering effects in a nesting driven charge-density-wave insulator: exact analysis of the spinless Falicov-Kimball model with dynamical mean-field theory*, Phys. Rev. B **82**, 155115 (2010). 10.1103/PhysRevB.82.155115.

[5] B. Moritz, T. P. Devereaux, and J. K. Freericks, *Temporal response of nonequilibrium correlated electrons*, Comp. Phys. Commun. **182**, 109 (2011). 10.1016/j.cpc.2010.05.020.

[6] J. K. Freericks, A. Y. Liu, A. F. Kemper, and T. P. Devereaux, *Pulsed high harmonic generation of light due to pumped Bloch oscillations in noninteracting metals*, to appear in Phys. Scripta (2012) .

THEORY OF FLUCTUATIONS IN SUPERCONDUCTORS

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1 PROJECT SCOPE

This DOE-supported program focuses on the fundamental theory of fluctuation phenomena in superconductors. The physical systems of interest include high-temperature cuprate superconductors, two-dimensional disordered superconducting films, superconducting proximity systems, superconducting heterostructures involving nanowires and ferromagnets, and topological superconductors. The main general goals of the project are to improve fundamental understanding of these systems and to provide solid theoretical basis for a number of relevant recent and ongoing experimental studies. A particularly important project is to further develop the theory of paired electron pockets in the underdoped cuprate superconductors and suggest new experiments that would unambiguously confirm or rule out this scenario of the pseudogap. Another ambitious component of this program is to develop a substantially new theoretical framework to investigate non-perturbative quantum fluctuation effects in broken-symmetry phases of quantum matter.

2 RECENT PROGRESS

2.1 ARPES in a current in the underdoped cuprates

One of the major questions in the field of high-temperature superconductivity is whether the pseudogap phase in the underdoped cuprates contains a "ghost" electron pocket that was possibly seen in the quantum oscillation experiments, but so far has not been directly visualized by any other means. Putting aside controversial debates about the nature of the pseudogap, it is reasonable to look for a new experiment that would unambiguously resolve the stand-alone question of the existence of the ghost pocket and provide a clear "yes" or "no" answer. Such an experiment involving ARPES in the presence of a current was first mentioned in Ref. [3], and recently the PI has made further progress in working out its detailed predictions assuming the paired electron pocket scenario [V. Galitski and S. Sachdev, Phys. Rev. B **79**, 134512 (2009)]. The logic is as follows: suppose that an electron pocket indeed forms due to a Brillouin zone folding and then a strong electron pairing occurs there, hiding the electron Fermi surface from low-energy ARPES. If a strong magnetic field is applied (for example, $B \sim 50\ T$ as in the quantum oscillation experiment), it disrupts Cooper pairing and opens up the electron pocket leading to the quantum oscillations. However, ARPES can not be performed in such a strong magnetic field and consequently direct visualization of a Fermi surface that gives rise to the oscillations is impossible. To access it, one needs to suppress strong pairing in the pocket by some other means without smearing out the

Fermi surface (hence, temperature and disorder alone are not appropriate). This however can be achieved by performing a photoemission experiment while running a current through the sample.

In a recent (to-be-published) work, the PI has developed a comprehensive theory of such an experiment. Two different regimes have been identified: (i) a strongly non-linear regime, where a strong current exceeds the critical current and opens up and shifts the electron pocket in a predictable way; and (ii) a linear regime, where a weak current is applied and ARPES is performed using photons with an energy, ω, just below the pseudogap. Without the current, only unpaired hole-like parts of the Fermi surface are seen, but even a small current applied in an antinodal direction effectively tilts the dispersion one way and makes a part of the electron pocket visible at the same energy. This predicted phenomenon is shown in Fig. 1, where the left panel has only hole-type Fermi pockets corresponding to zero current, while the right panel has the electron pocket showing up. The full picture of the ARPES in a current experiment is rather involved due to strong anisotropy, but the main phenomena of Fermi surface tilting and suppression of the pairing gap should provide a smoking gone test of the presence of electron pockets in the pseudogap phase.

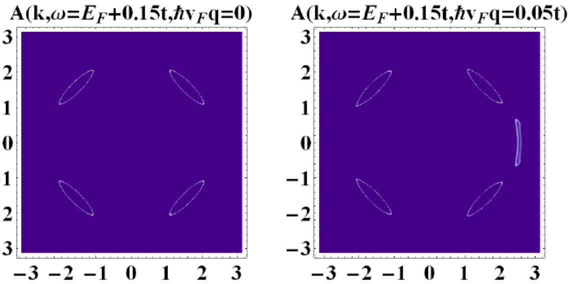

Figure 1: The left panel shows the spectral function for photon energy right below the pseudogap energy. In this regime, the electron pocket is hidden, while the hole pockets are visible. The right panel shows the same spectral function but in the presence of a current along the antinodal direction. Notice, a part of the electron pocket showing up.

2.2 Fluctuations in proximity systems

A very interesting recent experimental study has shown that a ferromagnetic Cobalt nanowire can be made superconducting by placing it in contact with a conventional superconductor (see, Fig. 2). Proximity-induced superconductivity was observed in the wire over a distance of a few hundred nanometers. A surprising and peculiar observation of Wang *et al.*, Nature Physics **6**, 389 (2010), was that transition to superconductivity was preempted by a large and sharp resistance peak (see, Fig. 2). The resistance peak disappears when the Co wire is replaced by a gold wire, indicating a direct connection between it and the ferromagnetism of the wire.

In a recent theoretical paper [5], the PI argued that the observed phenomena are consistent with the scenario of a ferromagnetic wire, proximity-coupled to a superconductor through a spin-orbit-coupled barrier, so that p-wave superconductivity is induced. As to the most surprising experimental finding – the resistance peak – it was naturally explained as a density-of-states (DOS) fluctuation effect. As we approach the transition temperature of the Tungsten electrodes, Cooper pair fluctuations grow. By virtue of the Rashba spin-orbit coupling at the W-Co interfaces, singlet Cooper pairs inside W are converted and triplet fluctuations permeate into the Co wire. The Aslamazov-Larkin correction to the conductivity arises due to the transport of these fluctuating Cooper pairs through the wire. However, Cooper pair tunneling across the interface is strongly suppressed because it is a higher-order process in both tunneling and the singlet-triplet conversion rate. The single-electron tunneling and the DOS correction, on the other hand, are

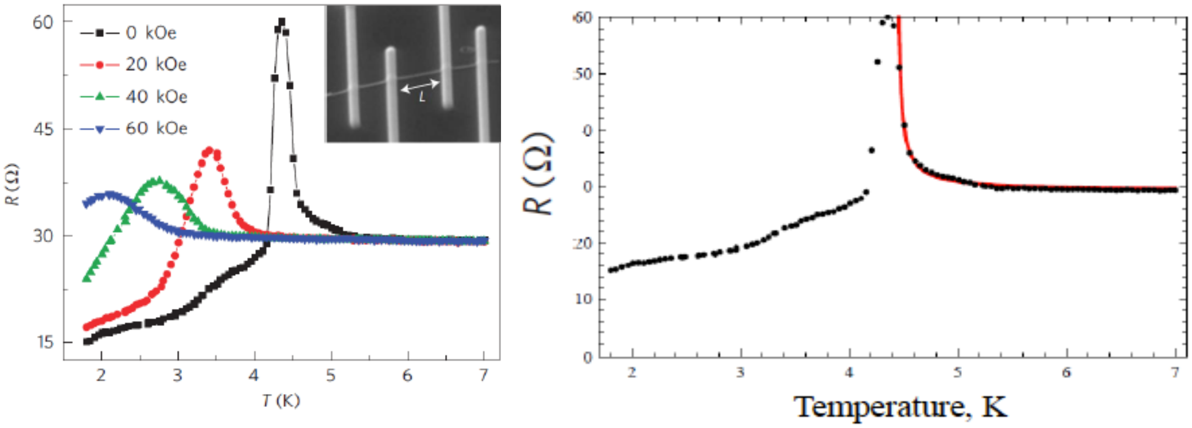

Figure 2: Left panel: Experimental data of Wang *et al.*, Nature Physics **6**, 389 (2010) – displays the typical T-dependence of the resistance of a fluctuating ferromagnet-superconductor proximity heterostructure. Note the surprising upturn in the resistance. Right panel: The data points here represent raw data (courtesy of J. Wang) for a 80 nm thick Cobalt nanowire in zero field. The red curves represent a theoretical fit that includes fluctuation corrections to the

lower-order tunneling processes that require no spin flipping. Therefore, the DOS correction is initially parametrically larger than the AL contribution, thus giving a negative overall correction to the Drude conductivity. This qualitatively explains the anomalous upturn in the resistance as a function of temperature. Fig. 2 (right panel) shows a comparison between the experimental data and a calculation that takes into account fluctuations in the Andreev scattering at the interface.

2.3 Topological superconductivity proximity-induced from a high-temperature superconductor

In Ref. [6] and ongoing work, we have considered topological superconductivity proximity-induced from a cuprate high-temperature superconductor (HTSC). We first considered a ballistic planar junction between a HTSC and a metallic ferromagnet. Bogoliubov-de Gennes equations were obtained by explicitly modeling the barrier, and taking account of the transport anisotropy in the HTSC. The self-consistent boundary conditions were derived. For a ferromagnet layer deposited on a (100) facet of the HTSC, triplet p-wave superconductivity is induced. For the layer deposited on a (110) facet, the induced gap does not have the p-wave orbital character, but has an even orbital symmetry and an odd dependence on energy. For the layer on the (001) facet, an exotic f -wave superconductivity is induced. We also consider the induced triplet gap in a one-dimensional half-metallic nanowire deposited on a (001) facet of a HTSC. Due to the breaking of translational symmetry in the direction perpendicular to the wire axis, the expression for the gap receives contributions from different perpendicular momentum eigenstates in the superconductor. We find that for a wire axis along the a-axis, these different contributions constructively interfere and give rise to a robust triplet p-wave gap. For a wire oriented 45 degrees away from the a-axis the different contributions destructively interfere and the induced triplet p-wave gap vanishes. For the appropriately oriented wire, the induced p-wave gap should give rise to Majorana fermions at the ends of the half-metallic wire that would exist in a much wider range of temperatures compared to the hybrid structures involving conventional superconductors.

3 PLANNED ACTIVITIES: 2012-2013

The following are the goals of PI's DOE research in 2012-2013:

1. To develop a quantitative theory of angle-resolved photoemission spectroscopy in the underdoped cuprates in the presence of currents in various theoretical scenarios. In particular, this theory will provide a means to unambiguously determine whether the enigmatic pseudogap phase contains a strongly fluctuating paired electron pocket.
2. To develop a theory of proximity effect from a fluctuating cuprate superconductor in the pseudogap phase into a normal metal. Recent experiments [Phys. Rev. Lett. **103**, 197003 (2009)] have observed a *proximity-induced pseudogap*, which strongly suggests that the latter indeed contains strongly fluctuating Cooper pairs - a scenario that the current project will help elucidate.
3. To study further topological superconductivity proximity-induced from a high-temperature superconductor [6]. In particular, the possibility of inducing Majoranas from the pseudogap phase will be explored. This project will both help increase temperature scales at which topological superconductivity is present and provide an additional insight into the nature of the pseudogap.
4. To further develop non-perturbative theoretical methods introduced by the PI in Refs. [1, 2] to describe quantum dynamics in fluctuating superconductors. In particular, the project will involve studies of possible quantum soliton excitations in superconducting/superfluid phases and explicitly identify the Higgs mode deep in the superfluid along with other competing non-linear modes. The importance of this project is in that it will shed light on the fundamentals of the spontaneous symmetry breaking phenomenon.

List of Publications in 2010 – 2012

[1] V. M. Galitski, "Non-perturbative Quantum Dynamics of the Order Parameter in the Pairing Model," Physical Review B **82**, 054511 (2010).

[2] V. M. Galitski, "Quantum-to-Classical Correspondence and Hubbard-Stratonovich Dynamical Systems, a Lie-Algebraic Approach," Physical Review A **84**, 012118 (2011).

[3] R. Sensarma and V. M. Galitski, "Three Projected Wave-Functions for a High-Temperature Superconductor," Rapid Communication in Physical Review B **84**, 060503(R) (2011).

[4] J. Mitchell, A. Gangopadhyay, V. M. Galitski, and M. Mueller, "Two-component Coulomb glass in insulators with a local attraction," Physical Review B **85**, 195141 (2012).

[5] S. Takei and V. M. Galitski, "Microscopic theory for a ferromagnetic-nanowire/superconductor heterostructure: Transport, fluctuations and topological superconductivity," to be published in Physical Review B (2012) [preprint: `http://arxiv.org/abs/1201.2180`].

[6] S. Takei, B. Fregoso, V. Galitski, and S. Das Sarma, "Topological superconductivity and Majorana fermions in heterostructures involving high-temperature superconductors," to be published in Physical Review B (2012) [preprint: `http://arxiv.org/abs/1206.3226`].

SEMICONDUCTOR NANOSTRUCTURES BY SCIENTIFIC DESIGN

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Project Scope

We develop and use quantum simulation techniques to predict structural, electronic, optical and transport properties affecting the scientific design of semiconductor nanostructures. We focus on the study of surfaces and interfaces at the nanoscale, in particular assembly and embedding of semiconductor nanoparticles, with the goal of providing a microscopic description of nanostructured materials in realistic environments, directly comparable with experimental conditions. We address four major problems: (i) devise realistic structural models of integrated nanostructures, e.g. quantum dots embedded in solid matrices; (iii) provide an accurate description of weak interactions (in particular van der Waals forces) within, e.g. self-assembled monolayers on surfaces; (iii) provide an efficient and accurate description of excited state properties of nanostructures, beyond standard Density Functional Theory; and (iv) provide an efficient and accurate description of thermal transport properties at the atomistic level. Our goal is to understand and predict properties of nanostructured materials of interest to renewable energy applications, for example solar conversion and thermoelectric devices.

Recent Progress

1. Electronic and thermal properties of semiconducting nanoparticles

1.1 Electronic structure calculation using many body perturbation theory

We recently completed the development of an algorithm and related codes to solve the Bethe-Salpeter equation (BSE) without the need to compute empty electronic states and inverting explicitly dielectric matrices [D.Rocca et al., JCP 2010]. In our approach, the quantum Liouville equation is solved iteratively within first order perturbation theory, with a Hamiltonian containing a static self-energy operator. This procedure is equivalent to solving the statically screened BSE. Full absorption spectra may be obtained with a computational workload comparable to ground state Hartree–Fock calculations. We obtained results for small molecules, for the spectra of 1- 2 nm Si clusters in a wide energy range, for a dipeptide exhibiting charge transfer excitations and for aromatic molecules. We also generalized our approach to solids and computed absorption spectra of elemental and compound semiconductors.

1.2 Embedded Nanoparticles

We carried out coupled classical and quantum simulations of 1 to 2 nm Si nanocrystals (NCs) embedded in amorphous SiO_2 [Li and Galli, PRL 2010] and we fond that by tuning the density of the oxide matrix, one may change the relative alignment of Si NC and SiO_2 electronic states at the interface. We found that interfacial strain plays a key role in determining the variation of the nanaoparticle gap as a function of size, as well as of conduction band offset with the oxide. In particular, our results show that it is the variation of the valence band offset with size that is responsible for the gap change. Our findings suggest that the elastic properties of the embedding matrix may be tuned to tailor the energy levels of small Si NCs so as to optimize their performance in opto-electronic devices and solar cells. Work is in progress on

Si nanoparticles embedded in nitride matrices, exploiting methods similar to those developed to study freezing of tetrahedral liquids from the melt [Li et al, JCP 2009 and Nat. Mat. 2009]; these methods will be used to derive structural models.

1.3 Thermal transport in nanoporous Si

We carried out molecular and lattice dynamics calculations of the thermal conductivity of nanoporous silicon (np-Si; see Fig.1) [He at al., ACS Nano 2011], for several samples generated using empirical potentials. We found that the thermal conductivity of np-Si may attain values 10-20 times smaller than in bulk Si for porosities and surface-to-volume ratios similar to those obtained in nanomeshes recently fabricated by the group of Prof. J.Heath at Caltech and in np-Si fabricated at UCB. Further reduction of almost an order of magnitude is obtained in thin films with thickness of 20 nm, in agreement with experiment. We found that the presence of pores has two main effects on heat carriers: appearance of non-propagating, diffusive modes and reduction of the group velocity of propagating modes. The former effect is enhanced by the presence of disorder at the pore surfaces; the latter is enhanced by decreasing the film thickness. Work is in progress to compute the figure of merit of small np-Si samples by carrying out a series of Boltzman transport calculations of the electronic conductivity and Seebeck coefficient.

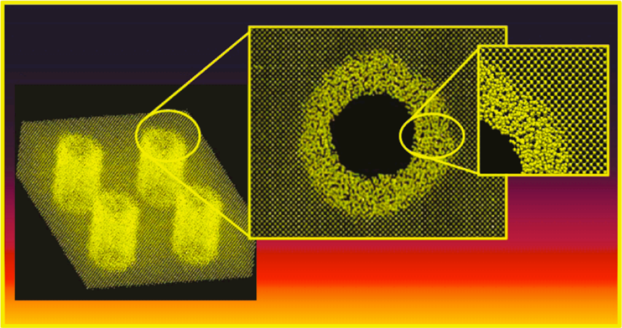


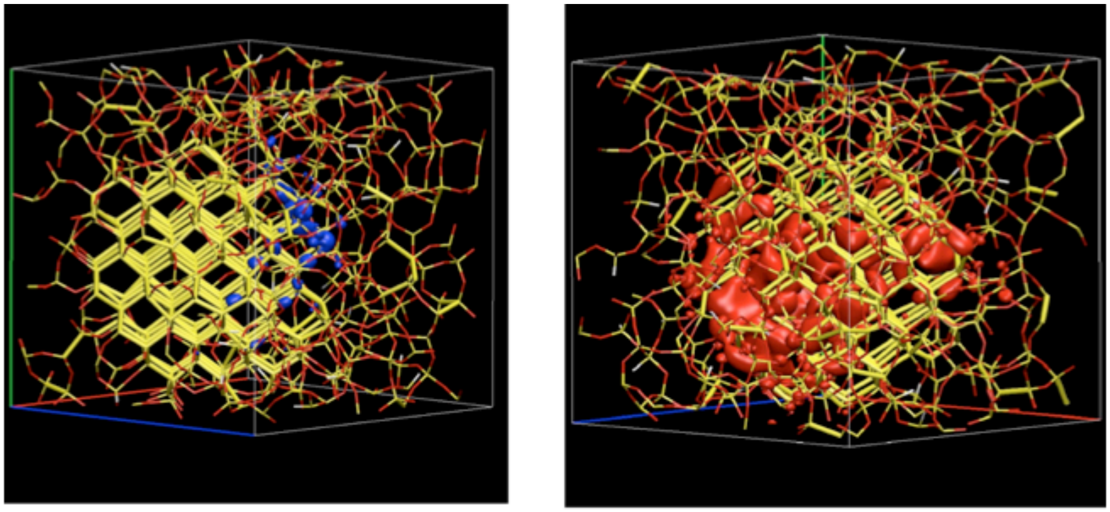
Figure 1: Representative microscopic picture of nanoporous Si investigated in the present work.

2. Self-assembled monolayers on surfaces and study of weak binding

We developed and applied techniques to study weak interactions between self-assembled monolayers on surfaces [Steele et al., PCCP 2009; Lu et al., PRL 2009; Li et al., JPCA 2010, and Li et al, JCTC 2009]. These techniques are based on the calculation of exact exchange and correlation energy within the Random Phase Approximation (RPA). The response functions involved in the evaluation of the RPA correlation energy were efficiently obtained with methods similar to those developed to compute excited state of molecules and solids, within many body perturbation theory. We also carried out accurate Quantum Monte Carlo calculations of weak binding energies, e.g. in graphite [Spanu, Sorella and Galli, PRL 2009]. Work is in progress to apply the approaches developed for flat surfaces to functionalized surfaces of nanoparticles and assemblies of nanoparticles.

Planned activities

We are continuing our investigations of embedded nanoparticles with two main goals: (i) generate realistic models of the nanoparticles by combined classical and ab-initio MD simulations; (ii) extract embedded semiconducting nanoparticles with an appropriately thick interface shell, and carry out excited state calculations using many body perturbation theory (see Fig. 2). We aim at providing an accurate description of semiconducting nanoparticles in realistic environments and at comparing directly with experiment.



HOMO

LUMO

Figure 2: Si nanoparticle embedded in a SiO_2 matrix; the left and right hand side show the square modulus of the highest occupied molecular orbital (HOMO, blue) and lowest unoccupied molecular orbital (LUMO, red) respectively. Identification of a interface shell is in progress.

We are developing Monte Carlo based techniques to solve the Boltzmann Transport Equation (BTE) and compute the thermal conductivity of complex, nanostructured materials with tens of thousands of atoms, e.g. the SiGe superlattices shown in Fig. 3. The technique is readily generalizable to ab initio Hamiltonians, although its tests are being conducted with empirical potentials. In addition, solutions of the BTE for electrons, with approximate lifetimes, will be implemented, so as to build an atomistic computational tool to compute the figure of merit of thermoelectric materials.

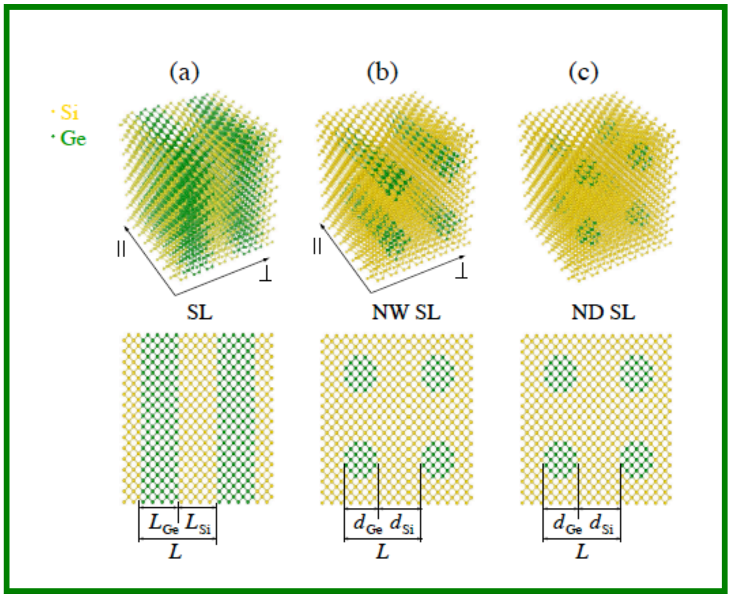


Figure 3 Superlattices (SL), embedded nanowire (NW) and embedded nanodots (ND) of SiGe; work is in progress to study heat transport in these nanostructured materials (as a function of the period L and the diameter d of the Ge and Si inclusions) using the Boltzmann transport equation and newly developed Monte Carlo based integration techniques.

Publications

Tailored Nanoheterojunctions for Optimized Light Emission", T. Li, F. Gygi, and G. Galli, *Phys. Rev. Lett.* **107**, 206805 (2011).

Transport in Nanoporous Silicon: Interplay between disorder at the mesoscopic and the atomic scale, Y. He, D. Donadio, J-H. Lee, J. C. Grossman, and G. Galli, *ACS Nano.* **5**, 1839 (2011).

Ab initio calculations of optical absorption spectra: Solution of the Bethe-Salpeter equation within density matrix perturbation theory, D. Rocca, D. Lu, and G. Galli, *J. Chem.* **33**, 154110 (2010).

Emerging Photoluminescence in Monolayer MoS_2, A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Nano Lett.* **10**, 1271 (2010).

Temperature dependence of the thermal conductivity of thin silicon nanowires, D. Donadio and G. Galli, *Nano Lett.* **10**, 847(2010).

Van der Waals interactions in molecular assemblies from first-principles calculations, Y. Li, D. Lu, H-V Nguyen and G. Galli, *J. Phys. Chem. A*, **114**, 1944-1952 (2010).

Structure, stability and electronic properties of nanodiamonds, G. Galli, to appear in: Springer Series on 'Carbon materials: Chemistry and Physics' (series Editors: F. Catadldo and P. Milani) (2010).

The 1,4-Phenylenediisocyande Dimer: Gas-phase properties and insights into organic self-assembled, R.P.Steele , R. A. DiStasio Jr., M. Head-Gordon, Y. Li and G. Galli, *Phys.Chem.Chem.Phys.* **12**, 82 (2009).

Nucleation of tetrahedral solids: A molecular dynamics study of supercooled liquid silicon, T.Li, D.Donadio, G.Galli, *J. Chem. Phys*. **131**, 224519 (2009).

High energy excitations in silicon nanoparticles, A.Gali, M.Vörös, D.Rocca, G. Zimanyi, and G.Galli, *Nano Lett*. **9**, 3780 (2009).

Nature and Strength of Interlayer Binding in Graphite, L. Spanu, S.Sorella, G.Galli, *Phys.Rev. Lett*. **103**, 196401 (2009).

Ab initio calculation of van der Waals bonded molecular crystals, D.Lu, Y.Li, D.Rocca and G.Galli, *Phys. Rev. Lett*. **102**, 206411 (2009).

Surface Induced Crystallization in Supercooled Tetrahedral Liquids, T.Li, D.Donadio, L.Ghiringhelli and G.Galli, *Nature Materials* **8**, 726 (2009).

Calculation of Quasi-Particle Energies of Aromatic Self-Assembled Monolayers on Au(111), Y. Li, D. Lu and G. Galli, *J. Comp. Theor. Chem*. **5**, 881 (2009).

ELECTRON COHERENCE AND INTERACTIONS IN NANOSTRUCTURES

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I. PROJECT SCOPE

The program addresses kinetic phenomena in quantum wires, metallic rings, and loops made of small Josephson junctions. In the part devoted to quantum wires, we are developing kinetic theory for interacting electrons with a generic dispersion relation (the nonlinear Luttinger liquid). We apply this theory to explain the observed particle-hole asymmetry of electron relaxation in single-mode wires, and to predict electron relaxation rates in edge modes formed in a two-dimensional electron liquid by a quantizing magnetic field. In the metallic rings direction, we are interested in the nonlinear dc response to a microwave field of an array of nanorings; the aim is to elucidate the effect of microwave radiation on the persistent currents. In the part devoted to quantum kinetics of Josephson junctions arrays, we consider the effects of coherent phase slips; we aim at understanding the relaxation mechanisms of low-energy excited states in a loop of junctions. All parts of the program are related to ongoing experiments.

II. RECENT PROGRESS

Electron energy partition and relaxation in quantum wires

Fabrication of semiconductors-based parallel quantum wires facilitated the studies of momentum-resolved electron tunneling. Experiments in the group of Prof. Amir Yacoby (Harvard University) revealed a puzzle: the relaxation of charge carriers apparently was strongly dependent on the polarity of the bias which injects the carriers into the wire. That prompted us to investigate the electron energy partition and relaxation in quantum wires.

Some energy re-distribution occurs already in the vicinity $\sim \hbar s/(eV)$ of the injection point (here s is the charge mode velocity, and V is the applied bias). In Ref. [1] we elucidated the salient features of that re-distribution. Tunneling, *e.g.*, of right-movers into a quantum wire disturbs the distributions of both right- and left-movers due to the interaction between them. In the case of momentum-conserving injection and energy-resolved sensing, see Fig. 1a, the non-equilibrium carriers would be detected at energies below $\epsilon^R_{\max} = (1/2)(eV + sk_V)$

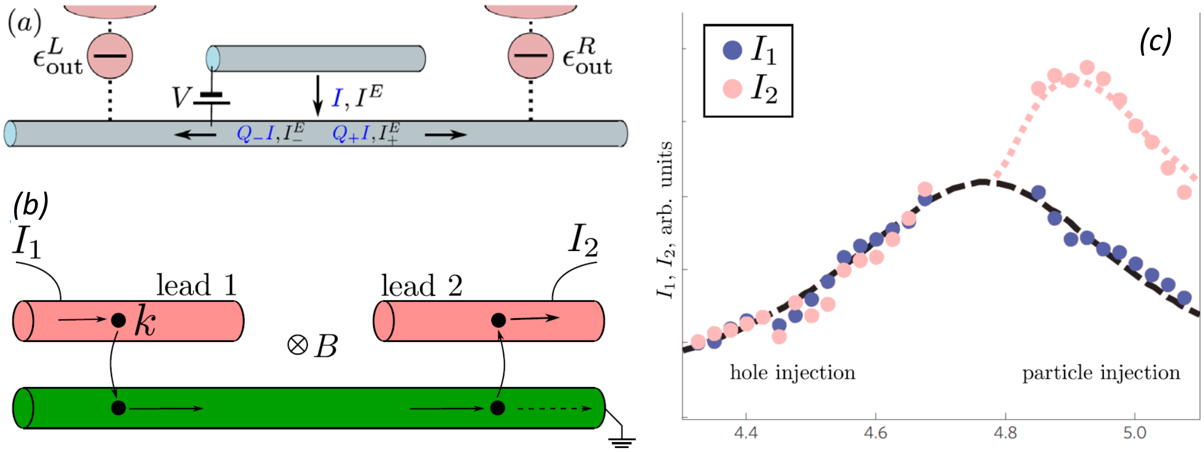

FIG. 1: (a) A setup to probe the energy partitioning. The momentum-conserving injection is achieved by tunneling between parallel quantum wires. Resonant tunneling currents through the quantum dots serve as the probes of energy partitioning. (b) Experimental setup used by Barak *et al.* [2]. A bias applied to lead 1 injects the current I_1 through the left tunnel junction into the grounded wire; the current I_2 through the right tunnel junction is collected in lead 2. Depending on the bias polarity, particles or holes are injected. The injection occurs in a window of momenta around a value k controlled by the magnetic field B. (c) Injected current I_1 (dark dots) and collected current I_2 (light dots) as a function of the magnetic field. The two currents coincide in the case of hole injection. If particles are injected, then the collected current exceeds the injected one due to relaxation. The dashed line is a theory plot obtained by solution of the rate equations. Adapted from Ref. [2]

and $\epsilon^L_{\max} = (1/2)(eV - sk_V)$ for the right- and left-movers, respectively (k_V is the excess momentum of electrons entering the wire). The differential conductances measured by the energy-resolving probes depicted in Fig. 1a are $dI_R/dV \propto (\epsilon^R_{\max} - \epsilon^R_{\text{out}})^{\phi-1}$ and $dI_L/dV \propto (\epsilon^L_{\max} - \epsilon^L_{\text{out}})^{3\phi-\sqrt{\phi(\phi-1)}}$, where $\phi = (K + 1/K - 2)/4$, and K is the Luttinger liquid parameter.

The linear Luttinger liquid theory predicts no further evolution of the distribution beyond the vicinity of the injection point and no difference in relaxation between particles and holes. That latter conclusion was in a clear contradiction to the results of the tunneling experiment [2]. The idea of the experiment is depicted in Fig. 1b. In the case of hole injection, the collected current $I_2 \approx I_1$, whereas in the case of particle injection the collected current I_2 was considerably *higher* than the injection current I_1, see Fig. 1c. That striking result found a natural explanation in the nonlinear Luttinger liquid theory [3]. It predicts slow relaxation of holes (which move with velocities less than s) and much faster relaxation of particles (having velocities higher than s). We developed a detailed perturbative theory of the particle-hole asymmetry of the relaxation rates for spin-degenerate electrons in a single-mode quantum wire [4]. The rate equations [2] based on the evaluated rates explained quantitatively the observations, see Fig. 1c.

III. RESEARCH AGENDA FOR THE NEXT ACADEMIC YEAR

Persistent currents under microwave irradiation

The persistent currents in normal-metal rings at equilibrium were measured with high precision in the group of Prof. Jack Harris at Yale University. Their results agree well with our detailed theory [5]. Next on the agenda is to elucidate the effect of external irradiation on the persistent currents. The preliminary data disagrees with the existing theoretical literature. While experiment indicates the current suppression, a string of theory papers predicts its giant enhancement. Our preliminary analysis indicates that at least some of the said papers are missing a family of diagrams which would cancel the large effect predicted there. However a correct and clear theory is not built as of yet. It must include the effects of rectification, charge pumping, and heating which in principle may affect the persistent currents. While the latter effect probably suppresses the current, the two former ones may increase the mesoscopic fluctuations of the current, and maybe even create a net average current. We plan to address these questions. We plan to employ the Cooperon-diffuson diagrammatic technique within Keldysh formalism to derive a proper kinetic equation. The latter should be sensitive to Aharonov-Bohm flux through the rings, as well as to the magnetic fields penetrating the rings.

Collective modes and charge disorder in long superconducting arrays

The notion of a static superconducting order parameter comes from the mean-field theory of superconductivity. In reality, order parameter in meso-scale superconductors exhibits quantum fluctuations. Quantum phase slips lead to tunneling between different classically-allowed states of the order parameter. Our theory [6] gave tools to recognize the phase slips interference in an experiment with a loop made of small superconducting islands connected by Josephson junctions. The observation of interference demonstrated the quantum nature of phase slips. The observation was made possible due to the charges which reside on the islands and cause the Aharonov-Casher effect in the phase slips interference (the Aharonov-Casher effect is dual to the broader-known Aharonov-Bohm effect). While consisting of relatively large ($N \approx 40$) number of junctions, the experimentally studied loops were apparently short enough for the electric field produced by the charges to stay inside the loop. In longer loops such electrostatic screening becomes ineffective, and the electric field does escape from the loop. That must modify the amplitudes of the phase slips and the interference conditions for slips occurring in different junctions of the array. We plan to extend our theory of quantum phase slips to include Josephson junctions arrays which are longer than the electrostatic screening length. We will also explore the role of Bogoliubov quasiparticles in the slow charge dynamics, extending some results of our earlier work [7].

IV. PUBLICATIONS

[1] Torsten Karzig, Gil Refael, Leonid I. Glazman, and Felix von Oppen, *Energy partitioning of tunneling currents into Luttinger liquids*, Phys. Rev. Lett. **107**, 176403 (2011).

[2] Gilad Barak, Hadar Steinberg, Loren N. Pfeiffer, Ken W. West, Leonid Glazman, Felix von Oppen, and Amir Yacoby, *Interacting electrons in one dimension beyond the Luttinger-liquid limit*, Nature Physics, **6**, 489 (2010).

[3] A. Imambekov, L.I. Glazman, *Universal theory of nonlinear Luttinger liquids*, Science **323**, 228 (2009).

[4] Torsten Karzig, Leonid I. Glazman, and Felix von Oppen, *Energy relaxation and thermalization of hot electrons in quantum wires*, Phys. Rev. Lett. **105**, 226407 (2010).

[5] Eran Ginossar, Leonid I. Glazman, Teemu Ojanen, Felix von Oppen, William E. Shanks, Ania C. Bleszynski-Jayich, J. G. E. Harris, *Mesoscopic persistent currents in a strong magnetic field*, Phys. Rev. B **81**, 155448 (2010).

[6] Vladimir E. Manucharyan, Nicholas A. Masluk, Archana Kamal, Jens Koch, Leonid I. Glazman, and Michel H. Devoret, *Evidence for coherent quantum phase slips across a Josephson junction array*, Phys. Rev. B **85**, 024521 (2012).

[7] G. Catelani, R. J. Schoelkopf, M. H. Devoret, and L. I. Glazman, *Relaxation and frequency shifts induced by quasiparticles in superconducting qubits*, Phys. Rev. B **84**, 064517 (2011).

[8] A. Kamenev, L.I. Glazman, *Dynamics of a one-dimensional spinor Bose liquid: a phenomenological approach*, Phys. Rev. A **80**, 011603 (2009)

[9] G. Katsaros, V. N. Golovach, P. Spathis, N. Ares, M. Stoel, F. Fournel, O. G. Schmidt, L. I. Glazman, and S. De Franceschi, *Observation of spin-selective tunneling in SiGe nanocrystals*, Phys. Rev. Lett. **107**, 246601 (2011).

[10] Ya.V. Fominov, M. Houzet, and L. I. Glazman, *Surface impedance of superconductors with weak magnetic impurities*, Phys. Rev. B **84**, 224517 (2011).

[11] Michael Schecter, Alex Kamenev, *Forming doublons by a quantum quench*, Phys. Rev. A **85**, 043623 (2012).

[12] Michael Schecter, Alex Kamenev, Dimitri Gangardt, Austen Lamacraft, *Critical velocity of a mobile impurity in one-dimensional quantum liquids*, Phys. Rev. Lett. **108**, 207001 (2012).

[13] M. Schecter, D.M. Gangardt, and A. Kamenev, *Dynamics and Bloch oscillations of mobile impurities in one-dimensional quantum liquids*, Annals of Physics, **327**, 639-670 (2012).

Quantum Quench Dynamics-Crossover Phenomena in Non-Equilibrium Correlated Quantum Systems

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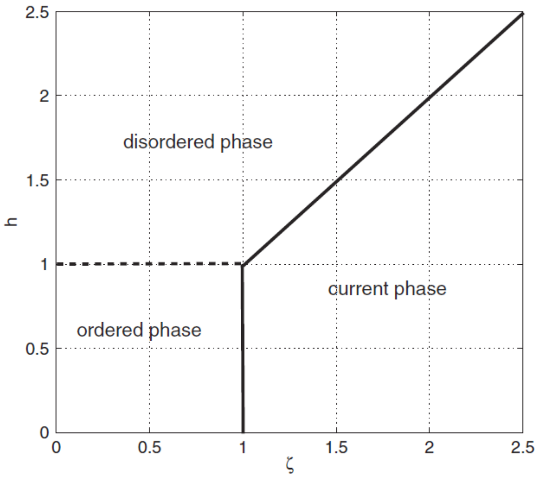
Project Scope

Transient and long time properties of quenched quantum systems have given rise to a wealth of theoretical activity as well as experimental applications. A combination of numerical methods and conformal field theory has been crucial to their understanding. The phenomenology of intermediate time behavior is potentially even richer, and often involves crossovers between different physical regimes - such as weak and strong coupling in the Kondo model. These crossovers are related to, but different from, other crossovers in out of equilibrium physics, such as those taking place when voltage or gate voltage are varied in tunneling experiments. While potential applications are numerous, the subject is not fully developed theoretically. In particular, the methods of conformal field theory apply only in very special cases, and therefore new, more involved approaches are needed. In this project, we develop such approaches by using ideas of integrability - in a nutshell, developing further the ideas of Bethe ansatz out of equilibrium. These ideas are combined with different numerical techniques - exact diagonalization and t-DMRG - and used to investigate a variety of interesting physical problems, such as non equilibrium transport through quantum point contacts.

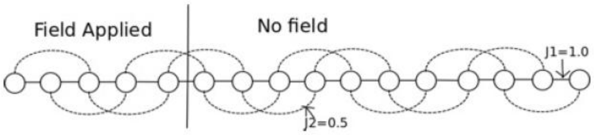
Recent Progress

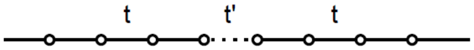
During the first year of this project, starting in September of 2011, we have developed in parallel analytical and numerical techniques to examine the dynamics of quantum systems, following a quench. In particular, we have devised a mean field approach to study the time evolution of entanglement in the presence of an energy current. Furthermore, we studied numerically the propagation of disturbances caused by local quenches in quantum systems with degeneracies. Finally, we used conformal field theory to examine the presence/absence of 'healing' effects in one-dimensional systems with impurity links. During the period covered by this report, these activities have resulted in a total of 2 published [1-2] papers and 1 submitted manuscript.

In the first project, we considered a one-dimensional Ising model with an additional Dzyaloshinskii-Moriya (DM) term, which introduces an effective energy current in the system. The phase diagram for this model, shown in the figure to the left, contains three phases, which are tuned by the applied magnetic field (shown on the y-axis) and the energy current (on the x-axis). In the absence of the energy current, there is an ordered ferromagnetic regime, separated from a disordered paramagnetic regime at a critical field h/J=1. The introduction of the energy current leads to a third, current-carrying phase. Studying the quench dynamics of entanglement in these three regimes, we considered two interesting quench protocols. The usual schemes consider quenches from an initial ground state. This scenario effectively corresponds to a quench from an initially excited state of the Ising spin chain in a transverse field (without DM interaction). The main result of this analysis showed that the ballistic picture previously presented by Cardy and Calabrese (P. Calabrese and J. Cardy, J. Stat. Mech.: Theory Exp. (2004) P06002.) is still valid, although with a significantly different aspect. In particular, the entanglement saturation time in the current-carrying phase depends on the details of the evolving Hamiltonian. This is an indication of the role played by the evolving Hamiltonian on the propagation of excitations. This result is of relevance in tuning the dynamics of the system in regions with a different rate for the propagation of entanglement. Furthermore, it also provides a characterization of the regions in the phase diagram that can be simulated more efficiently with DMRG-like techniques. From a general point of view, the scheme we considered also suggests a simple way to study the quench dynamics of initial excited states in integrable systems. The addition of a commuting term in the Hamiltonian causes a reshuffling of the spectrum that, without changing the integrability of the model, allows us to obtain nontrivial results about the excitations in the original model. The same trick can in principle be applied to other systems of interest.



In our second project, we examined the effects of local magnetic field quenches in a degenerate quantum system, i.e. the one-dimensional frustrated J_1 -J_2 Heisenberg Hamiltonian at and close to the Majumdar-Ghosh point. Quenches were considered using a local magnetic field. We found that the degenerate Majumdar-Ghosh ground state allows disturbances which carry quantum entanglement to propagate throughout the system and thus dephase the entire system within the degenerate subspace. These disturbances can also carry polarization, but not energy, as all energy is stored locally. The local evolution of the part of the system where energy is stored drives the rest of the system through long-range entanglement. We also examined approximations for the ground state of this Hamiltonian in the strong field limit and studied how couplings away from the Majumdar-Ghosh point affect the propagation of disturbances. We found that even in the case of approximate degeneracy, a disturbance can be propagated throughout a finite system.





In current work, we are examining the effects of impurity links on measures of entanglement and fidelity in one-dimensional systems, amenable to conformal field theory methods. The simplest non-interacting realization would be the set-up shown in this figure. Amazingly, even in this toy model, we observe an interesting differences between the cases of one vs. two-impurity links. While for one impurity link there is a strong dependence of these observables on the value of impurity coupling, for two adjacent impurity links we find large regimes for which the scaling properties of these observables are independent on t'. This can likely be attributed to the cancellation of two overlapping defect induced Kondo clouds, constituting a healing effect. We are currently studying this effect numerically, using exact numerical diagonalization, and are planning to investigate it in the context of interacting systems, such as Heisenberg chains.

Planned Activities

We are planning to study crossover phenomena for local quenches in a variety of systems. Our objective is twofold. On the one hand, transients are unavoidable in experiments, and it seems important to have an idea of what their main characteristics are. On the other hand, transients should also tell us a lot about systems and the associated renormalization group flows - screening in time being hopefully easier to access that screening in space such as occurs in the Kondo cloud problem. Numerically, we rely on a combination of exact diagonalization and time dependent density matrix renormalization group (t-DMRG) methods. Specifically, we wish to study the evolution of quantum states, i.e $|\varphi(t)> = \exp(-iHt)|\varphi(0)>$, where a quench on the initial state is performed at time t=0. This can either be achieved by direct time propagation, i.e. Trotter decomposition followed by iterative application of the Hamiltonian, or alternatively by full diagonalization of the Hamiltonian, followed by $|\varphi(t)> = \sum_n \exp(-iE_n t)\,|n><n|\varphi(0)>$, where $E_n$are the eigenenergies and $|n>$are the eigenstates. Both numerical techniques can be improved to achieve larger system sizes and higher accuracy. For direct time propagation, we will introduce Chebyshev polynomial expansions, which are already standard in quantum chemistry calculations, but have not been used in the present context, according to our knowledge. Regarding the alternative approach, we wish to explore truncated diagonalization schemes, such as Lanczos, which certainly will allow us to go to larger Hilbert spaces at the expense of sacrificing higher-frequency contributions. This trade-off needs to be carefully examined. Crossovers can also occur in steady regimes with systems involving several characteristic energy scales. Foremost in this direction are problems of transport through impurities, and the simplest of all systems in this case is probably the (spinless) interacting resonant level model. There, transport depends in a highly non trivial way on several energy scales: the thermal scale $k_B T$and the external voltage scale eV , but also a scale $(k_B T_{cr})$ (the equivalent of the Kondo scale in this case) associated with the tunneling through the impurity and the Coulomb interaction between the charge on the impurity and on the wires nearby. Highly non trivial I-V characteristics can be observed in this problem. Because the physics of interest occurs only in the presence of interactions and out of equilibrium, new methods have to be developed to obtain analytical results. Such

methods, based again on perturbed CFT and integrability, have been successfully used in the Interacting Resonant Level Model, with results for the current as well as the shot noise at vanishing temperature that have been recently checked against extensive t-DMRG calculations.
One of the physically most fascinating aspects of these problems in interaction is that they involve quasiparticles whose charge does not have to be the same as the electron charge. Such cases are well known in the fractional quantum Hall effect where charges $e^* = e/3$have been observed experimentally in the case of the filling fraction 1/3. In general, the crossovers involve smooth interpolations between the effective charge of the carriers being e^* in some regime and another charge simply related with the electron charge in another. In the quantum Hall, the crossover is thus between e/3 and e. In the Interacting Resonant Level Model the crossover is between 2e and e/2. How these crossovers affect for instance the full counting statistics is an entirely open question. Another question is how this FCS might be related with the entanglement rate in the system. Indeed, in the presence of a steady current owing between two wires connected by an impurity, entanglement between the wires is going to grow linearly with time, in a fashion that depends non-trivially on the voltage and other scales. It has been speculated that the rate might be connected to the even cumulants of the full counting statistics. While established in the free case, there is no evidence for or against the proposal in the interacting case. Note that, if true, this would be a most exciting result, as the FCS is in principle accessible experimentally, hence could lead via the proposal, to an experimental way of measuring entanglement.

Publications

1. A. Das, S. Garnerone, and S. Haas, Entanglement and its evolution after a quench in the presence of an energy current, Phys. Rev. A 84, 052317 (2011).
2. N. Chancellor and S. Haas, Propagation of disturbances in degenerate quantum systems, Phys. Rev. B 84, 035130 (2011).
3. B.P.W. de Oliveira and S. Haas, Electron-phonon bound states and impurity band formation in quantum wells, Phys. Rev. B 79, 155102 (2009).
4. R. Yu, T. Roscilde, and S. Haas, Revealing Novel Quantum Phases in Quantum Antiferromagnets on Random Lattices, Condensed Matter Physics 12, 519 (2009).
5. R. Yu, S. Haas and T. Roscilde, Universal phase diagram of disordered bosons from a doped quantum magnet, Euro. Phys. Lett. 89, 10009 (2010).
6. Y.C. Chang and S. Haas, Defect Induced Resonances and Magnetic Patterns in Graphene, Phys. Rev. B 83, 085406 (2011).

Computational Magnetism

within two FWP's:
Nanomagnetism, and Development of Theoretical Methods

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Scope

We are concerned with magnetic interactions where at least one dimension is on the order of nanometers (or less). Two examples will be presented. The first having to do with a predicted new type of surface magnetism involving the small gap antiferromagnetic insulator: $BaMn_2As_2$. The surface states are conducting and not spin degenerate. Another recent (submitted) project involves the resolution of a long time conundrum in understanding the physics of Sr doped $LaCoO_3$, a narrow gap, non-magnetic semiconductor, which becomes ferromagnetic with doping or even with increasing temperature. Hundreds of papers have been written about this material and we think we have a definitive analysis of the rather subtle physics involved. The work is in collaboration with x-ray scattering groups at Argonne and UC Santa Cruz. A large percentage of the work in the last two years has been in collaboration with local (Ames Lab) experimental groups who have had a great impact in the field of the new FeAs based superconductors and related compounds.

Recent Progress

FeAs Superconductors – There is a continuing surge of activity at Ames Laboratory on these materials. We have provided theoretical investigations and support for many of the studies of the structural, magnetic, electronic, and dynamical properties. Our early paper on the pressure dependence of the magnetism quenching with pressure in $CaFe_2Fe_2$ has well over 140 citations since published (2008). The most recent work (submitted) deals with the first principles calculation of the lattice dynamics. The comparison with measured phonon spectra of LaFeAsO at room temperature (above the AF ordering temperature) could be matched much better with spin polarized calculations, indicating the presence of magnetic fluctuations extending well above the Neél temperature.

$BaMn_2As_2$ - This material is a small gap antiferromagnetic semiconductor with the same crystal structure as the corresponding superconducting FeAs analogs. Our calculations show that the surface bands cross the Fermi level and are not spin degenerate! The calculations indicate the z-axis relaxation of the Mn surface atoms depends on the z-axis field, and can result in substantial net magnetization at the surface within the surface electronic states. Up until a few weeks ago, there was no experimental confirmation for these theoretical predictions. Recent magneto-optical imaging of the surface shows magnetic domains forming on the surface as the temperature is lowered below ~140K in the presence of a 500G field. These domains appear randomly positioned on the surface.

$La_{1-x}Sr_xCoO_3$ – The so-called LCO material has been the object of numerous studies. It is a small gap non-magnetic semiconductor, which becomes strongly ferromagnetic at high temperatures and also upon doping with Strontium. Our calculations using supercells are able to quantitatively explain the behavior of this material, including recent x-ray absorption and the x-ray magnetic circular dichroism data taken by collaborators. A manuscript has recently been submitted to PRL. Collaborators include: F. Bridges (UC Santa Cruz), J. W. Freeland and J. F. Mitchell (Argonne), and Yongbin Lee from Ames.

Some work has been with Kai Ming Ho and C. Z. Wang on Materials Discovery for magnetic materials using Petaflop computing as part of the INCITE program.

In the last year Bruce Harmon also chaired review panels for the DOE supercomputer operations at Argonne and ORNL; and also at the Swiss supercomputing center at Lugano.

Future Plans

We will undertake more careful and through analysis of the surface magnetism and conductivity of $BaMn_2As_2$ to understand the physics of the surface domain formation and determine if there are possible implications for spintronics.

We will continue work with local experimentalists exploring the properties and particularly the possible mechanisms of superconductivity in the FeAs materials.

We will push new approaches for materials discovery for desired magnetic properties.

We will undertake calculations in support of non-equilibrium phenomena at surfaces associated with femto-second (pump/probe) experiments in collaboration with Prof. Jigang Wang of Ames Lab / Iowa State University.

Publications (2009-2012)

257. "Lattice collapse and quenching of magnetism in CaFe2As2 under pressure: A single-crystal neutron and x-ray diffraction investigation", Goldman AI, Kreyssig A, Prokes K, Prokes K, Pratt DK, Argyriou DN, Lynn JW, Nandi S, Kimber SAJ, Chen Y, Lee YB, Samolyuk G, Leao JB, Poulton SJ, Bud'ko SL, Ni N, Canfield PC , **Harmon BN**, McQueeney RJ; Phys. Rev. B **79,** 024513 (2009).
258. Comment on "Dipolar Excitations at the L-III X-Ray Absorption Edges of the Heavy Rare-Earth Metals", Goldman AI, **Harmon BN**, Lee YB, and Kressig A. PHYSICAL REVIEW LETTERS Volume: **102** , Article Number: 129701, (2009)

259. “Magnetic ordering in EuRh2As2 studied by x-ray resonant magnetic scattering”, Nandi S, Kreyssig A, Lee Y, Singh Y, Kim JW, Johnston DC, **Harmon BN**, Goldman AI, Phys. Rev. **B79**, 100407 (2009). Rapids.
260. “Electronic properties of iron arsenic high temperature superconductors revealed by angle resolved photoemission spectroscopy (ARPES)”, Liu C, Kondo T, Palczewski AD, Samolyuk GD, Lee Y, Tillman ME, Ni N, Mun ED, Gordon R, Santander-Syro AF, Bud’ko SL, McChesney JL, Rotenberg E, Fedorov AV, Valla T, Cople O, Tanatar MA, Martin C, **Harmon BN**, Canfield PC, Prozorov R, Schmalian J, Kaminski A, PHYSICA C-SUPERCONDUCTIVITY AND ITS APPLICATIONS Volume: **469** Issue: 9-12 Pages: 491-497 Published: MAY-JUN 2009
261. “Influence of magnetism on phonons in CaFe2As2 as seen via inelastic x-ray scattering”, Hahn SE, Lee Y, Ni N, Canfield PC, Goldman AI, McQueeney RJ, **Harmon BN**, Alatas A, Leu BM, Alp EE, Chung DY, Todorov IS, Kanatzidis MG, PHYSICAL REVIEW B Volume: **79** Issue: 22 Article Number: 220511, **2009**. Rapids.
262. “Unusual magnetic, thermal, and transport behavior of single-crystalline EuRh2As2”, Singh Y, Lee Y, **Harmon BN**, Johnston DC, PHYSICAL REVIEW B Volume: **79** Issue: 22 Article Number: 220401, JUN 2009. Rapids.
263. Editorial on Exascale Computing, Journal of Phase Equilibria and Diffusion, **30**, 305, August 2009. **Harmon BN**
264. “The magnetic form factor of iron in $SrFe_2As_2$”, Y. Lee, David Vaknin, Haifeng Li, Wei Tian, Jerel L. Zarestky. N. Ni, S. L. Bud’ko, P. C. Canfield, R. J. McQueeney, and **B. N. Harmon**, Phys. Rev. B. **81** 060406 (2010). Rapids.
265. “Change or Perish”, editorial, Journal of Phase Equilibria and Diffusion, **v31**, n6, 497 (2010). **Harmon BN**
266. “Surface-driven electronic strcutre in LaFeAsO studied by angle-resolved photoemission spectroscopy”, C. Liu, Y. Lee, A.D. Palczewski, J.Q. Yan, T. Kondo**, B. N. Harmon**, R. W. McCallum, T. A. Lograsso, A. Kaminski, Phys. Rev. **B82**, Issue 7, Article 075135 (2010).
267. “Effect of Ligand Substitution on the Exchange Interactions in {Mn-12}-Type Single-Molecule Magnets, D. W. Boukhvalov, V. V. Dobrovitski, P. Koegerler, M. Al-Saqer, M. I. Katsnelson, A. I. Lichtenstein, **B. N. Harmon,** Inorganic Chemistry **v.49**, issue 23, 10902 (2010).
268. “Metallic surface electronic state in half-Heusler compounds RPtBi (R = Lu, Dy, Gd) “Liu, C , Lee, Y, Kondo, T, Mun, ED, Caudle, M. **Harmon, BN**, Bud'ko, SL, Canfield, PC, Kaminski, A, PhysRevB.**83**.205133 (2011).
269. Incommensurate Spin-Density Wave Order in Electron-Doped BaFe(2)As(2) Superconductors , Pratt, D. K., Kim, M. G., Kreyssig, A., Lee, Y., Tucker, G. S., Thaler, A., Tian, W., Zarestky, J. L., Bud'ko, S. L., Canfield, P. C., **Harmon, B. N.,** Goldman, A. I., McQueeney, RJ, PHYSICAL REVIEW LETTERS, **106**, 257001 (2011) .
270. “Fe K-edge X-ray resonant magnetic scattering from Ba(Fe1-x Co (x))(2)As-2 superconductors”, M. G. Kim, A. Kreyssig, Y.B. Lee, R. J. McQueeney; **B. N. Harmon**, A. I Goldman; European Physical Society – Special Topics, **208**, 157 (2012).
271. “$Ba_{1-x}K_xMn_2As_2$: An antiferromagnetic Local-moment metal”. A. Pandey, R.S. Dhaka, J. Lamsal, Y. Lee, V. K. Anand, A. Kreyssig, T.W. Heltmann, R.J. McQueeney, A. I. Goldman, **B. N. Harmon**, A. Kaminski, and D.C. Johnston. Physical Review Letters, **108**, issue 8, 087005, 2012.
272. “ Experimental and theoretical electronic structure of EuRh2As2“, Palczewski, AD, Dhaka, R. S., Lee, Y., Singh, Yogesh, Johnston, D. C., **Harmon, B. N.**, Kaminski, A; Phys. Rev. **B85**, 174509 (2012).

Theory of Novel Superconductors

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Project Scope

The research in this program is devoted to series of problems related to superconducting pairing, magnetism, and disorder in unconventional superconductors. While in the past phenomenological properties of such systems have been the focus, the P.I. and co-workers are moving towards studies directed towards understanding the microscopic mechanism of Fe-based and other novel superconductors, and developing quantitative and even predictive methods. The optimal materials for high-temperature superconductivity almost certainly represent a set of measure zero in the space of all possible materials. Finding them by conventional experience-based methods has proven frustrating. Working with collaborators in the ab initio community, we aim to develop computational methods to guide the search for new superconductors, focusing on *unconventional* pairing mediated by electronic excitations treated within the fluctuation exchange approximation. We will create an approximate ab initio method which can be applied to a family of materials, or a single material where an external control parameter like pressure, uniaxial strain or doping can be varied. The goal will not be a quantitative predictor of the critical temperature T_c for a given material, but an understanding of how crystal structure, Fermi surface electron orbital character, and local interactions influence it. Studies will include single-layer cuprates, a variety of Fe-based superconductor families, heavy fermion and other superconductors.

Recent Progress

THEORY OF SPIN FLUCUTAION PAIRING IN IRON PNICTIDE SUPERCONDUCTORS, with T. Maier, D.J. Scalapino, M. M. Korshunov, I.I. Mazin and A. Chubukov

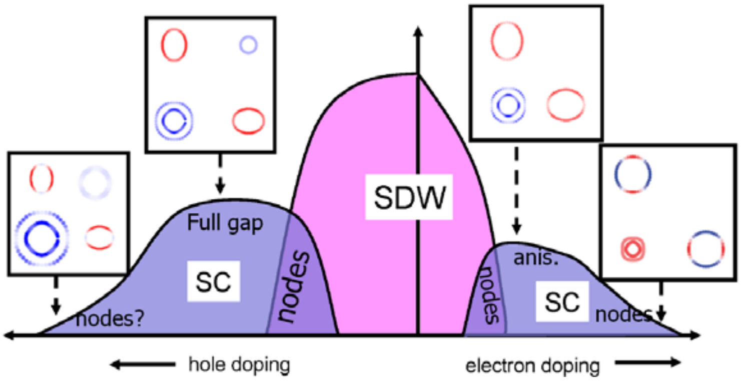

Figure 1. Spin fluctuation phase diagram of 122 Fe-pnictides. Inserts are gap maps with magnitude and sign of gap Δ(k) on displayed Fermi surface indicated by false color.

We have continued our Random Phase Approximation (RPA) calculations of the magnetic susceptibility and pairing interaction within a 5-band model accounting for Hubbard and Hund's rule interactions on each Fe site. The basic picture which emerges is summarized in Fig. 1. For both electron-and hole-doped systems, optimal doping corresponds to the most isotropic superconducting gap. Moving away from optimal doping, pair scattering processes which frustrate the basic $s_{+/-}$ interaction, including scattering processes between electron pockets and intraband Coulomb interaction, grow in importance. In Refs. 23 and 25, the RPA results were parameterized in terms of Fermi surface harmonics, allowing us to see the progressively more competitive d-wave channel grow in importance near the electron- and hole-doped "end points" of the phase diagram. On the hole-doped side, the isotropic state was stabilized further by the appearance (in the standard electronic structure model) of a third hole pocket of d_{xy} character which pair scatters with the electron pocket d_{xy} segments with the same $(\pi,0)$ wavevector as the basic $s_{+/-}$ interaction.

Future Plans

The really interesting systems which remain to be understood within this picture are therefore those which are so far overdoped that they consist of only hole (e.g. KFe_2As_2) or only electron pockets (e.g. KFe_2Se_2). According to conventional wisdom, the mechanism for spin-fluctuation induced $s_{+/-}$ pairing should fail in these situations. The former compound is a 7K anisotropic superconductor with nodes on the hole pockets which may be s or d-wave, while the latter is a mysterious system fabricated until now only in the form of multiphase samples that include a 31K superconductor coexisting with a antiferromagnet with nearly 600K Neel temperature and large 3 μ_B block ordered moment set between ordered Fe vacancies. We have focused out attention on the latter system since it is important to discover if there is an entirely new high-temperature mechanism at play. It could be that the superconducting phases are merely doped such that they have the conventional band structure (ARPES says this is not the case), or that interactions between electron pockets alone or with hole states away from the Fermi level, or that disordered vacancies can play a role. We have pursued two avenues: on one track we simply assume a Fermi surface like that found by ARPES and solving the RPA equations for the superconducting state; we find a d-wave state, which evolves into an s-wave state as one hole dopes, and made predictions for neutron scattering experiments which were recently confirmed by the Stuttgart group. In parallel, we have asked the question how such a Fermi surface can arise in the presence of the ordered AF state. We found, using an ab initio disorder method pioneered by Wei Ku's group, that disordered vacancies can induce a Fermi surface very similar to the one we assumed in the microscopic calculations (Berlijn et al, arXiv:1204.2849).

The next year or two of the grant will be primarily devoted to the systematizing of a code which calculates the downfolded tight-binding band structure near the Fermi level using DFT or LDA+DMFT and with it the pairing interaction, eigenvalues and eigenvectors (gap symmetry). While this will be within the same general spin fluctuation picture, we intend to include full 3D Fermi surfaces and self-energy effects. The goal will then be to try to understand systems where changing a single parameter (e.g. pressure or element on a given doping site) changes T_c strongly, to see if we can develop a semiquantitative understanding of these trends and relate them to structure, orbital character, etc.

Publications 2009-2012 supported by DOE-BES

1. "Inversion of specifc heat oscillations with in-plane magnetic field angle in 2D d-wave superconductors", G. R. Boyd, A. Vorontsov, P. J. Hirschfeld, and I. Vekhter, Phys. Rev. B 79, 064525 (2009).
2. "Extinction of quasiparticle interference in underdoped cuprates with coexisting order ", B. M. Andersen and P.J. Hirschfeld, Phys. Rev. B 79, 144515 (2009).
3. "Effect of oxygen chain defects on NMR response in YBCO", W. Chen and P.J. Hirschfeld, Phys. Rev. B 79, 064522 (2009).
4. "Near-degeneracy of several pairing channels in multiorbital models for the Fepnictides", S. Graser, P.J. Hirschfeld, T. Maier, and D.J. Scalapino, New J. Phys. 11, 025016 (2009).
5. " Lifting of nodes by disorder in extended-*s* state superconductors: application to ferropnictides", V. Mishra, G. Boyd, S. Graser, T. Maier, P.J. Hirschfeld, and D.J. Scalapino, Phys. Rev. B 79, 094512 (2009).
6. "Neutron Scattering Resonance and the Fe-pnictide Superconducting Gap", T. Maier, S. Graser, P.J. Hirschfeld, and D.J. Scalapino, Phys. Rev. B 79, 134520 (2009).
7. "Probing the pairing symmetry of the iron pnictides with electronic Raman scattering", G. Boyd, T.P. Devereaux, P.J. Hirschfeld, V.Mishra, and D.J. Scalapino, Phys. Rev. B 79, 174521 (2009).
8. "Origin of Gap Anisotropy in Spin Fluctuation Models of the Fe-pnictides", T. Maier, S. Graser, P.J. Hirschfeld, and D.J. Scalapino, Phys. Rev. B 79, 224510 (2009).
9. "Effects of cobalt doping and three-dimensionality in BaFe2As2", A. Kemper, C. Cao, P.J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B 80, 104511 (2009); erratum, Phys. Rev. B 80, 104511 (2009).
10. "Theory of Resistivity Upturns in Metallic Cuprates", W. Chen, B.M. Andersen and P.J. Hirschfeld, Phys. Rev. B 80, 134518 (2009).
11. "Theory of thermal conductivity in extended-*s* state superconductors: application to ferropnictides", V. Mishra, A. Vorontsov, P.J. Hirschfeld,and I. Vekhter, Phys. Rev. B 80, 224525 (2009).
12. "d-Wave superconductivity as a catalyst for antiferromagnetism in underdoped cuprates", M. Schmid, B.M. Andersen, P.J. Hirschfeld, and A. Kampf, New J. Phys. 12, 053043 (2010).

13. “How grain boundaries limit supercurrents in high temperature superconductors,”S. Graser, P.J. Hirschfeld, T. Kopp, R. Gutser, B.M. Andersen and J.Mannhart, Nat. Phys. 6, 609 (2010).
14. “Specific heat vs. field in the 30K superconductor BaFe2(As0:7P0:3)2”, J. S. Kim,P. J. Hirschfeld, G. R. Stewart, S. Kasahara, T. Shibauchi, T. Terashima, and Y. Matsuda, Phys. Rev. B 81, 214507 (2010).
15. ”Spin fluctuations and superconductivity in a 3D tight-binding model forBaFe2As2”, S. Graser, A. F. Kemper, T. A. Maier, H.-P. Cheng, P. J. Hirschfeld, and D. J. Scalapino, Phys. Rev. B 81, 214503 (2010).
16. “Sensitivity of superconducting state and magnetic susceptibility to key aspects of electronic structure in ferropnictides”, A. Kemper, T. Maier, S. Graser, H.-P. Cheng, P.J. Hirschfeld, and D.J. Scalapino, New J. Phys. 12 073030 (2010).
17. “Modulation of pairing interaction in Bi2Sr2CaCu2O8+_ by an O dopant: a DensityFunctional Theory study”, K. Foyevtsova, H. C. Kandpal, H. O. Jeschke, S. Graser, H.-P. Cheng, R.Valenti and P. J. Hirschfeld, Phys. Rev. B 82, 054514 (2010).
18. “Effect of disorder on Raman scattering in Fe-based superconductors”, G. Boyd, T. P. Devereaux, and P.J. Hirschfeld, Phys. Rev. B. 82, 134506 (2010).
19. “d wave pairing from spin fluctuations in the KFe_2 Se_2 superconductors”, T. A. Maier, S. Graser, P. J. Hirschfeld, and D. J. Scalapino, Phys. Rev. B 83, 100515 (2011).
20. “Transport properties of 3D extended s -wave states in Fe-based superconductors”, V. Mishra, S. Graser, and P.J. Hirschfeld, Phys. Rev. B 84, 014524 (2011).
21. “Anisotropic quasiparticle lifetimes in Fe-pnictides”, L. Kemper, M. Korshunov, and P.J. Hirschfeld, Phys. Rev. B 83, 184516 (2011).
22. “Probing superconducting gap structures in multiband superconductors with phonon anomalies”, T. Maier, S. Graser, P.J. Hirschfeld, and D.J. Scalapino, Phys. Rev. B 83, 220505 (2011).
23. “Evolution of superconductivity in Fe-based systems with doping”, S. Maiti, M. Korshunov, T. Maier, P.J. Hirschfeld, and A. Chubukov, Phys. Rev. Lett. 107, 147002 (2011).
24. “Impurity induced transition from $s_{+/-}$ to s_{++} in two-band superconductors, D.V. Efremov, M.M. Korshunov, O.V. Dolgov, A.A. Golubov, and P.J. Hirschfeld, Phys. Rev. B 84, 180512 (2011).
25. “Evolution of symmetry and structure of the gap in Fe-based superconductors with doping and interactions”, S. Maiti, M. Korshunov, T. Maier, P. Hirschfeld and A. Chubukov, Phys. Rev. B84, 224505 (2011).
26. “Gap symmetry and structure of Fe-based superconductors”, P.J. Hirschfeld, M.M. Korshunov, and I.I. Mazin, Rep. Prog. Phys. 74, 124508 (2011).
27. “Interface induced d-wave pairing”, C. Stephanos, T. Kopp, J. Mannhart, and P.J. Hirschfeld, Phys. Rev. B 84, 100510(2011).
28. “Volovik effect in a highly anisotropic multiband superconductor: experiment and theory”, Y. Wang, J.-S. Kim, G. Stewart, P.J. Hirschfeld, Y. Matsuda, T. Shibauchi, S. Graser, and I. Vekhter, Phys. Rev. B 84, 184524 (2011).
29. “Theory of quasiparticle vortex bound states in Fe-based superconductors: application to LiFeAs”, Y. Wang, P.J. Hirschfeld, and I. Vekhter, Phys. Rev. B 85, 020506 (2012).
30. “Spin-orbit coupling in Fe-based superconductors”, M.M.Korshunov, Yu. N. Togushova, I. Eremin, and P.J. Hirschfeld, submitted to Journal of Superconductivity and Novel Magnetism.
31. “Specific Heat to H_{c2}: Evidence for Nodes or Deep Minima in the Superconducting Gap of Under- and Overdoped $Ba(Fe_{1-x}Co_x)_2As_2$, J. S. Kim, Y. Wang and P.J. Hirschfeld, G. R. Stewart, K. Gofryk, F. Ronning, A. S. Sefat, K. Y. Choi, K. H. Kim, to be published in Phys. Rev. B.
32. “Evolution of neutron resonance in AFe$_2$Se$_2$”, T. Maier, P.J. Hirschfeld, and D.J. Scalapino, submitted to Phys. Rev. B.

Theory of topological quantum numbers in low dimensions

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Scope Many remarkable states in two dimensions, especially the fractional quantum Hall states, topological insulators, and Chern insulators, have topological underpinnings: their Hall conductance is characterized by a Chern number, which is the number of times a map from a 2-torus to a 2-sphere wraps around the latter. The insulating states with non-trivial Chern numbers are distinguished by the appearance of gapless modes at the boundary, i.e. at the edge for a two dimensional system and at the surface of a three dimensional system. It is theoretically predicted, though not yet experimentally confirmed, that the long distance properties of the edge states are also "quantized," and governed by the physics of the gapped state of the interior. In addition, some of these states, such as chiral p-wave paired state of composite fermions, present interesting topological aspects in the interior, such as Majorana zero modes obeying nonabelian statistics. The research supported by this grant has several goals including: (i) study of the 5/2 states, aiming for an understanding of the Majorana modes from a microscopic perspective and also of the role of Landau level mixing that selects between the Pfaffian and the anti-Pfaffian states; (ii) study of the edge states of the FQHE, hoping to explain why the observed edge exponents are not quantized, and under what conditions they would be quantized; (iii) exploring the possibility of other topological states, both in the context of the FQHE and topological insulators; (iv) collaboration with experimentalists on a subset of these topics.

Recent Progress We have made progress on a number of these issues, resulting in publications given at the end. Here is a brief description.

(i) *5/2 FQHE*: [Publication 3] The 5/2 FQHE state is believed to be a paired state of composite fermions (CFs), which supports two kinds of excitations: vortices and unpaired composite fermions (UCFs; these have also been called "neutral fermions" in the literature). Prior to our work, no satisfactory wave function was known for the unpaired composite fermion. In Ref. 3, we begin from a "bipartite" representation of the Pfaffian wave function for an even number of particles, in which composite fermions are divided into two equal partitions; they form 1/3 state in each partition; they have a simple inter-partition correlation; and the wave function is antisymmetrized with respect to all exchanges. We generalize this form to construct an explicit microscopic description of the state with an odd number of composite fermions, which ensures that one composite fermion is necessarily unpaired. This construction brings out an internal structure of the UCF as consisting of two Majorana quasiparticles (vortices). We demonstrate our description to be extremely accurate for a 3-body model interaction (namely the interaction for which the Pfaffian wave function is the exact ground state), and provide evidence that it is adiabatically connected to the Coulomb solution. Our theory shows how two quasiparticles can fuse into two distinct states, called ordinary and topological excitons, differing by one composite fermion, and that these two modes are degenerate when the two quasiparticles are far apart.

In addition, in Ref. 2, we consider the issue of whether Landau level mixing favors the Pfaffian or the anti-Pfaffian state at 5/2, which are believed to be topologically distinct and can have experimentally distinguishable signatures. We find that an effective interaction derived by Bishara and Nayak leads to the Pfaffian state as having lower energy. Our conclusion is inconsistent with another study by Simon and Rezayi, where they directly implement Landau level mixing at 5/2 in exact numerical diagonalizations. The experimental situation in this regard has been unclear and controversial.

(ii) *FQHE edge Luttinger liquid*: [Publications 4 and 5] The study of the FQHE edge has motivated many remarkable ideas by Wen and others, who argue that it is an example of a Luttinger liquid with quantized exponents. While experiments clearly show it to be a non-Fermi liquid, they also reveal that the exponents are not quantized. Earlier microscopic studies of the FQHE edge have focused largely on the 1/3 state. We have carried out extensive studies of the edge states at 2/5 [4] and 2/3 [5] for both spin polarized and spin singlet states. These are the simplest states beyond 1/3, in that they are described in terms of two filled CF Landau levels, and thus have two sets of edge modes. The addition of an electron at the edge is a nonperturbative process and it is not a priori obvious in what manner an added electron distributes itself over the different edges. The issue is of relevance to experiments that probe the nature of the edge modes by tunneling an electron into it. We show, from a microscopic calculation, that the addition of an electron at the edge of the 2/5 state, it is equivalent to adding a composite fermion in one of the edges, which does not create inter-edge excitations in the asymptotically low-energy limit. We also compute the spectral weights and find that while the individual spectral weights are complicated and nonuniversal, their sum is consistent with Wen's effective two-boson description of the 2/5 edge. Composite fermions experience a negative effective magnetic field at 2/3, which suggests backward moving edge modes. Our microscopic calculation shows that the 2/3 edge has a charge neutral mode moving in the up-stream direction (opposite to the direction of the current flow), which is a pure spin mode in the case of the 2/3 spin singlet state. The spin singlet 2/3 state thus constitutes a rather neat example of spin charge separation, with the spin and charge excitations moving in opposite directions. All of the results from our microscopic studies in Refs. [4,5] are consistent with Wen's effective theory.

(iii) *CF pairing beyond 5/2*: [Publication 6] It is of interest to ask if there might exist FQHE states other than 5/2 that owe their origin to pairing of composite fermions. We have predicted in Ref. [6] that 3/8 is a likely candidate, and should allow a study of physics similar to that envisioned in the context of the 5/2 state. At 3/8 composite fermions fill 1+1/2 levels, and we provide evidence from exact numerical studies, that the composite fermions in the half filled second level capture two additional vortices and form pairs. Furthermore, we find that the anti-Pfaffian is favored over the Pfaffian. Our work leads to several predictions, including: a FQHE state at 3/8 for fully spin polarized particles; presence of backward moving neutral modes; tunneling exponents; nonabelian braid statistics. Due to very small excitation gap this state is expected to be very fragile, but we are trying to get experimentalists interested in a more careful investigation of the 3/8 state; a resistance minimum here was seen more than a decade ago, and it is possible that, with improved mobility and lower temperatures available today, FQHE can be confirmed and studied.

(iv) *Fractional Chern insulator states*: [Publication 7] Fractional Chern insulators are lattice systems that produce bands with non-zero Hall conductance (non-zero Chern number) in a zero *net* field. (The system does break time reversal symmetry, but in a manner that preserves the lattice symmetry.) Recently there has been much interest in the possibility of gap openings due to interactions at partial fillings of these bands. We have shown that the nontrivial bands of Chern insulators in a zero net field can be adiabatically connected to the bands of a Hofstadter lattice in a uniform magnetic field. This gives a new handle on the fractional Chern insulator states – we can begin with the familiar fractional quantum Hall effect (FQHE) states of the Hofstadter lattice and then ask how many survive as we slowly modify the Hamiltonian to produce a Chern insulator. We have shown that the states at 1/3 and 1/2 fillings of the Chern bands are adiabatic cousins of the 1/3 and 1/2 FQHE states. Our work demonstrates that we can produce any FQHE state in the Chern insulator by taking a sufficiently complex unit cell.

(v) *Interaction effects in topological insulators*: [Publication 1] The experimental colleagues at Penn State have studied single crystal thin films of Bi_2Se_3 grown by molecular beam epitaxy, both with and without Pb doping. Angle-resolved photoemission data demonstrate topological surface states with a Fermi level lying inside the bulk band gap in the Pb doped films. Their transport data show weak localization behavior, as expected for a thin film in the two-dimensional limit (when the thickness is smaller than the inelastic mean free path). We carried out a detailed analysis within the standard theoretical framework of diffusive transport and found that the temperature and magnetic field dependences of resistance cannot be reconciled in a theory that neglects inter-electron interactions. We demonstrated that an excellent account of quantum corrections to conductivity is achieved when both disorder and interaction are taken into account. These results demonstrate that it is crucial to include electron-electron interaction for a comprehensive understanding of diffusive transport in topological insulators. While both the ordinary bulk and the topological surface states presumably participate in transport, our analysis does not allow a clear separation of the two contributions.

Plans for near future I list here a subset of the issues that we wish to pursue in the near future.

Pfaffian or anti-Pfaffian?: We will further investigate the issue of whether the Pfaffian or the anti-Pfaffian is stabilized in realistic situations. The question is a subtle one, given the rather small corrections, but we believe we can resolve the discrepancy between our results and those of Simon and Rezayi.

Multipartite CF states: Given the success of the bipartite representation of the Pfaffian wave function in capturing the physics of excitations, it is natural to ask if a tripartite, or a multi-partite, generalization of the FQHE will also be useful. A wave function proposed by Read and Rezayi can be cast in the tripartite form, and we plan to explore if its excitations can be described as combinations of excitations in each of the individual partitions. We will again first test this idea for a model interaction for which the Read-Rezayi ground state is exact, and then ask if the physics continues adiabatically to the Coulomb interaction.

Chern insulators: We showed that fractional Chern insulator states are similar to the FQHE states on a Hofstadter lattice. We plan to explore if this analogy helps us uncover new physics for fractional Chern insulators.

Unconventional excitations at 1/3?: While there has been much work on the nature of excitations of the 5/2 state, it is a less appreciated fact that we do not have a good understanding even of the excitations of the state at $2 + 1/3$. Exact diagonalization studies show that the quantum numbers of its excitations are different from that of the corresponding 1/3 state in the lowest Landau level, suggesting the interesting possibility of new physics. We have ideas on how CF pairing tendency may affect the nature of the $2 + 1/3$ state itself, which we plan to investigate.

Publications (since the beginning of the grant in August 2010)

1. Evidence for electron-electron interaction in topological insulator thin films, J. Wang, A.M. DaSilva, C.-Z. Chang, K. He, J.K. Jain, N. Samarth, X.-C. Ma, Q.-K. Xue, and M.H.W. Chan, Physical Review B **83**, 245538 (2011).
2. Bipartite composite fermion states, G. J. Sreejith, C. Toke, A. Wójs, and J.K. Jain, Physical Review Letters **107**, 086806 (2011).
3. Unpaired composite fermion, topological exciton, and zero mode, G.J. Sreejith, A. Wojs and J.K. Jain, Physical Review Letters **107**, 136802 (2011).
4. Microscopic study of the 2/5 fractional quantum Hall edge, G.J. Sreejith, S. Jolad, D. Sen, and J.K. Jain, Physical Review B **84**, 245104 (2011).
5. Microscopic study of edge excitations of spin-polarized and spin-unpolarized 2/3 fractional quantum Hall effect, Y.-H. Wu, G. J. Sreejith, and J. K. Jain, submitted to Physical Review B; arXiv:1207.3566.
6. Possible anti-Pfaffian pairing of composite fermions in the lowest Landau level, S. Mukherjee, S. S. Mandal, A. Wojs, and J. K. Jain, submitted to Physical Review Letters; arXiv:1207.2166.
7. Adiabatic continuity between Hofstadter and Chern Insulators, Y.-H. Wu, J. K. Jain, and K. Sun, submitted to Physical Review Letters; arXiv:1207:4439.

Correlation Effects and Magnetism in the Actinides: Elements and Compounds

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Project Scope

Actinide based materials are of fundamental important from a basic science perspective as model systems where we can explore the physics of strong correlations in elements and simple compounds. Understanding the solid state physics of actinides is also very important for the DOE in view of their applications as nuclear fuels and to ensure the safe storage of already accumulated radioactive material

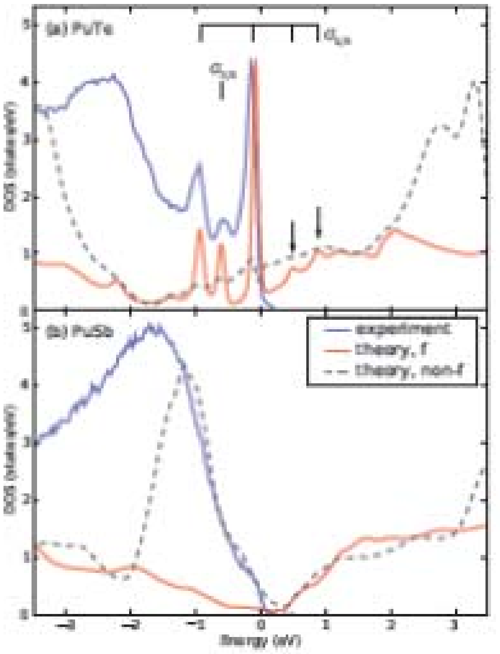
The objective of our research program is to achieve a fundamental understanding of the solid state phases of materials containing elements from the actinide series. To reach this goal we develop first principles relativistic electronic structure many body methods based on extensions of the Dynamical Mean Field Theory (DMFT) and apply them to elemental actinides and compounds. We then develop simplified models to guide the search for materials with desirable properties. We also develop DMFT based theoretical spectroscopies and use them to interpret the outcome of photoemission, optical conductivity and neutron scattering experiments.

Overview: In the last three year period of funding we carried out several important advances On the methodological side we carried out the first fully relativistic fully self consistent implementation of the GW method in an LAPW basis set. This will be the basis of an implementation of a GW+DMFT approach which will remove most of the ambiguities in the determination of parameters of the LDA+DMFT method. In the area of developments of theoretical spectroscopies, we added a new capablitity to the LDA+DMFT method, the ability to compute two particle responses including realistic calculations of elastic and inelastic neutron scattering. This approach yielded new insights into the mixed valent nature electronic structure of the high temperature superconductor PuCoGa5. This capability, has enabled a new collaborations with national laboratory facilities which is testing this method on the recently discovered iron based superconductors.

Recent Progress:

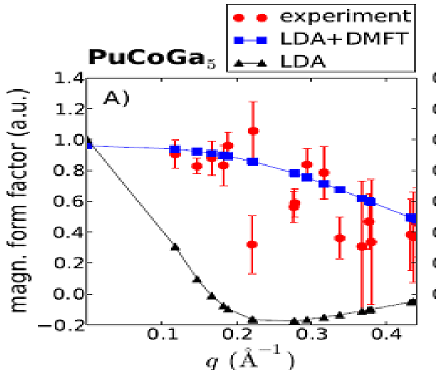
Study of photoemission spectra in plutonium pnicitides and chalgogenides: Valence Fluctuations and Quasiparticle Multiplets in Pu Chalcogenides and Pnictides . Chuck-Hou Yee, Gabriel Kotliar, Kristjan Haule, Phys. Rev. B 81, 035105 (2010)

We applied the LDA+DMFT methodology to understand pnictides and chalcogenides.
The spectra of Pu chalcogenides and pnictides were computed with LDA+DMFT and interpreted with the aid of valence histograms and slave-boson calculations. We find the chalcogenides are mixed-valent (nf = 5:2) materials with a strongly T-dependent low-energy density of states and atriplet of quasiparticle peaks below the Fermi level. Furthermore, we predict a doublet of peaks above the Fermi level. In the pnictides, the raising of f6 states relative to f5 suppresses valence fluctuations, resulting in integral-valent (nf = 5:0) local moment metals. This sheds new light on the the quasiparticle multiplets ad spectroscopic fingerprints of multiplets in the low energy spectra of plutonium compounds.



Photoemission spectra of two complex actinide compounds with different degree of localization of the f electron adapted from Chuck-Hou Yee, Gabriel Kotliar, Kristjan Haule, Phys. Rev. B 81, 035105 (2010)

We introduced a new formalism to compute the neutron magnetic form factor within a first-principles LDA+DMFT approach. The approach treats spin and orbital interactions on the same footing and reduces to earlier methods in the fully localized or the fully itinerant limit. We test the method on various actinides of current interest NpCoGa5, PuSb and PuCoGa5, and we show that PuCoGa5 is in a mixed valent state, which naturally explains the measured magnetic form factor.



The magnetic form factor of delta Pu is not described by either atomic physics or band theory. LDA+DMFT is in reasonable agreement with the experimental data and highlight the mixed valent character of Pu . Experiments from theory from Pezzoli Haule and Kotliar Phys. Rev. Lett. **106**, 016403 (2011).

We developed the methodology to study the momentum and frequency dependent spin susceptibility within LDA+DMFT . At this point formalism ignores the effects of spin orbit coupling but treats the Hunds rule coupling and the Hubbard interaction. We tested our approach in a BaFe2As2 a 3d compound which is the subject of extensive experimental investigations, and which shares almost all the difficulties (strong itinerancy , strong correlations, substantial effects of spin orbit coupling) with the actinides, but where we can neglect the spin orbit coupling. The results are in excellent agreement with experiments performed at ONRL.

We developed a relativistic fully self consistent GW, and quasiparticle GW code. This work will be a platform for a relativistic GW +DMFT for actinide materials which will remove the most important remaining shortcomings in the DMFT machinery for the treatment of actinide materials.

Planed Activities: 2012-2013:

We will generalize our calculations of the inelastic neutron scattering to the relativistic case, including the spin orbit coupling in a fully self consistent manner. We will expand our earlier LDA+DMFT CTQMC studies of the delta phase, and use the previous development
to compute the inelastic scattering cross section of delta Pu. The results will be compared with ongoing experiments at LANL.

We will compute the magnetic form factor of delta Pu using the methodology previously developed and tested on Pu and Np 115’2.

We will carry out a comparative study of the Plutonium 115’s and delta Pu to elucidate how important differences emerge at low energies, given their similarities at high energies.

We will begin investigations of the sctructural the properties of the alpha phase of Plutonium, using a recently developed slave boson solver including all the multiplets and crystal field states. This study will be a first test of the degree of site differentiation that takes place I this compound, and the results will be compared to those of the delta phase, to guide the development of a theory of the physical factors that govern the phase stability in this class of materials. The studies will serve to guide future calculations planned for alpha Pu with LDA+DMFT+CTQMC at a later stage.

List of publications resulting from this program 2009-2012

1) Valence Fluctuations and Quasiparticle Multiplets in Pu Chalcogenides and Pnictides Chuck-Hou Yee, Gabriel Kotliar, Kristjan Haule Phys. Rev. B 81, 035105 (2010)

2) Computational modeling of actinide materials and compounds Per Soderlind G. Kotliar, K. Haule, P. Oppeneer and D. Guillaumong, MRS Bulletin vol 35, 883, (2010).

3) Jian-Xin Zhu, P.H. Tobash, E.D. Bauer, F. Ronning, B.L. Scott, K. Haule, G. Kotliar, R.C. Albers, and J.M. Wills . Europhysics Letters 97 (2012) 57001.

4) Neutron Magnetic Form Factor in Strongly Correlated Materials: Maria Elisabetta Pezzoli, Kristjan Haule, and Gabriel Kotliar Phys. Rev. Lett. **106**, 016403 (2011)

5) Maria E. Pezzoli, Matthias J.Graf, Kristjan Haule, Gabriel Kotliar and Alexander V. Balatsky. Accepted for publication in physical review B.

6) Andrey Kutepov, Kristjan Haule, Sergey Y. Savrasov, and Gabriel Kotliar Phys. Rev. B **85**, 155129 (2012)

7) Nature of magnetic excitations in superconducting BaFe_{1.9}Ni_{0.1}As_{2}, Mengshu Liu, Leland W. Harriger, Huiqian Luo, Meng Wang, R. A. Ewings, T. Guidi, Hyowon Park, Kristjan Haule, Gabriel Kotliar, S. M. Hayden, Pengcheng Dai. Nature Physics 8, 376-381 (2012)

Effective medium theory

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Project scope

This project includes theoretical study of wave processes in different media: ordered and disordered. The main goal is to derive analytical results for the effective parameters -- index of refraction, bulk modulus, mass density, localization length, transmission coefficient, etc. For the ordered (periodic) systems the effective parameters completely define wave propagation in the long-wavelength limit. Calculation of the effective parameters becomes important in relation with recent progress in fabrication of so called metamaterials, i.e. structures with 'exotic' properties. New theoretical methods – transformation optics and transformation acoustics -- proposed for manipulation with waves in metamaterials require acoustic and dielectric materials with prescribed anisotropy. Here we concentrate on the theory of homogenization for anisotropic and absorbing periodic and plasmonic structures. Acoustic transmission through narrow fluid channels is a long-standing problem of fluid dynamics. Here, in relation with recent experiments, we reconsider the old results and propose a new theory which takes into account excitation of coupled Rayleigh waves. Study of disordered systems is concentrated on calculations of Anderson localization in real DNA molecules. The nucleotide sequence in DNA exhibit long-range correlations which strongly affect electron transport. The strength and spatial extension of the correlations are different in exons and introns, which are the cording and "junk" segments of DNA respectively. Our goal is to demonstrate that there are energy bands with extended quantum states in exons, unlike introns, which contain only localized states. Finite conductivity due to extended states inside exons may be relevant to the ability of the DNA molecules to detect and heal mutations (including cancerous ones).

Recent progress

Dissipative photonic crystals A periodic arrangement of parallel cylinders with dissipative dielectric constants is considered and a general formula for the effective dielectric constant $\varepsilon_{eff} = \varepsilon'_{eff} + i\varepsilon''_{eff}$ is derived using the plane waves expansion method [1]. The results for the real and imaginary part are represented in a form of expansions over the reciprocal-lattice vectors. Fig. 1 shows angular plots for ε'_{eff} and ε''_{eff} vs direction of propagation in a rectangular lattice. Later we performed a series of experiments in the laboratory of Prof. Sánchez-Dehesa at the Polytechnic University of Valencia (Spain) measuring the electromagnetic absorption for a photonic crystal of FR4 cylinders [1] and for alumina (Al_2O_3) cylinders in air [2]. In both cases we obtained a good agreement between theory and experiment for the *E*- and *H*-polarized modes. We also measured the anisotropy of the real and imaginary parts of the effective dielectric constant for the *H*-polarization. Theory predicts stronger anisotropy for the imaginary part (see the plot in Fig. 1), which was confirmed in the experiments.

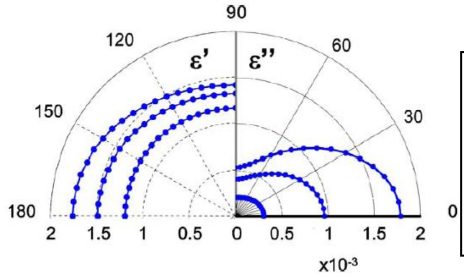

Fig. 1. Polar plot of the real and imaginary part of the effective dielectric constant vs direction of propagation in the x−y plane for three photonic crystals of alumina cylinders with $\varepsilon_a = 9.4(1 + 0.006i)$ and filling fractions $f = 0.1$, 0.2, and 0.26. The unit cell is a rectangle with ratio 2:1 of side lengths along x and y. Note much stronger anisotropy for the imaginary part, Ref. [2].

Surface plasmons on anisotropic substrates The main source of attenuation for a propagating surface plasmon is Joule losses in the metal. At room temperatures there are very limited options for variation of the propagation length. One possibility is to affect the level of dissipation through the properties of the substrate. In particular, we propose the use of dielectric substrates with high optical anisotropy oriented appropriately in order to maximize the propagation length [3,4]. We consider that the dielectric slabs on either side of the metal film possess uniaxial anisotropy. In order to determine the most favorable orientation of the optical axis of the dielectric substrates with respect to the interface, we calculated the propagation length. In Refs. [3,4] we analyze the plasmon propagation length over a wide range of frequencies, including the telecommunication wavelengths (1.3–1.6 μm) and determine which orientation of the optical axis is most favorable from the point of view of dissipation losses. In Ref. [3] we also propose a solvable Kronig-Penney model for a plasmonic anisotropic crystal.

Metafluid with anisotropic mass density Here we propose a method for calculating the dynamic mass density tensor of a fluid with embedded lattice of solid cylinders [5]. A homogeneous fluid is isotropic, i.e. longitudinal sound propagates with the speed $c = \sqrt{B/\rho}$ independent of the direction of propagation. If, however, an anisotropic structure of solid scatterers is embedded into this fluid, the medium behaves in the long-wavelength limit as a homogeneous metafluid with anisotropic mass density. This kind of anisotropic medium with coordinate-dependent anisotropy is required for the design of an acoustic cloak. The method of calculation of the mass density tensor is based on our previous result for the effective speed of sound in phononic crystal, *Phys. Rev. Lett.* ***91***, *264302 (2003)*. The obtained results are shown in Fig. 2 for a square lattice of Al cylinders in air. The anisotropy of the lattice is due to the rectangular cross-section of the cylinders with an aspect ratio of 1:5.

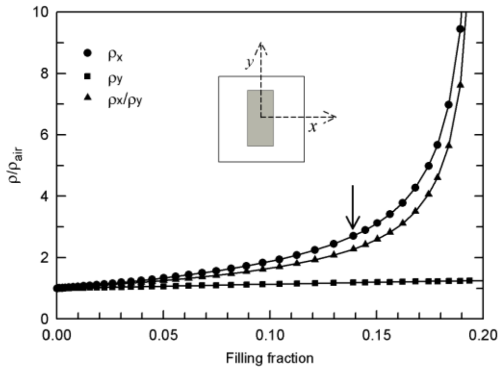

Fig. 2. Dynamical mass density (normalized to the density of air) calculated vs filling fraction of Al cylinders. Arrow indicates the filling fraction f = 0.14 of the phononic crystal studied experimentally by L. Zigoneanu, *et al.*, *J. Appl. Phys.* ***109***, *054906 (2011)*. At f = 0.14 we obtained the values ρ_x / ρ_{air} = 2.70 and ρ_y / ρ_{air} = 1.19 that are indistinguishable from those reported in the experiment. Insert shows the unit cell of the phononic crystal.

Resonant excitation of coupled Rayleigh waves The effect of coupling of Rayleigh waves through a narrow fluid channel was studied theoretically and compared with the experiment on acoustic transmission for the set up shown in Fig. 3. The Rayleigh waves propagate along the surfaces of metals. A fluid is apparently a weak link since the acoustic impedance of a fluid is much less than that of the metals. Thus, the coupling of two Rayleigh waves is a rather subtle effect that may be observed only under special conditions. We observed minima at the frequencies which can be calculated from a transcendental equation derived in Ref. [6]. This equation takes into account the effect of weak coupling. Two modes, symmetric and anti-symmetric have been studied in Refs. [6,7] for the channels formed by identical and different metals, respectively. A new effect of frequency cut-off for acoustic transmission has been predicted and observed.

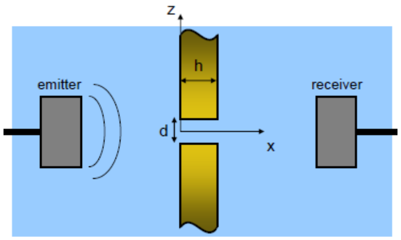

Fig. 3. Experimental setup for observation of the effect of resonant coupling of Rayleigh waves.

Josephson plasma waves in slabs of layered superconductors We studied propagation of electromagnetic waves within a layered type II superconductor [8]. Layered superconductors are either artificially grown stacks of Josephson junctions, such as Nb/Al-AlO$_x$/Nb, or natural high-temperature superconductors, such as $Bi_2Sr_2CaCu_2O_{8+\delta}$. We calculate the spectrum of Josephson plasma waves in a finite-thickness slab. Unlike most previous publications, we take into account the impedance boundary conditions and classify a rich spectrum of collective modes. We have found two types of eigenwaves: The "true" surface modes, which decay exponentially from the slab boundaries, and the waveguided modes, the fields of which oscillate across the layers. As an example, we also study theoretically the problem of excitation of one of the waveguide modes by the attenuated-total-reflection method. For certain geometrical parameters, we predict an interesting effect: Total suppression of specular reflection due to resonant excitation of the waveguided modes.

Swelling kinetics of a microgel shell Here we studied experimentally and theoretically the kinetics of the swelling of a polymer gel -- poly-N- isopropylacrylamide (PNIPAM). The swelling of polymer gels is one of the classical problems in both macromolecular science and technology. The previous studies have focused on the swelling kinetics of solid gel structures, i.e. structures without internal cavities. What actually motivates this work is the current synthesis of monodisperse polymer gel shells using microfluidic devices. These gel shells have radii of ∼60 μm and have characteristic swelling times that range around several tens of seconds. The kinetics of these shells is easily measurable, but there is a lack of theoretical description. The study of the swelling kinetics of gels with shell structure may aid in the development of applications ranging from controlled drug release to cell encapsulations. In Ref. [9] we propose a theoretical model which is applicable to the case of a shell and obtain a good agreement between our theoretical and experimental results.

Anderson localization of conduction electrons in DNA molecules The parts of DNA sequences known as exons and introns play very different roles in the coding and storage of genetic information. Here we show that their conducting properties are also quite different. Taking into account long-range correlations among the four basic nucleotides that form the double-stranded DNA sequence, we calculate the electron localization length for exon and intron regions. By analyzing different DNA molecules, we find that the exons have narrow bands of extended states, unlike the introns where all the states are well localized. These bands of extended states arise due to a specific form of the binary correlation function of the sequence of basic DNA nucleotides. Some results of our study based on the two-stranded model of DNA molecule are shown in Fig. 4.

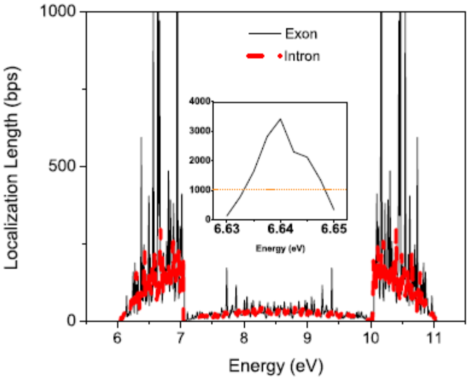

Fig. 4. Localization length for human ADAM10 gene measured in the number of base pairs. The length of the exon (intron) is 1,030 (31,752) bps. Inset shows the fine structure of one of the peaks. Exon regions contain narrow bands of practically delocalized states. By comparison, introns contain *only* well-localized states, i.e. they are insulators.

Memory effects in fractional Brownian motion Fractional Brownian motion (FBM) is a generalization of ordinary Brownian motion that has been the subject of active research because the anomalous scaling and the memory properties of many diffusion processes are considered to be the attributes of FBM. There are two important parameters associated with FBM: the Hurst exponent H and the persistent exponent θ. These two exponents are related and it is commonly believed that $H = 1 - \theta$. In Ref. [10] we show that the relation between H and θ depends on H. In particular, we prove, both analytically and numerically, that that within the interval $0 < H < 1/3$ the previous relation is replaced by $H = \theta/2$. We show that for $0 < H < 1/3$ the memory effect on the trajectories of the FBM are much stronger than for the case of 1/3 < H < 1. The new relation means that previous studies of the FBM based on the renewal assumption must be reconsidered.

Review on Anderson localization in disordered systems with correlations This recently published review [11] is a result of a 3-year cooperative effort with my co-authors from the Universidad Autònoma de Puebla (Mexico) to summarize the recent progress in the theory of Anderson localization within disordered systems with special correlations in the disordered potentials. It contains results on low-dimensional systems with diagonal and off-diagonal disorder. We also consider short- and long-range correlations in the tight-binding and Kronig-Penney discrete models. This comprehensive review covers the results obtained in the field of Anderson localization during the last 15 years.

Future plans

I am going to study a new mechanism of non-plasmonic enhancement of photoluminescence in hybrid metal-semiconductor quantum structures. This effect has been recently observed experimentally in the optical laboratory led by Prof. Neogi at the University of North Texas (UNT). Our theoretical explanation for the experimental results is based on Coulomb interaction between the carriers in a semiconductor quantum well and the metallic inclusions. The enhancement has been observed for InGan/GaN quantum well with gold nanoparticles imbedded in the body of the quantum well. Since the frequency of the plasmonic resonance for Au is well below the frequency of emitted light, the known plasmonic mechanism of enhancement is completely ruled out. Our results show that the observed enhancement is due to attractive forces between the electrons and holes and neutral metal nanoparticles. This mechanism is a non-resonant one and may be applicable for wide-band solid state light emitters.

References

1. J. Carbonell, F. Cervera, J. Sánchez-Dehesa, J. Arriaga, L. Gumen, A. Krokhin, Homogenization of two-dimensional anisotropic dissipative photonic crystal, *Appl. Phys. Lett.* ***97****, 231122 (2010).*
2. J. Carbonell, J. Sánchez-Dehesa, J. Arriaga, L. Gumen, A. Krokhin, Electromagnetic absorption in anisotropic photonic crystal of alumina cylinders, *Metamaterials* ***5****, 74 (2011).*
3. Nagaraj Nagaraj, A.A. Krokhin, Long-range surface plasmons in dielectric-metal-dielectric structure with highly anisotropic substrates, *Phys. Rev. B* ***81****, 085426 (2010).*
4. L. Gumen, Nagaraj, A.Neogi, A. Krokhin, Long-range surface plasmons on highly anisotropic dielectric substrates, *Journal of Nonlinear Optical Physics & Materials* ***19****, 613 (2010).*
5. L. Gumen, J. Arriaga, A. Krokhin, Metafluid with anisotropic dynamic mass, *Low Temp. Phys.* ***37****, 975 (2011).*
6. V. M. García-Chocano, T. López-Rios, A. Krokhin, J. Sánchez-Dehesa, Resonant excitation of coupled Rayleigh waves in a short and narrow fluid channel clad between two identical metal plates, *AIP Advances* ***1****, 041501 (2011).*
7. V. M. García-Chocano, Nagaraj, T. López-Rios, L. Gumen, J. Sánchez-Dehesa, A. Krokhin, Resonant coupling of Rayleigh waves through a narrow fluid channel causing extraordinary acoustic absorption, *accepted to J. Ac. Soc. Am., 2011.*
8. T. M. Slipchenko, D. V. Kadygrob, D. Bogdanis, V. A. Yampol'skii, A. A. Krokhin, Surface and waveguide Josephson plasma waves in slabs of layered superconductors, *Phys. Rev. B* ***84****, 224512 (2011).*
9. Joshua Wahrmund, Jin-Woong Kim, Liang-Yin Chu, Changjie Wang, Yong Li, Alberto Fernandez-Nieves, David A. Weitz, Arkadii Krokhin, Zhibing Hu, *Macromolecules* ***42****, 9357 (2009).*
10. M. Bologna, F. Vanni, A. Krokhin, P. Grigolini, Memory effects in fractional Brownian motion with Hurst exponent H < 1/3, *Phys. Rev. E* ***82****, 020102 (R) (2010).*
11. F.M. Izrailev, A.A. Krokhin, N.M. Makarov, Anomalous localization in low-dimensional systems with correlated disorder, *Phys. Rep.* **512**, 125 (2012).

Electronic properties of transition-metal-compound nanotubes

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Project scope

In direct connection to one of the department's main thrust in functional correlated materials, this program intends to conduct first-principles-based theoretical studies of electronic structure and excitation properties of transition metal compounds that are of great scientific and technical interest. Particular focus will be given to the physics of nano-scale short-range correlations and effects of nano-scale disorder in these materials. These include the newly discovered Fe-based superconductors, high-T_c cuprates, thermoelectric cobaltates, intercalated graphite, transition metal dichalcogenides, Ir-based correlated materials, and doped semi-conductors alloys. Besides having intriguing properties that challenge our current fundamental understanding, these materials also possess great potential in a wide range of energy-related applications essential to the central missions of DOE-BES and BNL.

Recent progress

Electronic structure of Fe-based high-temperature superconductors

The newly discovered Fe-based high-temperature superconductors has triggered intense investigations of this new class of materials. This program has actively contributed to this rapid evolving field:

1. Essential role of ferro-orbital correlation: Our DFT solution indicates that the system has a strong tendency to break the degeneracy between *xz* and *yz* orbital (c.f.: Fig. 1) and that the higher-temperature structure transition is in fact an ferro-orbital order transition. This "nematic" correlation leaves only one of the orbital active in boosting up the stiffness of C-type magnetic correlation that is intimately tied to the superconductivity.

2. Unified picture of rich magnetic structure: Our DFT+model analysis shows that the rich and variable magnetic structure in families of Fe-SC (C-type, E-type, and block-type) can all be understood from the competition between kinetic energy of the itinerant carriers, and the exchange energy of the local carriers, under the strong Hund's coupling.

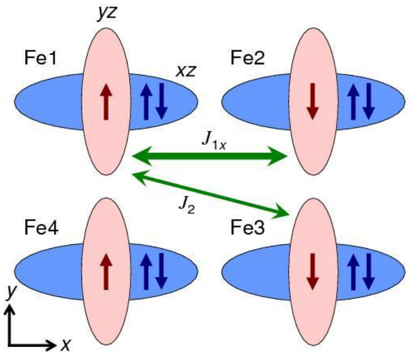

Fig. 1 Leading coupling paths, and ferro-orbital / C-type AF correlation.

3. Special parity-switching band folding from alternating As position: Our DFT analysis of the effects of translational symmetry breaking due to alternating As position has revealed a non-trivial "parity switching" folding of the band structure that alter the orbital character of each bands across 1-Fe zone boundary. The study not only explains the puzzling 1-Fe like neutron and ARPES spectra, but also indicates that the essential electron pockets are only created because of the broken translational symmetry, implying important roles of electron-lattice coupling in short-range correlation.

4. Effects of disordered chemical substitution of Fe: Fe-SC can be doped by substituting Fe with Co and other close transition metals. The role of such a substitution has recently been under heavy debate. Some theoretical and experimental studies propose that the substitution is actually isovalent and thus not doping. We conducted the first DFT calculation with random disorder and clarified that the substitution does dope additional carriers, but at the same time, some of the itinerant carriers become more diffusive in nature. This opens doors to potential new mechanisms of enhancing superconductivity.

Novel first-principles methods

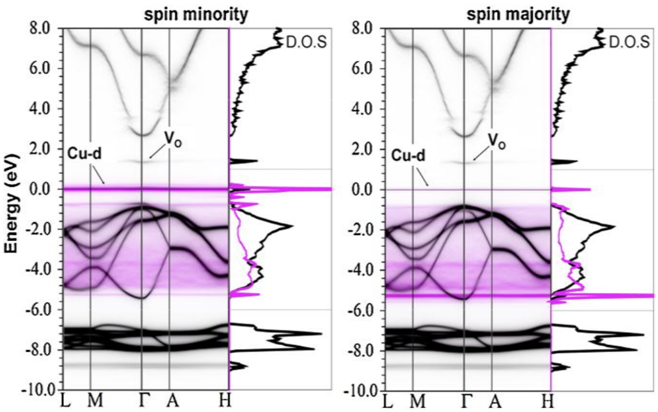

Fig. 2 One-particle spectral function of Zn$_{1-x}$CuxO$_{1-y}$ showing partially ordered Cu moment and large-sized oxygen vacancy orbital.

To help investigating the short-range correlation, we have recently developed two methods:

1. Unfolding first-principles band structure: We have proposed a simple method to reveal the influence of broken translational symmetry (due to presence of impurities or long-range / short-range order) on the one-particle propagator, by representing the propagator in the more periodic basis. The information that used to be hidden in the wave functions is then explicitly shown in spectral weight.

2. One-particle propagator of materials with disordered impurities: Introduction of impurities (substitution, intercalation, vacancy) is one of the most common methods to trigger experimentally the rich behavior of correlated functional materials. However, the physical effects of the accompanied disorder have been mostly ignored. We have developed a first-principles based method that allows efficient computation of averaging large systems containing disordered configurations. Figure 2 shows the resulting spectral function containing clear impurity levels of local Cu moments and large-sized oxygen vacancy orbitals, which clearly has a strong momentum dependent (non-local) self-energy.

First-principles theory for exciton propagation

We have recently developed a new theory to describe the propagation of tightly bound excitons. By integrating out the de-pair degree of freedom, the tightly bound exciton can then be viewed as a composite object, with a irreducible hopping kernel that gives the propagation. This description is exact in both weak and strong coupling limit and has a natural approximation of high quality. The real-space nature of the theory allows applications in lower dimension, or in the presence of impurities or surfaces. It also allows a more accurate treatment of local interaction for strongly correlated materials.

Future Plans

Effects of nano-scale disorders in real material

We plan to extend our study of disorders in real materials to resolve the following scientific questions:

1. Effects of Fe vacancy in Fe-SC: The newest member of the Fe-SC family is the so-called 245 system K$_2$Fe$_4$Se$_5$. This family is particularly interesting due to its rich behaviors and the large amount (20%) of Fe vacancy. With a good vacancy order, the system is known to be a magnetic insulator. However, the system often contains "other region" (some considers it phase separation) that contains either no vacancy, or disordered vacancy. It is currently unclear why the ARPES measurements don't see a strong reconstruction of the band structure reflecting the Fe-vacancy order. Furthermore, it is currently mostly unclear how disordered Fe vacancy would modify the electronic structure.

2. Missing interlayer bands in intercalated graphite: Intercalated graphite demonstrated interesting superconducting property. Almost all theoretical studies points to the important role of electron-phonon coupling involving the intercalant band. However, these bands are never observed in ARPES. We plan to investigate this by considering the local rattling of the intercalant.

3. Impurity Level and Band Gap Bowing in Doped Semiconductor: The functionality of most semiconductors is derived from introduction of dopings or vacancies that give rise to the n-type or p-type carriers residing in the impurity levels within the band gap. The energy of the impurity level is however difficult to calculate accurately with current DFT methods. As shown in Fig. 2 above, our method allows a direct production of the impurity level, localized or semi-localized. Since we have the information unfolded back to the regular normal cell, the result even gives direct information of the intensity of optical process involving the impurity levels. A related well known phenomenon is the band gap bowing. It is often found that the alloys of semiconductors show a smaller

fundamental gap than a naïve linear interpolation between the pure compounds. A simple general microscopic mechanism for this observation, however, is not yet available. At least two possible scenarios can be formulated as the potential mechanism. It could be that the bowing is related to reduction of bonding-anti-bonding splitting as a result of frustrated kinetic energy. Or, it could be that it is actually the impurity levels that define the band gap and thus controls the band gap bowing. We plan to investigate this general property of the semiconductor alloys and provide a simple intuitive picture in real materials.

Effects of strong short-range correlation on one-particle spectral function

Strongly correlated materials often possess large correlation functions at short-range, regardless whether the correlations develop into long-range orders. The short-range correlations should in principle manifest themselves in the one-particle spectral function as well. We plan to extend our method to include fluctuating local order parameters and study their influence:

1. Thermal fluctuation of large spin moment in paramagnetic phase: In DFT community, paramagnetic phase is often restricted to the Pauli paramagnetism. Recent ARPES measurement of the paramagnetic phase of EuO offers a good example of non-trivial development of one-particle spectral function within Curie paramagnetism. We plan to conduct formal extension of DFT to describe the thermal fluctuation of the local moment and compute the corresponding one-particle spectral function. The new theory should allow a Mott gap in the paramagnetic phase.
2. Nematic phase of Fe-based superconductors above orbital/magnetic transition temperature: The new theory would allow an investigation of the so-called nematic phase in Fe based superconductor. We plan to investigate whether thermal fluctuation of the local order parameter can explain the experimentally observed strong nematic susceptibility in the absence of long-range order, and how the correlation extend to such a high temperature.

Publications

1. "Do transition metal substitutions dope carriers in iron-based superconductors?"
   Tom Berlijn, Chai-Hui Lin, William Garber and Wei Ku, Phys. Rev. Lett. **108**, 207003 (2012)
2. "Relevance of the Heisenberg-Kitaev Model for the Honeycomb Lattice Iridates A_2IrO_3"
   Yogesh Singh, et al., Phys. Rev. Lett. **108**, 127203 (2012)
3. "Magnetic softness in iron-based superconductors", Weiguo Yin, Chi-Cheng Lee, and Wei Ku, Supercond. Sci. Technol. **25**, 084007 (2012)
4. "One-Fe versus Two-Fe Brillouin Zone of Fe-Based Superconductors: Creation of the Electron Pockets via Translational Symmetry Breaking"
   Chia-Hui Lin, Tom Berlijn, Limin Wang, Chi-Cheng Lee, Wei-Guo Yin, and Wei Ku, Phys. Rev. Lett. **107**, 257001 (2011)
5. "Kinetics-Driven Superconducting Gap in Underdoped Cuprate Superconductors Within the Strong-Coupling Limit"
   Y. Yildirim and Wei Ku, Phys. Rev. X **1**, 011011 (2011)
6. "Can disorder alone destroy the e_g' hole pockets of $Na_{0.3}CoO_2$?"
   Tom Berlijn, Dmitri Volja, and Wei Ku, Phys. Rev. Lett. **106**, 077005 (2011)
7. "*dd* excitations in three-dimensional q-space: A nonresonant inelastic X-ray scattering study on NiO", N. Hiraoka, M. Suzuki, K. D. Tsuei, H. Ishii, Y. Q. Cai, M. W. Haverkort, C. C. Lee and W. Ku, Europhys. Lett. **96**, (2011)
8. "Local-moment magnetism in superconducting $FeTe_{0.35}Se_{0.65}$ as seen via inelastic neutron scattering"
   Zhijun Xu, Jinsheng Wen, Guangyong Xu, Songxue Chi, Wei Ku, Genda Gu, and J. M. Tranquada, Phys. Rev. B **84**, 052506 (2011)
9. "Nanospheres of a New Intermetallic FeSn(5) Phase: Synthesis, Magnetic Properties and Anode Performance in Li-ion Batteries"
   XL Wang, M Feygenson, HY Chen, CH Lin, CH, Wei Ku, JM Bai, MC Aronson, TA Tyson, TA, WQ Han, JACS **133**, 11213 (2011)

10. "Long-range magnetic ordering in Na_2IrO_3"
X. Liu, T. Berlijn, W.-G. Yin, W. Ku, A. Tsvelik, Young-June Kim, H. Gretarsson, Yogesh Singh, P. Gegenwart, and J. P. Hill, Phys. Rev. B **83**, 220403(R) (2011)
11. "X-ray diffuse scattering study of local distortions in $Fe_{1+x}Te$ induced by excess Fe"
X. Liu, C.-C. Lee, Z. J. Xu, J. S. Wen, G. Gu, W. Ku, J. M. Tranquada, and J. P. Hill, Phys. Rev. B **83**, 184523 (2011)
12. "Room temperature magnetism of Cu-doped ZnO films probed by soft X-ray magnetic circular dichroism"
T.S. Herng, et al., Phys. Rev. Lett. **105**, 207201 (2010)
13. "A unified picture for magnetic correlations in iron-based high-temperature superconductors"
Wei-Guo Yin, Chi-Cheng Lee, and Wei Ku, Phys. Rev. Lett. **105**, 107004 (2010)
14. "Dynamical Linear Response of TDDFT with LDA+U Functional: Strongly hybridized Frenkel excitons in Mott insulators"
Chi-Cheng Lee, Hung-Chung Hsueh, and Wei Ku, Phys. Rev. B **82**, 081106 (R) (2010)
15. "Unfolding first-principles band structures"
Wei Ku, Tom Berlijn, and Chi-Cheng Lee, Phys. Rev. Lett. **104**, 216401 (2010)
16. "Experimental observation of the crystallization of a paired holon state"
A. Rusydi, W. Ku, et al., Phys. Rev. Lett. **105**, 026402 (2010)
17. "Effect of covalent bonding on magnetism and the missing neutron intensity in copper oxide compounds"
Andrew C Walters, et al., Nature Physics **5**, 867 (2010)
18. "Charge Ordering in Half-Doped Manganites: Weak Charge Disproportion and Leading Mechanisms"
D. Volja, W.-G. Yin, and Wei Ku, Europhys. Lett. **89** 27008 (2010)
19. "Coupling of spin and orbital excitations in the iron-based superconductor $FeSe_{0.5}Te_{0.5}$"
S.-H. Lee, et al, Phys. Rev. B **81**, 220502 (2010)
20. "Nanoscale disorder and local electronic properties of $CaCu3Ti_4O_{12}$: An integrated study of electron, neutron and x-ray diffraction, x-ray absorption fine structure and first principles calculations"
J.C. Zheng, et al., Phys. Rev. B **81**, 144203 (2010)
21. "Ferro-Orbital Order and Strong Magnetic Anisotropy in the Parent Compounds of Iron-Pnictide Superconductors"
Chi-Cheng Lee, Wei-Guo Yin, and Wei Ku, Phys. Rev. Lett. **103**, 267001 (2009)
22. "Tuning Hole Mobility, Concentration, and Repulsion in High-Tc Cuprates via Apical Atoms"
W.-G. Yin and Wei Ku, Phys. Rev. B **79**, 214512 (2009)
23. "Flavored-Twisted Boundary Conditions for the Quantum World: between Big and Small"
Wei-Guo Yin, and Wei Ku, Phys. Rev. B **80**, 180402(R) (2009)
24. "Electronic Properties of Thin Film Periodic Nanostructures"
Travis Sjostrom, Daniel C. Mattis, Weiguo Yin, and Wei Ku, J. Comput. Theor. Nanosci. **6**, 403–417 (2009)
25. "GGA+U calculations of correlated spin excitations in LaCoO3"
Karel Knizek, Zdenek Jirak, Jiri Hejtmanek, Pavel Novak, and Wei Ku, Phys. Rev. B. **79**, 014430 (2009)
26. "Effect of Number of Walls on Plasmon Behavior in Carbon Nanotubes"
M. H. Upton, R. F. Klie, J. P. Hill, T. Gog, D. Casa, W. Ku, Y. Zhu, M. Y. Sfeir, J. Misewich, G. Eres, D. Lowndes, Carbon **47** (1), 162 (2009)

STRUCTURE AND DYNAMICS OF MATERIAL SURFACES, INTERPHASE INTERFACES AND FINITE AGGREGATES

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Project Scope

Investigations of fundamental materials physical and chemical processes and of the microscopic origins of materials properties, and explorations aiming at novel materials preparation and design, are major thrusts of our research. This research program emphasizes the development and implementation of computational and simulation methodologies of predictive capabilities, and their use as tools of discovery in a broad range of materials problems of fundamental and technological interest, with a focus on nanoscale systems, where "small is different". Topics of our research and educational program include:

1. Joint First-principles theoretical and experimental investigations of atomic-scale mechanisms of mutations in DNA, involving proton-coupled electron transfer reactions of ionized DNA with water. The targets of our research are reactions of one-electron ionized A/T-rich regions in DNA and fundamental understanding of the sequence dependence and pathways of reactions underlying mutations, caused by endogenous and exogenous one-electron oxidation of A/T rich DNA, which are implicated in early stages of cancer development.

2. Investigations of metal/water cluster complexes, and first-principles explorations of the elementary steps of charging and water splitting reactions. These first-principles simulations, joint with laboratory experiments, aim at contributing to the development artificial photosynthesis systems.

3. Computational explorations of the properties of confined electron systems which exhibit highly correlated electron states and spontaneous symmetry breaking, weak disorder in two-dimensional electron gases underlying Wigner crystallization under fractional quantum Hall effect conditions, semiconducting, metal, and graphene quantum dots (QDs) at field-free conditions and under the influence of magnetic fields, Aharonov-Bohm oscillations in graphene, edge reconstruction and edge states engineering of the properties of graphene QDs, and optical properties of small graphene QDs targeted for possible application in photo-voltaics.

Recent Progress

Proton-Coupled Electron Transfer (PCET) mechanism of thymine deprotonatoion One-electron oxidation, endogenous and exogenous, of A/T-rich DNA leads to mutations at thymine. Experimental investigation of DNA containing methyl-deuterated thymine reveals a large isotope effect establishing that cleavage of this carbon-hydrogen bond is involved in the rate-determining step of the reaction. Extensive first-principles quantum simulations reveal that the radical cation (electron hole) generated by DNA oxidation, initially located on adenines, localizes on thymine as the proton is lost from the methyl group demonstrating the role of proton-coupled electron transfer (PCET) in thymine oxidation. Proton transport by structural diffusion along a segmented "water-wire" culminates in proton solvation in the hydration environment, serving as an entropic reservoir that inhibits reversal of the PCET process. These findings provide insight into replication fork stalling in A/T-rich DNA that is implicated in early-stage carcinogenesis.

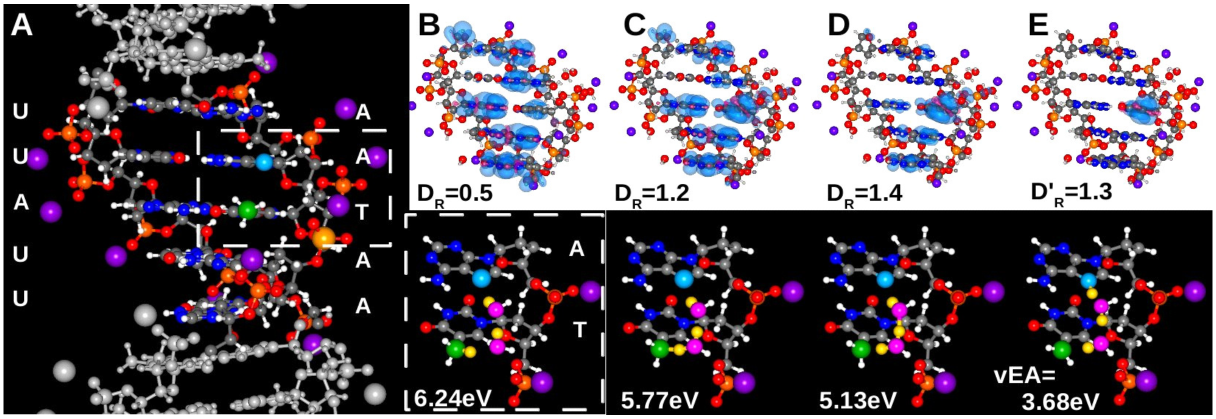
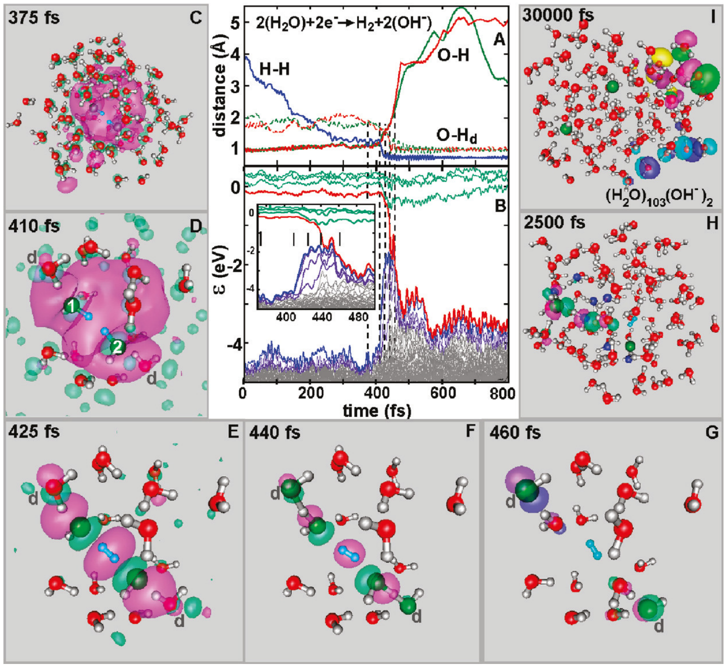


Figure: **(A)** Atomic configuration (side-view) of part of the 11-base-pair DNA duplex used in QM/MM simulations of the PCET deprotonation process. The central region (colored atoms) comprises the five base-pair segment (5′–UUAUU-3′)/(5′-AATAA-3′) is treated quantum mechanically (QM). **(B)** Bottom panel: a close-up view of the PCET reaction region. **(C-E)** evolution of the PCET process – (bottom) atomic configuration , and (top) corresponding spin-density (hole) distributions (blue iso-surfaces) , illustrating initial delocalization, and final (E) localization on the thymine.

Dielectrons & Hydrogen evolution in charged water clusters

Figure: Dielectron hydrogen evolution reaction mechanism in a $(H_2O)_{105}^{-2}$ cluster, evaluated with steered first-principles quantum MD simulations.



Binding of excess electrons to nanosize water droplets, with a focus on the hitherto largely unexplored properties of doubly-charged clusters, were investigated experimentally using mass spectrometry and theoretically with large-scale first-principles simulations based on spin-density-functional theory, with all the valence electrons (that is, 8e per water molecule) and excess electrons treated quantum mechanically. Singly-charged clusters $(H_2O)_n^{-1}$ were detected for n = 6 - 250, and our calculated vertical detachment energies agree with previously measured values in the entire range $15 \leq n \leq 105$, giving a consistent interpretation in terms of internal, surface and diffuse states of the excess electron. Doubly charged clusters were measured in the range of $83 \leq n \leq 123$, with $(H_2O)_n^{-2}$ clusters found for $83 \leq n \leq 105$, and mass-shifted peaks corresponding to $(H_2O)_n^{-2}$ $(OH^-)_2$ detected for $n \geq 105$.

The simulations revealed surface and internal (see figure) dielectron, e^-_2, localization modes and elucidated the mechanism of the reaction $(H_2O)_n^{-2} \rightarrow (H_2O)_{n-2}$ $(OH^-)_2 + H_2$ (for $n \geq 105$), which was found to occur via concerted approach of a pair of protons belonging to two water molecules located in the first shell of the dielectron internal hydration cavity, culminating in formation of a hydrogen molecule $2H^+ + e^-_2 \rightarrow H_2$. Instability of the dielectron internal localization impedes the reaction for smaller ($n < 105$) doubly charged clusters.

Unified microscopic theory of pinned-Wigner-solid and liquid behavior of the lowest Landau-level states in the neighborhood of ν = 1/3

Most recent microwave absorption observation showing experimental signatures associated with a pinned Wigner crystal in the immediate neighborhood of $\nu = 1/3$ represents a rather surprising development. Using the rotating-and-vibrating electron-molecule (RVEM) theory developed in our earlier work, in conjunction with exact diagonalization, a unified microscopic approach was developed, Our work reveals that away from the exact fractional fillings, weak pinning perturbations (due to weak disorder) may overcome the energy gaps between adjacent global states and generate pinned broken symmetry ground states as a superposition of symmetry-conserving LLL states with different total angular momenta. The electron densities of such mixed states (without good angular momentum quantum numbers) exhibit oscillating patterns that correspond to molecular crystallites. These pinned Wigner crystallites represent finite-size precursors of the bulk Wigner-solid state. It is further shown that the emergence of these molecular crystallites is a consequence of the presence of RVEM components in the symmetry-conserving LLL states.

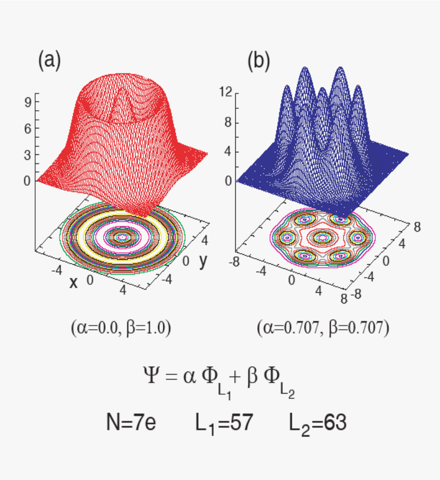


Figure: Electron densities of wave function constructed as a superposition of two good angular momentum eigenstates of a rotationally invariant Hamiltonian in the lowest Landau level (7 electrons). (a) the electron density corresponding to a vanishing coefficient α illustrating a uniform azimuthal density for $L_2 = 63$. (b) the electron density corresponding to equal coefficient α and β, illustrating an oscillatory azimuthal density, corresponding to the broken symmetry crystalline Wigner crystallite state. Underlying the formation of the rotationally symmetry broken state is a pining potential caused by disorder.

Planned activities: 2012 – 2013

In addition to continuation of our current work on grapheme quantum dots, metal nanocrystals, and post-ionization of DNA, we plan the following studies:

1. First-principles quantum simulations of charging of water nanoclusters (with up to 100 water molecules) through the attachment of multiple excess electrons, in the presence of solvated metal ions. Dependencies of the excess electrons attachment modes (surface and interior attachment) and of the excess-charge-limit (ecl, namely the maximum number of excess electrons bound to a given cluster) as a function of the number and chemical identity of the metal ions (in particular valence structure), as well as a function of the nanocluster size, will be explored. Water-splitting (hydrogen evolution) reactions will be investigated, as well as the effect of an externally applied electric fields which are expected to distort the shape of the water naosclusters. Electric-field induced phase transformations will be studied.

2. Exploration of the adsorption of metal clusters (e.g. palladium clusters with 10 to20 atoms) on a monolayer of graphene supported on a metal substrates (e.g. Ru(0001)), with an emphasis on: (i) the optimal adsorption sites on the graphene/metal Moire; (ii) the nature of binding (i.e., cluster-induced graphene rehybridization); (iii) cluster isomerization and dimensionality crossovers (two-dimensional and three dimensional clusters), and (iv) cluster diffusional characteristics. Moreover, the chemical reactivity and catalytic activity of the supported metal clusters will be explored, using the catalyzed oxidation of CO (to form CO_2) as a test reaction.

Publications

1. "Quantal molecular description and universal aspects of the spectra of bosons and fermions in the lowest Landau level", C. Yannouleas, U. Landman, Phys. Rev. A, **81**, 023609 (2010).
2. "Unified microscopic approach to the interplay of pinned-Wigner-solid and liquid behavior of the lowest Landau-level states in the neighborhood of ν = 1/3", C. Yannouleas, U. Landman, Phys. Rev. B **84**, 165327 (2011).
3. "Edge and bulk components of lowest-Landau-level orbitals, correlated fractional quantum Hall effect incompressible states, and insulating behavior in finite graphene samples", C. Yannouleas, I. Romanovsky, U. Landman. Phys. Rev. B **82**, 125419 (2010) .
4. "Unique nature of the lowest Landau level in finite graphene samples with zigzag edges: Dirac electrons with mixed bulk-edge character", C.Yannouleas, I. Romanovsky, and U. Landman, Phys. Rev. B 83, 045421 (2011).
5. "Patterns of the Aharonov-Bohm oscillations in graphene nanorings", I.Romanovsky, C. Yannouleas, U. Landman, Phys. Rev. B**, 85**, 165434 (2012).
6. "Oxidation of DNA: Damage to Nucleobases", S. Kanvah, J. Joseph, G. B. Schuster, R.N. Barnett, C.L. Cleveland, U. Landman, Accounts of Chemical Research, **43**, 280 (2010).
7. "Oxidative Thymine Mutation in DNA: Water-Wire-Mediated Proton-Coupled Electron Transfer", R. N. Barnett, J.J. Joseph, U. Landman, G. B. Schuster, J. Am. Chem. Soc. (submitted, 2012).
8. "Methane Activation and Catalytic Ethylene Formation on Free Au_2^+", S.M. Lang, T.M. Bernhardt, R.N. Barnett, U. Landman, Angew. Chem. Int. Ed. **49**, 980 (2010).
9. "Ultra thin magnesia films as support for molecules and metal clusters: tuning reactivity by thickness and composition", M.E. Vaida, T.M. Bernhardt, C. Barth, F. Esch, U. Heiz, U. Landman, Phys. Stat. Solid. (feature article), Physica Status Solidi B **247**, No. 5, 1001 (2010). (2010).
10. "Size dependent binding energies of methane to small god clusters", S.M. Lang, T.M. Bernhardt, R.N. Barnett, U. Landman, ChemPhysChem **11**, 1570 (2010).
11. "Dielectron Attachment and Hydrogen Evolution Reaction in Water Clusters" R. N. Barnett, R. Giniger, O.Cheshnovsky, U. Landman, J. Phys. Chem. A **115**, 7378 (2011).
12. "Shell-correction and orbital-free density-functional methods for finite systems", C. Yannooleas, U. Landman, in "Orbital Free Density Functional Methods", Editor A. Wang (Word Scientifi, Singapore, 2012).
13. "Chiral tunneling in metallic carbon nanotubes" A. V. Parafilo, I. V. Krive, E. N. Bogachek,, U. Landman, R. I. Shekhter, M. Jonson, Phys. Rev. B **83**, 045427 (2011).
14. "Chiral effects in normal and superconducting carbon nanotube-based nanostructures", A. V. Parafiloa, I. V. Krive, E. N. Bogachek, U. Landman, R. I. Shekhter, M. Jonson, Low Temp. Phys. **36** (10/11), 959 (2010)**.**
15. "Superconducting phase-dependent force in SNS junctions with a movable scatterer", A.V. Parafilo, I.V.Krive, E.N. Bogachek, and U. Landman, Low Temperature Physics/Fizika Nizkikh Temperatur, **38** (4), 446-450 (2012).

Superconductivity in correlated and spin-orbit materials

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Project scope

The research in this program studies superconductivity in correlated materials. The program focuses most heavily on iron-based superconductors, less on cuprates, and search for topological superconductors. The main goal of the proposed research on the iron-based superconductor is to understand the recent potential paradigm-shifting experimental results: for $K_yFe_{2-x}Se_2$ ($T_{c,max}$=48K under pressure) , and a single-unit-cell-thick FeSe on $SrTiO_3$ substrate (T_c>55K) *there is no hole pockets at the Brillouin zone center*. This is in conflict with the conventional wisdom that antiferromagnetic fluctuations associated with the "stripe" ordering wavevector is the primary trigger of Cooper pairing. In the proposed research focus will be on the contribution to Cooper pairing due to magnetic fluctuations associated with other ordering wavevector and phonons. For the cuprates focus will be on the exciting recent discovery of incipient checkerboard charge density ordering in (Y,Nd)Ba2Cu3O(6+x) by resonant soft X-ray scattering. Six years ago the PI proposed such charge density wave ordering is responsible for the large pseudogap. In addition, efforts will be made to understand the recent light induced transient superconductivity at room temperature in YBCO. For topological superconductivity the focus will be on non-centrosymmetric systems with large Rashba spin-orbit interaction.

Recent progresses

Iron based Superconductors

Functional renormalization group (FRG) and variational Monte-Carlo calculations were combined to study the pairing mechanism of iron-based superconductors [1]. The main results indicate that, like cuprates, the iron-based superconductors possess many competing instabilities: superconductivity, antiferromagnetism, Fermi surface (Pomeranchuk) instability, and charge density wave instability [2]. These are shown in figure 1.

FRG places the main cause of these instabilities as the high energy magnetic fluctuations at [1,2]. Aside from superconductivity the Fermi surface instability

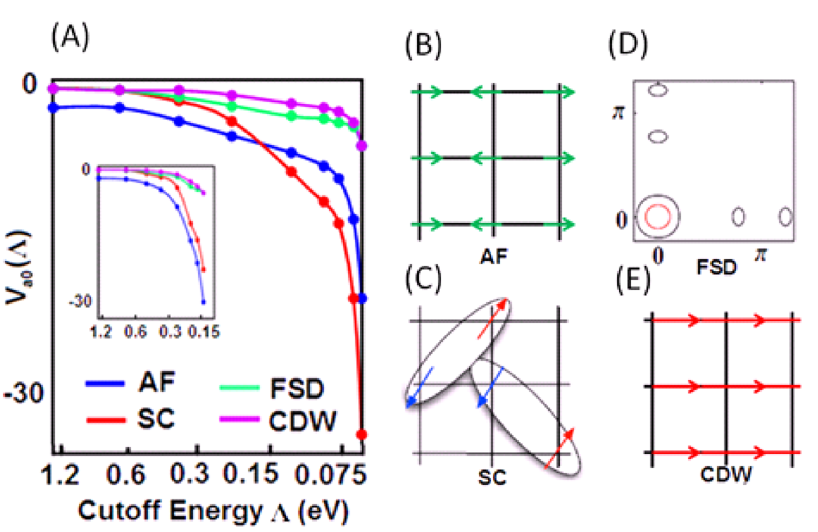

Figure 1 (A) Evolution of the antiferromagnetic (AF), superconducting (SC), Fermi surface distortion (FSD), and charge density wave (CDW) ordering tendencies with the energy cutoff (or the temperature) of the functional renormalization group calculation in a superconducting sample (main panel) and an AF sample (inset). The vertical axis is ameasure of the degree of instability: more negative values imply stronger instability. Schematics of the four competing instabilities are shown. (B) AF order. The green arrows represent the magnetic moments. (C) Superconductivity. The oblong shape denotes a Cooper pair. (D) FS distortion. The circles are all hole-like FSs. (E) Charge density order. The red arrows represent the direction of bond current.

is also interesting. It is found a Fermi surface reshaping which breaks the 90° rotation symmetry of the crystal is a close rival of antiferromagnetism and superconductivity. This band version of “orbital order” couples to antiferromagnetism strongly hence they reinforce each other. This Fermi surface distortion is likely to be closely related to the growing evidences of a non-magnetic ``nematic'' state. The above instabilities are also confirmed by a variational Monte-Carlo calculation [3]. The significance of this is the fact that, unlike FRG, the variational Monte-Carlo is an inherently strong coupling approach; hence the agreement reinforces the reliability of FRG.

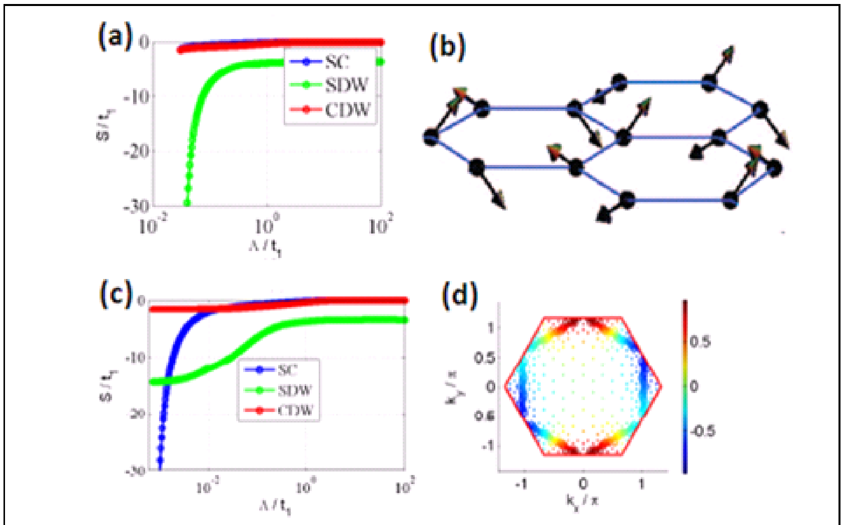

Figure 2. Results for the ¼ electron doped graphene. (a) theFRG flow of the most negative singular values in the SC (blue), SDW (green) and CDW (red) channels. (b) The chiral SDW order on honeycomb lattice. (c) Same as in (a) but for doping level 0.194. (d) The color scale encodes the gap function (real-part) in band basis generated by one of the degenerate pairing modes.

Topological superconductivity Near 1/4 doping in graphene

The electronic instabilities of near 1/4 electron doped graphene was studied using the FRG and variational Monte-Carlo method [3]. At 1/4 doping the ground state is a chiral spin density wave exhibitting quantized anomalous Hall effect. When the doping drops below 1/4, the $d_{x^2-y^2}$+i

d_{xy} Cooper pairing becomes the leading instability. This result suggests near 1/4 electron or hole doping graphene is either a topological insulator or a time-reversal breaking topological superconductor (see figure 2). Hopefully in the recent future material fabrication will allow the quarter doped graphene to be realized.

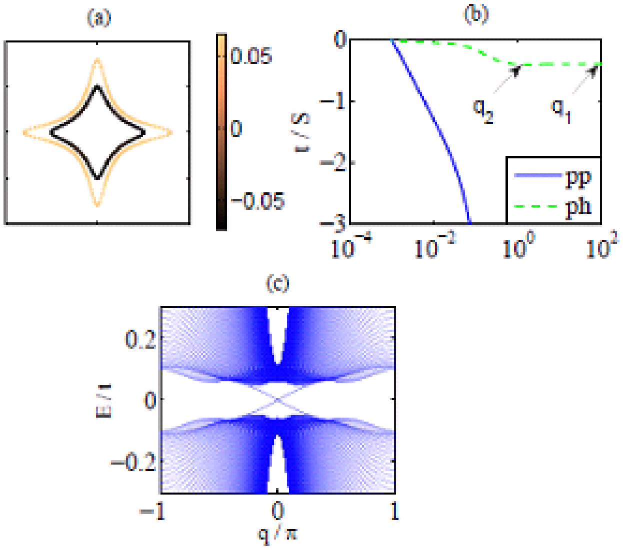

Figure 3 FIG. 2: (a) The spin-split Fermi surfaces of a two dimensional model with Rashba spin-orbit interaction. Different colors indicates the gap function have opposite sign on the two Fermi surfaces. (b) The FRG flow of the inverse of the most negative singular values associated with the superconducting pairing (pp) and spin density wave (ph) instability. Arrows mark the evolution of the spin density wave vector during the FRG flow (q_1 is an antiferromagnetic wavevector and q_2 is the eventually more diverging ferromagnetic wavevector.) (c) The low energy quasiparticle eigen spectrum in a strip (open along one of the principal crystalline axis) as a function of the momentum parallel to the edge.

Time reversal invariant topological superconductivity

The condition favoring time reversal invariant topological superconductivity in systems lacking inversion symmetry was studied using FRG[4]. The results imply the most favorable condition for topological pairing is near ferromagnetic instability. A model calculation demonstrating this is shown in figure 3.

Many non-centrosymmetric superconductors appear near antiferromagnetic phase rather than the ferromagnetic phase. These include $CePt_3Si$, $CeRhSi_3$, $CeIrSi_3$ and $CeCoGe_3$. For these materials topological superconductivity is unlikely. There are also many materials where superconductivity appears near ferromagnetism. Examples include Li_2Pd_3B, URhGe, $HoMo_6Se_8$, ErRh4B_4, Fe under pressure and the interface superconductivity of $LaAlO_3/SrTiO_3$. In these systems topological pairing should more likely to be found.

Planned activities: 2012-2013

The recently discovered high T_c in pressurized $K_yFe_{2-x}Se_2$ [1] and single-unit-cell-thick FeSe on $SrTiO_3$ [2] call for an reexamination of the “conventional wisdom” concerning the Cooper pairing mechanism in iron-based superconductors. According to which the magnetic fluctuation associated with the so-called “stripe”

ordering wavevector, which scatters a pair of electron from the hole pockets to the electron pockets is responsible Cooper pairing [5]. What's found in the new materials is *there is no hole Fermi surfaces.* As a result the stripe magnetic fluctuation cannot even scatter electrons among Fermi surfaces. In an earlier theory we proposed magnetic fluctuations associated with a different wavevector is responsible for the pairing in $K_yFe_{2-x}Se_2$ [6]. If long range order associated with this wavevector is realized, the magnetic pattern will be checkerboard rather than stripe like. In addition, recently we found polar phonons in $SrTiO_3$ can screen the long-range part of the Coulomb interaction and sufficiently raise T_c [7]. We propose to further investigate these possibilities.

Six years ago we proposed a checkerboard charge density wave is responsible for the large pseudogap in the cuprates [4]. Very recently resonant soft x-ray scattering has discovered an incipient checkerboard charge density wave ordering in underdoped $(Y,Nd)Ba_2Cu_3O_{(6+x)}$. This result gives one the hope that the understanding of the origin of pseudogap is within reach. This makes revisiting our proposal for the pseudogap very timely and pressing.

In searching for new topological superconducting materials, focuses will be on non-cenrosymmetric systems with large Rashba coupling. An example is the recently discovered BiTeI with a very interesting Fermi surface topology. We propose to explore the possibility of topological superconductivity in this new material.

Publications

1. **"*A Funtional Renormalization Group Study of the Pairing Symmetry and Pairing Mechanism of the FeAs Based High Temperature Superconductors*", F. Wang, H. Zhai, Y. Ran, A. Vishwanath, and D.-H. Lee, Phys. Rev. Lett. <u>102</u>, 047005 (2009).**

2. **"*The Electron-Pairing Mechanism of Iron-Based Superconductors*", Fa Wang and Dung-Hai Lee, Science <u>332</u>, 200 (2011).**

3. **"The electronic instabilities of the Iron-based superconductors: a variational Monte-Carlo study", F. Yang, H. Zhai, F. Wang and D.-H. Lee, Phys. Rev. B <u>83</u>, 134502 (2011).**

4. **"Functional renormalization group and variational Monte Carlo studies of the electronic instabilities in graphene near 1/4 doping" W. Wang,Y. Xiang, Q. Wang,F. Wang,F. Yang,and D.-H. Lee, Phys. Rev. B <u>85</u>, (2012).**

5. **"Time reversal invariant topological superconductivity in correlated non-centrosymmetric systems", Y. Xiang, W. Wang, Q. Wang, and D.-H. Lee, PRB in press.**

Production and Detection Schemes of Majorana Bound States

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Project Scope

A Majorana fermion is a fermion which is its own antiparticle. It is sometimes described as half a fermion because a conventional creation operator can be written as $f^\dagger = a + ib$, where a and b are Majorana operators satisfying $a = a^\dagger$, $b = b^\dagger$. If a Majorana fermion is localized in space, it is expected to obey non-Abelian statistics, i.e., the exchange of two such localized objects lead to a new state vector in the Hilbert space, as opposed to a sign change or a change in the phase of the wavefunction in the case of fermions or anions. These objects have attracted great interest because they have been proposed as the first step towards fault tolerant topological quantum computers. Regardless of potential applications, it is clear that these objects are of fundamental interest in their own right, but up to now they have not been seen in Nature.

In solid state physics we are familiar with Bogoliubov quasiparticles in superconductors which are superpositions of particles and holes with amplitude u and v, respectively. If $|u| = |v|$ and if the quasiparticles are localized, they will form Majorana bound states (MBS) and will possess all the exotic properties described above. Under suitable circumstances, the MBS arises as a *single* zero energy mode in the solution of the Bogoliubov-deGennes (BdG) equation. (It is important to be single because two MBS will hybridize to form one fermion.) For example, in a spin aligned $p_x + ip_y$ paired superconductor, a single MBS is predicted to exist as a zero mode in the vortex core. Another example is the proposal by Kitaev that MBS exists at the ends of a chain of p wave superconductors. Unfortunately, $p_x + ip_y$ superconductors are not common in Nature. The goal of this project is to study practical schemes to produce MBS in the laboratory and to verify their existence.

Recent Progress

While many schemes have been put forward, we have focused our attention on making wires using materials with Rashba spin-orbit coupling and proximity coupled to a conventional superconductor. In the presence of a magnetic field, $p_x + ip_y$ pairing is induced and MBS are predicted to exist at the end of the wires. This proposal was originally made for semiconductor nanowires by Sau *et al* and Oreg *et al.* We realized that the nanowire scheme which was originally proposed for the strictly one dimensional situation, i.e., restricted to the lowest transverse sub-band, is in fact readily generalized to multi sub-bands.[R1] The only requirement is that the wire width has to be smaller or comparable to the superconducting coherence length, which is typically thousands of angstrom. We found that MBS alternately appears and disappears as each sub-band becomes occupied as a function of chemical potential. Furthermore, this even-odd picture is highly robust, and remains even if the transverse width is randomized to the extent that the notion of transverse sub-band is no longer meaningful.[R2] This opens up the quasi-one dimensional geometry to a much broader class of materials than the nanowires.

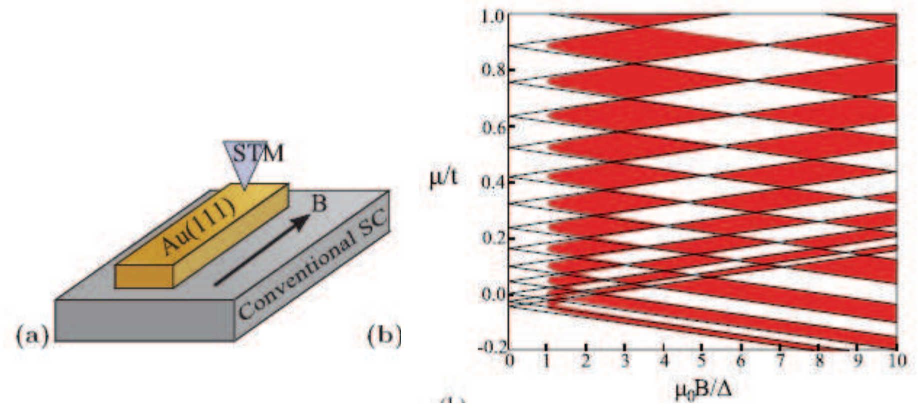

FIG. 1: (a) Proposed geometry to create Majorana bound states (MBS). Superconductivity is induced in the Au film and in the surface states on the top Au (111) surface by proximity effect. Upon application of a magnetic field parallel to the wire, MBS appears at the wire ends. The requirement is simply that the film width is smaller than the superconductivity coherence length. (b) Phase diagram for the topological regime (red color) which supports MBS as a function of chemical potential μ/t where t is the hopping parameter and parallel magnetic field B/Δ where Δ is the induced pairing gap. For example, at a fixed chemical potential, MBS appears and disappears as a function of B. A first step to detect MBS is by tunneling to observe a zero bias peak as shown in (a).

We went on to study the effect of disorder on the various schemes to produce MBS.[R3] We found that the Fu-Kane scheme using topological insulators is immune to disorder, because that system preserves time reversal symmetry, and a form of Anderson theorem holds. In contrast, the scheme using Rashba and magnetic field breaks time reversal, and impurity is pair breaking. The strength of the pair breaking depends crucially on the relative size of Rashba energy and the Zeeman splitting due to the magnetic field. If this ratio is small, the induced superconductivity is hyper-sensitive to disorder, i.e., the induced gap closes even if the mean free path is much greater than the coherence length. Unfortunately, the semiconductor nanowire is in this regime. Due to the relatively large cross-section of the nanowire, the Rashba energy which comes from the surface effect is very small, estimated to be 50 μV or 0.5 K. This means that all other parameters need to be optimized to see the MBS, and even then very low temperature of order mK will be needed.

We then turn to look for other systems where the Rashba energy scale is much larger.[R4] A promising example we found is the well studied surface state on the (111) surface of Au and Ag. The Rashba splitting of the parabolic surface state in Au was measured by ARPES to be of order 20 meV, several hundred times larger than that of the semiconducting nanowires. Furthermore, we found that the even-odd appearance of MBS persists up to many sub-bands. (See Fig. 1b.) We propose a simple structure where a thin film of Au of width one to two thousand angstrom is deposited on a conventional superconductor (Fig. 1a.). When a magnetic field is applied parallel to the length of the film, MBS are predicted to appear and disappear at the ends of the long film as a function of the magnetic field strength. We are currently collaborating with Jagadeesh Moodera's group at the Magnet Lab at MIT to develop this idea experimentally.

Besides the creation of MBS, an important question is how to detect them once they are created. The first step is likely to be the observation of a zero bias peak in the tunneling spectrum. Indeed, a recent experiment reporting the signature of MBS is based on the observation of the zero bias peak under certain conditions. However the predicted signature that the peak conductance should reach $2e^2/h$ [R5] has not yet been verified. The next key experiment will likely be the verification of the so-called 4π Josephson effect, first pointed out by Kitaev. Due to the existence of a zero energy quasiparticle, there should be a Josephson current which depends on the pair phase ϕ as $J_0 \sin(\phi/2)$, in addition to the conventional Josephson current $J \sin \phi$. We have studied the robustness of this prediction in the presence of the so-called mini-gap states located at the ends of the wire.[R6] We have found from our studies of multi-channel wires that with the filling of every two sub-bands, a new low energy quasiparticle appears.[R2] Thus the MBS in generally accompanied by in-gap fermion states which are called mini-gap states. We have found numerically that the level spacing scales as $\frac{\Delta}{\sqrt{N}}$ where N is the number of filled sub-bands. The presence of these mini-gap states is a cause of concern for the robustness of the 4π Josephson effect. In pub. (R6) we showed in a general model where mini-gap states exist on both sides of the tunnel junction and are coupled to the MBS with arbitrary strength, the 4π Josephson effect survives. However, its amplitude is suppressed at finite temperatures by thermal excitations to the mini-gap states and we predict that at finite temperatures, the 4π Josephson effect is exponentially suppressed once the temperature exceeds the mini-gap spacing. This makes the 4π Josephson junction difficult, but not impossible to detect.

Planned Activities

Recent reports by the Delft group and several others reporting a "signature" of Majorana bound states have generated a great deal of excitement in the community. The main observational evidence is the appearance of a zero bias peak which appears in certain ranges of gauge voltage and applied magnetic field parallel to the nanowires. We are suspicious of this claim because based on our previous work, we think that the Rashba coupling in the InSb wires are too weak and the disorder too strong to support MBS. We have been carrying out simulations of the quantum wires using realistic parameters and we are finding that zero bias peaks are fairly common features. They may occur because the disorder is pair breaking in the presence of a magnetic field and can induce low energy bound states in the gap. We will continue this study and try to gain more understanding of this phenomenon analytically.

I also plan to explore realization of MBS beyond electronic systems. An interesting possibility is to use cold atoms. It has been demonstrated that artificial gauge magnetic field and spin-orbit coupling can be generated using a two photon Raman transition. Recently, my colleague Martin Zwierlein and collaborators have applied this to a degenerate Fermi gas of Li atoms and observed the Rashba split bands by a special form of spectroscopy. Their Hamiltonian corresponds to an equal sum of Rashba and Dresselhaus terms. I have been discussing with them the possibility of creating quasi-one dimensional confinement of the Li gas and creating MBS at chain ends. An interesting twist is that the gas is generally confined by a smooth parabolic potential along the chain. As a result, one expects transitions between segments where even and odd number of transverse sub-bands are occupied. The MBS will then live at the junction of these segments. We plan to do some calculation to optimize the length L of the sub-band segments which can be controlled by tuning the parabolic potential. If the segments are too long the MBS will be accompanied by many long energy sub-gap states whose energy spacing will scale as $1/L$. If the segments are too short, the MBS will tunnel and annihilate each other. It will be useful to estimate what the optimal segment length is. The advantage of the cold atom system is that the Rashba energy can be controlled and disorder is less of an issue. As a first step, the MBS can be observed as zero energy states by a special form of spectroscopy which amounts to a form of photoemission spectroscopy. This is not a conclusive demonstration of MBS and I plan to explore ways to find more definitive signatures of MBS.

Publications(2009–2012)

R1 Andrew C. Potter and Patrick A. Lee, "Multichannel Generalization of Kitaev's Majorana End States and a Practical Route to Realize Them in Thin Films," Phys. Rev. Lett. **105**, 227003 (2010).

R2 Andrew C. Potter and Patrick A. Lee, "Majorana End States in Multi-band Microstructures with Rashba Spin-orbit Coupling," Phys. Rev. B **83**, 094525 (2011).

R3 Andrew C. Potter and Patrick A. Lee, "Engineering a $p+ip$ Superconductor: Comparison of Topological Insulator and Rashba Spin-orbit Coupled Materials," Phys. Rev. B **83**, 184520 (2011); Erratum B **84**, 159906 (2011).

R4 Andrew C. Potter and Patrick A. Lee, "Topological Superconductivity and Majorana Fermions in Metallic Surface States," Phys. Rev. B **85**, 094516 (2012).

R5 K.T. Law, P.A. Lee and T.K. Ng, "Majorana Fermion Induced Resonant Andreev Reflection," Phys. Rev. Lett. **103**, 237001 (2009).

R6 K.T Law and Patrick A. Lee, "Robustness of Majorana Fermion Induced Fractional Josephson Effect," Phys. Rev. B **84**, 081304(R) (2011).

R7 Karen Michaeli, Andrew C. Potter and Patrick A. Lee, "Superconductivity and Ferromagnetism in Oxide Interface Structures: Possibility of Finite Momentum Pairing," Phys. Rev. Lett. **108**,117003 (2012).

R8 Wing-Ho Ko and Patrick A. Lee, "Magnetism and Mott Transition: A Slave-rotor Study," Phys. Rev. B **83**, 134515 (2011).

R9 Wing-Ho Ko and Patrick A. Lee, "Proposal for Detecting Spin-Chirality Terms in Mott Insulators via Inelastic X-ray Scattering," Phys. Rev. B **84**, 125102 (2011).

R10 P. Ribeiro and Patrick A. Lee, "Magnetic Impurity in a U(1)-Spin Liquid with a Spinon Fermi-Surface," Phys. Rev. B **83**, 235119 (2011).

R11 Saeed Saremi, Patrick A. Lee, and T. Senthil, "Unifying Kondo Coherence and Antiferromagnetic Ordering in the Honeycomb Lattice," Phys. Rev. B **83**, 125120 (2011).

Studies of the Marginally Jammed Solid

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Project Scope:

A collection of idealized spheres can jam into a disordered solid when it is compressed at zero temperature and zero shear stress. Our work has shown that this jamming transition is singular, in that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. In the manner of an ordinary critical point, this singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our project addresses the following questions: (1) How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important? Our preliminary results show that the most anharmonic vibrational normal modes are at low-frequency where they are quasi-localized. These modes are exquisitely sensitive to stress or temperature because they have low energy barriers to particle rearrangements. Can these modes be used to predict where local failure might occur? Can we predict from the harmonic spectrum or the anharmonic response how close a system is to the edge of failure? At the jamming transition, anharmonic effects diverge. How do they evolve as the system is compressed above that transition? (2) What is the effect of temperature? Could the anharmonic quasi-localized modes herald the existence of two-level systems or dynamical heterogeneities? How is the jamming transition related to the glass transition? (3) How do generalizations of the model, such as non-spherical particle shapes, attractive interactions and three-body interactions affect the picture developed for idealized spheres?

Recent progress:

Heat transport in model jammed solids:

We calculated numerically the normal modes of vibrations in three-dimensional jammed packings of soft spheres as a function of the packing fraction and obtain the energy diffusivity, a spectral measure of transport that controls sound propagation and thermal conductivity. The crossover frequency between weak and strong phonon scattering is controlled by the coordination and shifts to zero as the system is decompressed toward the critical packing fraction at which rigidity is lost. We present a scaling analysis that relates the packing fraction dependence of the crossover frequency to the anomalous scaling of the shear modulus with compression. Below the crossover, the diffusivity displays a power-law divergence with inverse frequency consistent with Rayleigh law, which suggests that the vibrational modes are primarily transverse waves, weakly scattered by disorder. Above it, a large number of modes appear whose diffusivity plateaus at a nearly constant value before dropping to zero above the localization frequency. The thermal conductivity of a marginally jammed solid just above the rigidity threshold was calculated and related to the one measured experimentally at room temperature for most glasses.

Anharmonicity and quasi-localization of the excess low-frequency vibrations in jammed solids:

A starting point for understanding any solid is a calculation of its harmonic vibrational excitations. However, many important properties require an understanding of anharmonic effects as well. For example, in a crystal, heat transport and thermal expansion are governed by anharmonic coupling of the modes. Anharmonic effects become even more essential when one considers how a solid, be it crystalline or amorphous, disintegrates and loses rigidity. Such behavior requires the system to depart from the harmonic regime as it continually moves over potential-energy barriers to explore different configurations. We studied harmonic and anharmonic properties of the vibrational modes in 3-dimensional jammed packings of frictionless spheres interacting via repulsive, finite-range potentials. A crossover frequency is apparent in the density of states, the diffusivity and the participation ratio of the normal modes of vibration. At this frequency, which shifts to zero at the jamming threshold, the vibrational modes have a very small participation ratio implying that the modes are quasi-localized. The lowest-frequency modes are the most anharmonic, with the strongest response to pressure and the lowest-energy barriers to mechanical failure.

Mapping the slowdown of the dynamics of soft spheres onto hard sphere behavior:

Relaxation in a liquid proceeds by numerous pathways that each depend on temperature and pressure. It has remained an enduring challenge to delineate different modes of relaxation and to bring them into a common framework where they can be treated on a common footing. To reach such a goal, it is necessary to understand what combinations of variables control liquid dynamics in different regimes of temperature and pressure. We have shown that dynamics of soft repulsive spheres near their glass transition can be described in terms of the dynamics of hard spheres by introducing an effective hard sphere diameter that is determined via the Andersen-Weeks-Chandler approximation. We have shown that this approximation, which is known to describe static properties of liquids remarkably well, also describes a dynamical quantity, the relaxation time. These results indicate that the dynamics of soft spheres depend on an effective free volume in a universal way.

Soft spots in disordered packings

Like liquids, solids can flow under applied shear stresses. Crystalline solids flow via rare rearrangements controlled by a population of lattice defects, namely dislocations. In disordered solids, rearrangements tend to be localized, but despite several decades of effort, there has been no obvious way to identify defects that might control them. Can these rare localized rearrangements occur anywhere, as in a liquid, or do glasses possess a population of “soft spots,” analogous to dislocations in a crystalline solid, which are structurally distinct and susceptible to rearrangement? We used quasilocalized low-frequency modes, previously identified (see first paragraph above) to have unusually low energy barriers to rearrangements, to identify a population of soft spots. We showed that rearrangements occur at soft spots, that the soft spot population evolves slowly compared to the time between rearrangements, and that they are structurally different from the rest of the system, suggesting that soft spots are good candidates for the elementary defects that control flow in disordered packings.

Future plans:

We are currently studying the nature of rearrangements under mechanical load, focusing on how they depend on the conditions under which load is applied and their connection to the low-frequency density of vibrational states. This will allow a better understanding of plastic flow in disorder solids as well as a direct comparison with the low-temperature properties of glasses where there is also an excess number of low-energy excitations.

We wish to continue our study of anharmonic effects near the jamming threshold. In particular we are interested in see how the stability of the amorphous solid is influenced by anharmonicity.

We are interested in seeing how plane waves affect the normal modes of vibration in a jammed system. This will be achieved by looking at the entire system as a crystal with a very large unit cell. The plane waves will then coexist with quasilocalized modes in the same frequency range.

We will continue to simulate the affect of small temperatures and small applied shear stresses on a model system that is close to the transition at Point J. This has to do with the shear modulus mentioned above but we also will continue to study how the relaxation time varies with temperature and pressure near the onset of jamming. We are interested in studying the affect of shear stress on the first peak in g(r) to see if it behaves in the same way as it does due to an increase in the pressure. In the case of pressure, this was observed in experiment as well as simulation. We would like to see if the effect of shear can also be seen in experiment.

We will also continue to study soft spots identified from low-frequency quasilocalized modes, to determine how robust they are to thermal fluctuations.

A list of papers resulting from DOE sponsored research since 2009:

1. “Energy transport in jammed sphere packings,” N. Xu, V. Vitelli, M. Wyart, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. **102**, 038001 (2009).
2. “Normal modes in model jammed systems in three dimensions,” L. E. Silbert, A. J. Liu and S. R. Nagel, Phys. Rev. E **79**, 021308 (2009).
3. “Thermal vestige of the zero-temperature jamming transition, ”Z. Zhang, N. Xu, D. T. N. Chen, P. Yunker, A. M. Alsayed, K. B. Aptowicz, P. Habdas, A. J. Liu, S. R. Nagel and A. G. Yodh, Nature **459**, 230 (2009).
4. “Excitations of ellipsoid packings near jamming,” Z. Zeravcic, N. Xu, A. J. Liu, S. R. Nagel and W. van Saarloos, Europhys. Lett. **87**, 26001 (2009).

5. “Elasticity and response in nearly isostatic periodic lattices,” A. Souslov, A. J. Liu and T. C. Lubensky, Phys. Rev. Lett. **103**, 205503 (2009).
6. “Equivalence of glass transition and colloidal glass transition in the hard-sphere limit,” N. Xu, T. K. Haxton, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. **103**, 245701 (2009).
7. “Heat transport in model jammed solids,” V. Vitelli, N. Xu, M. Wyart, A. J. Liu, S. R. Nagel, *Phys. Rev. E* **81**, 021301 1-14 (2010).
8. “Anharmonicity and quasi-localization of the excess low-frequency vibrations in jammed solids,” N. Xu, V. Vitelli, A. J. Liu, and S. R. Nagel, *Europhys. Lett.* **90**, 56001 1-6 (2010).

9. “The jamming transition and the marginally jammed solid,” A. J. Liu and S. R. Nagel, *Annual Reviews of Cond. Mat. Phys.* **1**, 347-369 (2010).
10. “Granular and Jammed Materials,” A. J. Liu and S. R. Nagel *Soft Matter*, **6**, 2869-2870 (2010); editorial for focus issue on Jamming. Guest editors: A. J. Liu and S. R. Nagel.
11. “The jamming scenario — an introduction and outlook,” A. J. Liu, S. R. Nagel, W. van Saarloos, and M. Wyart in *Dynamic heterogeneities in glasses, colloids, and granular media*, edited by L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, W. van Saarloos, accepted (Oxford University Press, 2011).
12. “Kinetic heterogeneities at dynamical crossovers,” T. K. Haxton and A. J. Liu, Europhys. Lett. **90**, 66004 (2010).
13. “Low-frequency vibrations of soft colloidal glasses,” K. Chen, W. G. Ellenbroek, Z. Zhang, D. T. N. Chen, P. J. Yunker, S. Henkes, C. Brito, O. Dauchot, W. van Saarloos, A. J. Liu and A. G. Yodh, Phys. Rev. Lett. **105**, 025501 (2010).
14. “Jamming mechanisms and density dependence in a kinetically-constrained model,” Y. Shokef and A. J. Liu, *Europhys. Lett.* **90**, 26005 (2010).
15. “Rotational and translational phonon modes in glasses composed of ellipsoidal particles,” by P. J. Yunker, K. Chen, Z. Zhang, W. G. Ellenbroek, A. J. Liu and A. G. Yodh, *Phys. Rev. E* **83**, 011403 (2011).
16. “Universal jamming phase diagram in the hard-sphere limit,” T. K. Haxton, M. Schmiedeberg and A. J. Liu, Phys. Rev. E **83**, 031503 (2011).
17. “Mapping the slowdown of the dynamics of soft spheres onto hard sphere behavior,” M. Schmiedeberg, T. K. Haxton, S. R. Nagel, and A. J. Liu, *Europhys. Letts.* **96**, 36010 (2011).
18. “Direct determination of the size of basins of attraction of jammed solids,” N. Xu, D. Frenkel and A. J. Liu, Phys. Rev. Lett. **106**, 245502 (2011).
19. “Measurement of correlations between low-frequency vibrational modes and particle rearrangements in quasi-two-dimensional colloidal glasses,” K. Chen, M. L. Manning, P. J. Yunker, W. G. Ellenbroek, Z. Zhang, A. J. Liu and A. G. Yodh, Phys. Rev. Lett. **107**, 108301 (2011).
20. “Vibrational modes identify soft spots in a sheared disordered packing,” M. L. Manning and A. J. Liu, Phys. Rev. Lett. **107**, 108302 (2011).
21. “Mapping the glassy dynamics of soft spheres onto hard-sphere behavior,” M. Schmiedeberg, T. K. Haxton, S. R. Nagel and A. J. Liu, Europhys. Lett. **96**, 36010 (2011).
22. “Temperature-pressure scaling for air-fluidized grains near jamming,” L. J. Daniels, T K. Haxton, N. Xu, A. J. Liu and D. J. Durian, Phys. Rev. Lett., **108**, 138001 (2012).

23. “Finite-size scaling at the jamming transition,” C. P. Goodrich, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. (in press, 2012).

Theory of Materials Program

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Project Scope

The goal of this program is to understand and compute material properties and behaviors, covering a range of systems that include complex materials, surfaces and interfaces, nanostructures, superconductors, and strongly correlated electron systems. Novel materials and new concepts are explored. A variety of theoretical techniques is employed, ranging from first-principles electronic structure methods and many-body perturbation theory approaches to new conceptual and computational frameworks suitable for complex materials/nanostructures and strongly interacting systems. One emphasis is to investigate realistic systems employing microscopic first-principles approaches, including many-electron effects. Model systems are also examined. Close collaboration with experimentalists is maintained. Another emphasis is to push theory beyond the Landau paradigm toward a framework suitable for very strongly correlated systems. New phenomena, new phases, and new organization principles may be discovered. Equally important is the development of computational methods suitable for increasingly complex materials and strongly correlated materials.

Recent Progress

Activities since 2009 covered several areas including: topological insulators; many-electron effects in graphene structures; transport through single-molecule junctions; superconductivity; electron-phonon interactions; photovoltaics; quantum spin Hall systems, strongly correlated electron systems; new theoretical and computational methods. Since Neaton and Wang have been part of this program for only past weeks, we describe here publications and progress made before their joining. Since 2009, seventy (70) papers were published by the program which included 15 *Phys. Rev. Letters,* 4 *Nano Letters,* 1 *Nature Physics,* 1 *Nature Nanotech., 1 PNAS,* 17 *Phys. Rev. B,* etc. Some selected results are:

- *Ab initio* studies of topological insulators, leading to accurate surface-state spin texture
- Explored new phases of matter (e.g., under pressure or magnetic field) and cold atoms in optical lattices
- *Ab initio* theory of quasiparticles in graphene systems, explained ARPES and STS measurements
- Predicted “*artificial* graphene” from patterned 2D electron gas (now verified by experiment)
- Discovered a transformation mapping graphene in a 1D magnetic field to that in an electric field
- Predicted strong excitonic effects in graphene and bilayer graphene (now confirmed by experiment)
- Discovered the novel phenomenon of *anti-screening* in carbon nanotubes and other 1D systems
- Theory of edge states and structure and dynamics of atoms on graphene edges, explaining experiments
- Improved methods for *ab initio* calculations of ground- and excited-state properties of materials
- Development of public domain codes: the EPW code for electron-phonon coupling and the BerkeleyGW code for excited-state (spectroscopic) properties
- *Ab initio* theory of charge/thermal transport through single-molecule junctions, explaining experiments
- Showed localized metal-induced gap states as origin of noise in SQUIDs and superconducting qubits
- Electron-phonon coupling and Eliashberg theory of superconductivity in doped and layered systems
- *Ab initio* study of electron-phonon renormalization of properties of solids, including iron pnictides

- Theory of behaviors of Dirac fermions of topological insulators in curved 2D spaces
- Studied the effects of interaction on quantum spin Hall insulators
- Exploration of optical properties of materials for photovoltaics

Future Plans

Planned activities focus in these areas: superconductivity and superconductor/insulator interfaces; excited states of novel materials, interfaces, and nanostructures; methodology developments; new phases of matter; and transport through molecular and nanostructured junctions. Some selected projects include:

A new class of states, "symmetry protected topological states" (SPT states), will be explored, in particular the nature of phase transition between topologically trivial and non-trivial phase, and the relation between free Fermion SPT states and bosonic SPT ones. We will also study the magnetic properties of iron-based superconductors for possible connection between magnetism and superconductivity, and investigate the nature and possible control of local magnetic states at superconductor-insulator interfaces to eliminate a critical noise source in such systems.

Excited-state properties (quasiparticle and optical spectra) of novel materials (e.g., topological insulators), defects (e.g., NV^- centers), nanostructures (sheets, tubes, ribbons), and systems relevant to energy research will be investigated. We will continue development of theories and algorithms for *ab initio* excited-state calculations, in particular, development of methods appropriate for open-shell systems and those going beyond the standard GW approximation (e.g., the cumulant expansion technique) for accurate satellite structures in valence and core spectra. The effects of matrix elements on the photoelectron spectra from Dirac fermions will be investigated and calculated.

Calculations of electronic and transport properties of molecular junctions and well-defined inorganic-organic interfaces will be performed, as well as development of viable frameworks for predicting current-voltage (I-V) characteristics of open systems at finite bias voltage. Interface geometries, level alignment, currents, current-induced forces, and absorption properties for experimentally-relevant junctions will be explored.

Publications from 2009-present

1. W. Luo, M.L. Cohen, J.W. Morris, Jr., "On the possibility of cleavage in Nb," Phil. Mag. Lett. **89**, 23 (2009).
2. H.J. Choi, S.G. Louie, and M.L. Cohen, "Anisotropic Eliashberg Theory for Superconductivity in Compressed and Doped MgB_2," Phys. Rev B **79**, 094518 (2009).
3. J. Noffsinger, F. Giustino, S.G. Louie, and M.L. Cohen," Origin of Superconductivity in Boron-Doped Silicon Carbide from First Principles," Phys. Rev B **79**, 104511 (2009).
4. S.R. Leslie, J. Guzman, M. Vengalattore, J.D. Sau, M.L. Cohen, and D.M. Stamper-Kurn, "Amplification of fluctuations in a spinor Bose-Einstein condensate," Phys. Rev. A **79**, 043631 (2009).
5. J. Deslippe, M. Dipoppa, D. Prendergast, M.V.O. Moutinho, R.B. Capaz, and S.G. Louie, "Electron-Hole Interaction in Carbon Nanotubes: Novel Screening and Exciton Excitation Spectra," Nano Lett. **9**, 1330 (2009).
6. J. Noffsinger, S.G. Louie, F. Giustino, and M.L. Cohen, "Role of Fluorine in the Iron Pnictides: Phonon Softening and Effective Hole Doping," Phys. Rev. Lett. **102**, 147003 (2009).
7. C.D. Spataru, M.S. Hybertsen, S.G. Louie, and A.J. Millis, "GW Approach to Anderson Model Out of Equilibrium: Coulomb Blockade and False Hysteresis in the I-V Characteristics," Phys. Rev. B **79**, 155110 (2009).
8. S.Y. Quek, M. Kamenetska, M.L. Steigerwald, H.J. Choi, S.G. Louie, M.S. Hybertsen, J.B. Neaton, and L. Venkataraman, "Mechanically Controlled Binary Conductance Switching of a Single-Molecule Junction," Nature Nanotechnology **4**, 230 (2009).
9. G.M. Zhang, Y.H. Su, Z.Y. Lu, Z.Y. Weng, D.H. Lee, and T. Xiang, "Universal linear-temperature dependence of static magnetic susceptibility in iron pnictides," Europhys. Lett. **86**, 37006 (2009).
10. C.-H. Park and S.G. Louie, "Making Massless Dirac Fermions from a Patterned Two-Dimensional Electron Gas," Nano Lett. **9**, 1793 (2009).
11. C.-H. Park, Y.-W. Son, L. Yang, M.L. Cohen, and S.G. Louie, "Landau Levels and Quantum Hall Effect in Graphene Superlattices," Phys. Rev. Lett. **103**, 046808 (2009).
12. R. Vijay, J.D. Sau, M.L. Cohen, and I. Siddiqi, "Optimizing anharmonicity in nanoscale weak link Josephson junction oscillators," Phys. Rev. Lett. **103**, 087003 (2009).
13. J.D. Sau, S.R. Leslie, D.M. Stamper-Kurn, and M.L. Cohen, "Theory of domain formation in inhomogeneous ferromagnetic dipolar condensates within the truncated Wigner approximation," Phys. Rev. A **80**, 023622 (2009).
14. H.J. Choi, S.G. Louie, and M.L. Cohen, "Prediction of Superconducting Properties of CaB_2 Using Anisotropic Eliashberg Theory," Phys. Rev. B **80**, 064503 (2009).

15. L. Yang, J. Deslippe, C.-H. Park, M.L. Cohen, and S.G. Louie, “Excitonic effects on the optical response of graphene and bilayer graphene” Physical Review Lett. **103**,186802 (2009).
16. K. Nomura, S. Ryu, and D.-H. Lee, "Field-Induced Kosterlitz-Thouless Transition in the N=0 Landau Level of Graphene," Phys. Rev. Lett. **103**, 216801 (2009).
17. D.-H. Lee, "Surface States of Topological Insulators: The Dirac Fermion in Curved Two-Dimensional Spaces," Phys. Rev. Lett. **103**,196804 (2009).
18. S.K. Choi, D.-H. Lee, S.G. Louie, and J. Clarke, "Localization of Metal-Induced Gap States at the Metal-Insulator Interface: Origin of Flux Noise in SQUIDs and Superconducting Qubits," Phys. Rev. Lett. **103**, 197001 (2009).
19. S.Y. Quek, H.J. Choi, S.G. Louie, and J.B. Neaton, "Length Dependence of Conductance in Aromatic Single-Molecule Junctions," Nano Lett. **9**, 3949 (2009).
20. C.-H. Park, F. Giustino, C.D. Spataru, M.L. Cohen, and S.G. Louie, “Angle-resolved photoemission spectra of graphene from first-principles,” Nano Lett. **9**, 4234 (2009).
21. D. Prendergast and S. G. Louie, “Bloch-state-based interpolation: An efficient generalization of the Shirley approach to interpolating electronic structure, Phys. Rev. B **80**, 235126 (2009).
22. J. Noffsinger and M. L. Cohen, “Electronic and structural properties of ununquadium from first principles,” Phys. Rev. B **81**, 073110 (2010).
23. P. Ghaemi, S. Ryu and D.-H. Lee, "The quantum valley Hall effect in proximity-induced superconducting graphene: an experimental window for deconfined quantum criticality," Phys. Rev. B **81**, 081403 (2010).
24. J. L. Janssen, M. Côté, S.G. Louie, and M.L. Cohen, “Electron-Phonon Coupling In C_{60} Using Hybrid Functionals,” Phys. Rev. B **81**, 073106 (2010).
25. F. Giustino, M.L. Cohen, and S.G. Louie, “GW Method with the Self-Consistent Sternheimer Equation,” Phys. Rev. B **81**, 115105 (2010).
26. B.D. Malone, S.G. Louie, and M.L. Cohen, “Electronic and Optical Properties of Body-Centered Tetragonal Si and Ge,” Phys. Rev. B **81**, 115201 (2010).
27. L.Z. Tan, C.-H. Park, and S.G. Louie, “Graphene Dirac Fermions in One-dimensional Inhomogeneous Field Profiles: Transforming Magnetic to Electric Field,” Phys. Rev. B **81**, 195426 (2010).
28. M. Kamenetska, S.Y. Quek, A.C. Whalley, M.L. Steigerwald, H.J. Choi, S.G. Louie, C. Nuckolls, M.S. Hybertsen, J.B. Neaton, and L. Venkataraman, “Conductance and Geometry of Pyridine-linked Single-molecule Junctions,” J. Am. Chem. Soc. **132**, 6817 (2010).
29. J. Noffsinger and M.L. Cohen, “First-principles calculation of the electron-phonon coupling in ultrathin Pb superconductors: Suppression of the transition temperature by surface phonons,” Phys. Rev. B **81**, 214519 (2010).
30. J.D. Sau, S.R. Leslie, M.L. Cohen, and D.M. Stamper-Kurn, “Spin squeezing of high-spin, spatially extended quantum fields,” New J. of Physics **12**, 085011 (2010).
31. G.-S. Do, J. Kim, S.-H. Jhi, C.-H. Park, S.G. Louie, and M.L. Cohen, “Ab Initio Calculations of Pressure-induced Structural Phase Transitions of GeTe,” Phys. Rev. B **82**, 054121 (2010).
32. M.L. Cohen, “The physics of energy bands,” in *Giuseppe Franco Bassani: Man and Scientist*, eds. G. Grosso and G. La Rocca (Società Italiana di Fisica, Bologna, Italy, 2010) p. 263.
33. M.L. Cohen, “Emergence in condensed matter physics,” in *Visions of Discovery: New Light on Physics, Cosmology, and Consciousness*,” eds. R.Y. Chiao, M.L. Cohen, A.J. Leggett, W.D. Phillips, and C.L. Harper, Jr. (Cambridge University Press, Cambridge, 2010) p. 496.
34. B.-C. Shih, Y. Xue, P. Zhang, M.L. Cohen, and S.G. Louie, “Quasiparticle band gap of ZnO: High accuracy from the conventional G^0W^0 approach,” Phys. Rev. Lett. **105**, 146401 (2010).
35. M.L. Cohen, “Predicting and explaining T_c and other properties of BCS superconductors,” Modern Phys. Lett. B **24**, 2755 (2010). Also in *Bardeen, Cooper, and Schrieffer: 50 Years*, eds. L.N. Cooper and D. Feldman (World Scientific, Singapore, 2010).
36. T. Bazhirov, J. Noffsinger, and M.L. Cohen, “Superconductivity and electron-phonon coupling in lithium at high pressures,” Phys. Rev. B **82**, 184509 (2010).
37. H. Yao and D.-H. Lee, "Topological insulators and topological nonlinear sigma models," Phys. Rev. B **82**, 245117 (2010).
38. J. Noffsinger, F. Giustino, B.D. Malone, C.-H. Park, S.G. Louie, and M.L. Cohen, “EPW: A program for calculating the electron-phonon coupling using maximally localized Wannier functions,” Comput. Phys. Comm. **181**, 2140 (2010).
39. F. Giustino, S.G. Louie, and M.L. Cohen, “Electron-phonon renormalization of the direct band gap of diamond,” Phys. Rev. Lett. **105**, 265501 (2010).
40. E. Kioupakis, M.L. Tiago, and S.G. Louie, “Quasiparticle Electronic Structure of Bismuth Telluride in the *GW* Approximation,” Phys. Rev. B **82**, 245203 (2010).
41. O.V. Yazyev, J.E. Moore, and S.G. Louie, "Spin Polarization and Transport of Surface States in the Topological Insulators Bi_2Se_3 and Bi_2Te_3 from First Principles," Phys. Rev. Lett. **105**, 266806 (2010).
42. M.L. Cohen, “Electron-phonon induced pairing and its limits for superconducting systems,” Physica E **43**, 657 (2011).

43. D. Zheng, G.-M. Zhang, T. Xiang, and D.-H. Lee, "Continuous quantum phase transition between two topologically distinct valence bond solid states associated with the same spin value," Phys. Rev. B **83**, 014409 (2011).
44. S.Y. Quek, H. J. Choi, S. G. Louie, and J. B. Neaton, "Thermopower of Amine–Gold-linked Aromatic Molecular Junctions from First Principles," ACS Nano **5**, 551 (2011).
45. J. Noffsinger and M.L. Cohen, "Superconductivity in monolayer Pb on Si (111) from first principles," Solid State Comm. **151**, 421 (2011).
46. D.-H. Lee, G.-M. Zhang and T. Xiang, "Topological term in the non-linear σ model of the SO(5) spin chains," Nucl. Phys. B **846**, 607 (2011).
47. T. Koretsune, S. Saito, and M.L. Cohen, "One-dimensional alkali-doped C_{60} chains encapsulated in BN nanotubes," Phys. Rev. B **83**, 193406 (2011).
48. M.L. Cohen and B.D. Malone, "Wave-function engineering: Other phases of Si for photovoltaic applications," J. Appl. Phys. **109**, 102402 (2011).
49. T. Bazhirov, J. Noffsinger, and M.L. Cohen, "Electron-phonon coupling in bcc lithium," Phys. Rev. B **84**, 125122 (2011).
50. H. Oh, H.J. Choi, S.G. Louie, and M.L. Cohen, "Fermi Surfaces and Quantum Oscillations in the Underdoped High-T_c Superconductors $YBa_2Cu_3O_{6.5}$ and $YBa_2Cu_4O_8$," Phys. Rev. B **84**, 014518(2011).
51. D.A. Siegel, C.-H. Park, C. Hwang, J. Deslippe, A.V. Federov, S.G. Louie, and A. Lanzara, "Many-body Interactions in Quasi-freestanding Graphene," Proc. Natl. Acad. Sci. U.S.A. **108** 11365 (2011).
52. H. Yao and D.-H. Lee, "Fermionic Magnons, Non-Abelian Spinons, and the Spin Quantum Hall Effect from an Exactly Solvable Spin-1/2 Kitaev Model with SU(2) Symmetry," Phys. Rev. Lett.**107**, 087205, (2011).
53. C. Tao, L. Jiao, O.V. Yazyev, Y.-C. Chen, J. Feng, X. Zhang, R.B. Capaz, J.M. Tour, A. Zettl, S.G. Louie, H. Dai, and M.F. Crommie, "Spatially Resolving Edge States of Chiral Graphene Nanoribbons," Nature Physics **7**, 616 (2011).
54. H.C. Hsueh, G.Y. Guo, and S.G. Louie, "Excitonic Effects in the Optical Properties of an SiC Sheet and Nanotubes," Phys. Rev. B **84**, 85404 (2011).
55. G.P. Zhang, D.A. Strubbe, S.G. Louie, and T.F. George, "First-principles Prediction of Optical Second-order Harmonic Generation in the Endohedral N@C_{60} Compound," Phys. Rev. A **84**, 023837 (2011).
56. S. Blackburn, M. Cote, S.G. Louie, and M.L. Cohen, "Enhanced Electron-phonon Coupling Near the Lattice Instability of Superconducting $NbC_{1-x}N_x$ from Density-Functional Calculations," Phys. Rev. B **84**, 104506 (2011).
57. G. Samsonidze, M. Jain, J. Deslippe, M.L. Cohen, and S.G. Louie, "Simple Approximate Physical Orbitals for *GW* Quasiparticle Calculations, " Phys. Rev. Lett **107**, 186404 (2011).
58. M.L. Cohen, "Conceptual progress for explaining and predicting semiconductor properties," J. Mater. Res. **26**, 2815 (2011).
59. D.-H. Lee, "Effects of Interaction on Quantum Spin Hall Insulators "Phys. Rev. Lett. **107**, 166806 (2011).
60. L.-T. Huang and D.-H. Lee, "Topological insulators on a Mobius strip," Phys. Rev. B **84**, 193106 (2011).
61. G. Samsonidze, M.L. Cohen, and S.G. Louie, "Compensation-doped Silicon for Photovoltaic Applications," Phys. Rev. B **84**, 195201 (2011).
62. B.D. Malone and M.L. Cohen, "Prediction of a metastable phase of silicon in the *Ibam* structure," Phys. Rev. B **85**, 024116 (2012).
63. D.A. Strubbe, L. Lehtovaara, A. Rubio, M.A.L. Marques, and S.G. Louie, "Response Functions in TDDFT: Concepts and Implementation," in *Fundamentals of Time-Dependent Density Functional Theory* (LNP **837**); eds. M.A.L. Marques, N.T. Maitra, F.M.S. Nogueira, E.K.U. Gross, A. Rubio (Springer, Heidelberg, 2012).
64. B.D. Malone and M.L. Cohen, "First principles study of phosphorus and boron substitutional defects in Si-XII," J. Phys.: Condens. Matter **24**, 055505 (2012).
65. O.V. Yazyev, E. Kioupakis, J.E. Moore, and S.G. Louie, "Quasiparticle Effects in the Bulk and Surface-state Bands of Bi2Se3 and Bi2Te3 Topological Insulators," Phys. Rev. B **85**, 161101 (2012).
66. J. Noffsinger, E. Kioupakis, C.G. Van de Walle, S.G. Louie, and M.L. Cohen, "Phonon-assisted Optical Absorption in Silicon from First Principles," Phys. Rev. Lett. **108**, 167402 (2012).
67. S. Bhattacharjee, Y. B. Kim, S.-S. Lee and D.-H. Lee, "Fractionalized topological insulators from frustrated spin models in three dimensions," Phys. Rev. B **85**, 224428 (2012).
68. J. Deslippe, G. Samsonidze, D.A. Strubbe, M. Jain, M.L. Cohen, and S.G. Louie, "BerkeleyGW: A Massively Parallel Computer Package for the Calculation of the Quasiparticle and Optical Properties of Materials and Nanostructures," Comp. Phys. Comm. **183**, 1269 (2012).
69. M. Orlita, L.Z. Tan, M. Potemski, M. Sprinkle, C. Berger, W. A. de Heer, S. G. Louie, and G. Martinez, "Resonant Excitation of Graphene K-Phonon and Intra-Landau-Level Excitons in Magneto-Optical Spectroscopy," Phys. Rev. Lett. **108**, 247401 (2012).
70. X. Andrade, J. Alberdi-Rodriguez, D.A. Strubbe, M.J.T. Oliveira, F. Nogueira, A. Castro, J. Muguerza, A. Arruabarrena, S.G. Louie, A. Aspuru-Guzik, A. Rubio, and M.A.L. Marques, "Time-dependent Density-functional Theory in Massively Parallel Comuter Architectures: the OCTOPUS Project," J. of Phys. – Cond. Matter **24**, 233202 (2012).

Geometric phases and topological effects in graphene and magnetic systems

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Project scope

This research project focuses on the electronic properties of crystals in which the orbital chararacter of band states changes rapidly with wavevector. These materials tend to have large momentum space Berry curvatures and Berry phases, and can have topological order. The project has in the past made important contributions to progress by emphasizing the important role played by geometric phases in the anomalous Hall effect. The project's scope encompasses both the momentum space Berry phases of perfect crystals, real-space Berry phase effects associated with quasiparticle Hamiltonians that change slowly on an atomic length scale, and geometric phases that involve a mixed dependence on position and momentum. Space-dependent Hamiltonians are normally associated with order-parameter textures. Our current focus is on electronic properties associated with order-parameter textures in ferromagnetically and antiferromagnetically ordered metals, and on the physics of Dirac-like two-dimensional electron systems including those that occur at the surface of three-dimensional topological insulators and in graphene single-layer and multilayer materials. The single layer and multi-layer graphene case, in which phase differences between Bloch state projections onto different sublattices have a strong momentum dependence, has been a particularly strong focus because these two-dimensional electron systems are exceptionally robust and because they are describable by a variety of distinct simple models over a very broad range of energy. Graphene-based two-dimensional electron systems exhibit an extremely wide variety of properties, depending on doping, gating, and in the multilayer case also stacking arrangements. Our program also includes a strong interest in the growth of materials with interesting momentum or real space structures, including graphene and graphene multilayers and topological insulators.

Recent progress

Engineering Topological Phases in Graphene Systems

We have investigated the possibility of engineering various topological phases in graphene systems. (1) Previously we found that when both Rashba spin-orbit coupling and Zeeman field are present, a nontrivial bulk gap opens to host a quantum anomalous-Hall state. This is now substantiated by our first principles study of adsorbing magnetic metal atoms on graphene. (2) In bilayer graphene, an interlayer potential difference breaks inversion symmetry and opens a bulk gap to support the quantum valley-Hall state. We show that Rashba spin-orbit coupling can induce a topological phase transition from the quantum valley-Hall effect to a Z2 topological insulator. When the Zeeman field is also included, a rich variety of topological phases emerge. (3) If the interlayer potential difference varies spatially, a topologically protected 1D state arises along domain walls. Based on the Green's function technique and Landauer-Buttiker formula, we demonstrate that this type of topological 1D state exhibits zero bend-resistance and extremely long mean free path in relatively clean samples. We further point out that this topologically protected 1D state can be tailored in graphene nanoroads in boron nitride sheets. In a four-terminal set up, our numerical results indicate that this 1D state obeys a current partition law, which is only dependent on the angle of incidence. (4) In a gated trilayer graphene, we show that unbalanced edge modes can appear along zigzag boundaries. (5) We have also investigated Valley-selective circular dichroism of monolayer molybdenum disulphide, an effect that we predicted before for a single layer graphene with AB sublattice symmetry breaking, which has been investigated extensively experimentally.

Suppression of grain boundaries in the epitaxial growth of graphene on metals

Grain boundaries (GBs) are widespread undesirable defects in epitaxial graphene samples grown on metal substrates like Cu. Using density functional theory calculations, we have established that misorientations of carbon islands nucleated on a Cu(111) surface leads to the formation of GBs as the islands coalesce. We have proposed a two-step kinetic pathway to effectively suppress the formation of GBs. In the first step, large aromatic hydrocarbon molecules are deposited onto a superstructured Cu-Mn alloyed surface to seed initial carbon clusters with a common orientation; in the second step, the seeded islands are enlarged through normal chemical vapor deposition of methane to form a complete graphene sheet. This approach promises to overcome a fundamental obstacle which has stood in the way of large scale single-crystal graphene fabrication.

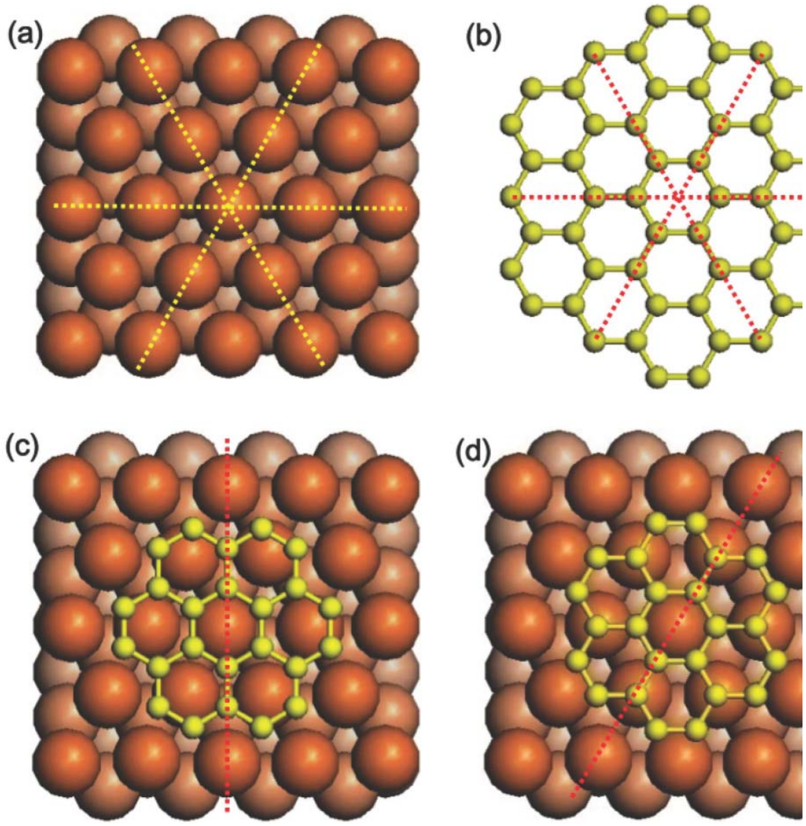

Figure X: (a) and (b) llustrations of the Cu (111) substrate and graphene structures. The yellow and red dashed lines show respective high-symmetry axes. (c) and (d) Illustrations of two geometries where a 7CR carbon cluster has a high-symmetry orientation on the Cu(111) surface. In (c), the edge C atoms reside at the 3-fold hollow sites; in (d), the edge C atoms are at the bridge sites between two surface Cu atoms.

Graphene Cavity QED

The Dicke model of

cavity quantum electrodyamics (CQED) is approximately realized in condensed matter when the cyclotron transition of a two-dimensional electron gas is nearly resonant with a cavity photon mode. Graphene is an attractive material for realization of the strong coupling CQED limit because its cyclotron resonance frequency is lowered and disorder effects reduced when its Fermi level is displaced from the Dirac carrier-neutrality point. Because of graphene's linear band crossing, minimal substitution in the Dirac model leads to a theory of light-matter coupling which is linear in the electric field. Along with collaborators from Scuola Normale is Pisa Italy we have examined the theory of graphene cavity cyclotron resonance, showing that a dynamically generated quadratic term neglected in previous work plays an essential role. The presence of this quadratic term implies that the superradiant quantum phase transition, which famously occurs in Dicke models of CQED, cannot occur in graphene. We have been able to derive an analytic expression for the Fermi-level dependence of the quadratic coupling term for the case of a graphene two-dimensional electron gas in the presence of a quantizing external magnetic field.

III. Planned activities: 2012-2013

Exchange Coupling between Magnetic Nanoparticles Mediated by Dirac 2DEG's

We are in the process of studying the properties of magnetic particles on the surface of two-dimensional Dirac-model systems. A fairly exhaustive study of cobalt nanoparticles on a gatable graphene substrate has been completed. We have found that the exchange interactions between cobalt and graphene have sublattice-independent and sublattice-dependent components. Graphene mediated interactions between two different cobalt nanoparticles can therefore be sublattice dependent. The strength and the sublattice dependence of the exchange interactions can be tuned by external gate voltages, although the change in the exchange interactions is generally smaller than the magnetic anisotropy of individual nanoparticles. Separately we have explored a novel and promising approach to effectively introduce local magnetic moments and long-range ferromagnetic order in graphene, via n-p codoping, by exploiting charge-compensated co-doping of non-magnetic B and magnetic Ni.

Casimir Forces Between 2D Dirac systems

We are developing the theory of Casimir interactions between two-dimensional Dirac systems, for example the interaction between graphene sheets, in the quantum Hall regime. Because the current-current correlation functions in this regime can be dominated by their Hall conductivity responses, Casimir interactions can be repulsive. We are also exploring the possibility that separate contacting between nearby two-dimensional electron gases can enable electrical measurement of Casimir forces.

Selected Publications

1. Di Xiao, Juren Shih, D.P. Clougherty and Qian Niu, “Polarization and Adiabatic Pumping in Inhomogeneous Crystals”, Phys. Rev. Lett, **102**, 087602, (2009).
2. Hua Chen, Wenguang Zhu, Efthimios Kaxiras, and Zhenyu Zhang, "Optimization of Mn Doping in Group-IV-semiconductor-based Diluted Magnetic Semiconductors by Additional Electronic Dopants", Phys. Rev. B **79**, 235202 (2009).
3. Shengyuan A. Yang, Geoffrey S. D. Beach, Carl Knutson, Di Xiao, Qian Niu, Maxim Tsoi, and James L. Erskine, “Universal Electromotive Force Induced by Domain Wall Motion”, Phys. Rev. Lett. **102**, 067201 (2009).
4. Ke Zhao, M. C. Troparevsky, Di Xiao, Adolfo G. Eguiluz, and Zhenyu Zhang, "Electronic Coupling and Optimal Gap Size between Two Metal Nanoparticles", Phys Rev Lett **102**, 186804 (2009).
5. Tianyi Cai *et al.* “Magnetoelectric Coupling and Electric Control of Magnetization in Ferromagnet-Ferroelectric-Metal Superlattices”, Phys Rev B **80**, 140415 (R) (2009).
6. Wang-Kong Tse and A.H. MacDonald, “Interaction effects in the optical conductivity of bilayer graphene: Drude-interband coupling and screening”, Phys. Rev. B **80**, 195418 (2009).
7. F. Zhang, H. Min, M. Polini and A.H. MacDonald, “Spontaneous inversion symmetry breaking in graphene bilayers”, Phys. Rev. B **81**, 041402(R) (2010).
8. Di Xiao, Ming-Che Chang, Qian Niu, “Berry Effects on Electronic Properties”, Rev. Mod. Phys. **82**, 1959-2007 (2010).
9. F. Zhang, B. Sahu, H. Min and A.H. MacDonald, “Band structure of ABC-stacked graphene trilayers”, Phys. Rev. B **82**, 035409 (2010).
10. Wang-Kong Tse and A.H. MacDonald, “Giant Magneto-optical Kerr Effect and Universal Faraday Effect in Thin-film Topological Insulators”, Phys. Rev. Lett. **105**, 057401 (2010).
11. Giovanni Borghi, Marco Polini, Reza Asgari and A.H. MacDonald, “Compressibility of the electron gas in bilayer graphene”, Phys Rev B **82**, 155403 (2010).
12. Shengyuan A. Yang, Geoffrey S. D. Beach, Carl Knutson, Di Xiao, Zhenyu Zhang, Maxim Tsoi, Qian Niu, A.H. MacDonald, and James L. Erskine, “Topological electromotive force from domain-wall dynamics in a ferromagnet”, Phys Rev B **82**, 054410, (2010).
13. Hua Chen, Wenguang Zhu,and Zhenyu Zhang, "Contrasting Behavior of Carbon Nucleation in the Initial Stages of Graphene Epitaxial Growth on Stepped Metal Surfaces", Phys Rev Lett **104**, 186101 (2010).
14. Di Xiao, Yugui Yao, Wanxiang Feng, Jun Wen, Wenguang Zhu, Xing-Qiu Chen, G. Malcolm Stocks, and Zhenyu Zhang, “Half-Heusler Compounds as a New Class of Three-Dimensional Topological Insulators”, Phys. Rev. Lett. **105**, 096404 (2010).

15. J. Velasco Jr., L. Jing, W. Bao, Y.Lee, P. Kratz, V. Aji, M. Bockrath, C.N. Lau, C. Varma, R. Stillwell, D. Smironov, Fan Zhang, J. Jung, A.H. MacDonald, “Transport Spectroscopy of Symmetry-Broken Insulating States in Bilayer Graphene”, Nature Nanotechnology, Jan. 22 (2012).

16. Rosario E.V. Profumo, Reza Asgari, Marco Polini, A.H. MacDonald, “Double-layer graphene and topological insulator thin-film plasmons”, Phys. Rev. B **85**.085443 (2011).
17. Fan Zhang, Dagim Tilahun, A.H. MacDonald, “Hund’s Rules for the N=0 Landau Levels of Trilayer Graphene”, Phys. Rev. B **85**.165139 (2012).
18. Jeil Jung, Zhenhua Qiao, Qian Niu, A.H. MacDonald, “Transport Properties of Graphene Nanoroads in Boron-Nitride Sheets”, Nano Lett **12**.2936 (2012).
19. Inti Sodemann, D.A. Pesin, and A.H. MacDonald, “Interaction-Enhanced Coherence Betweeen Two-Dimensional Dirac Layers”, Phys Rev B **85**, 195136(2012).

Many-body effects in chiral electron transport

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Project scope

We study physics of chiral electron states, whose properties depend on the direction of electron propagation. Such states exist in a variety of practical realizations: two-dimensional electron gas in semiconductor quantum wells with spin-orbit interaction, Dirac fermions in graphene (2D) or carbon nanotubes (quasi-1D), protected surface states in topological insulators, etc. The emphasis is on investigating transport phenomena and effects of electron-electron interactions from a general perspective, on elucidating features common to various chiral systems, and on applying to newer materials the techniques previously successful for other chiral systems. As an example, the method of transport equations used by us in 2004-2005 to study spin Hall effect was subsequently applied to the problem of optical conductivity in graphene, within the scope of this project. The PI was the first who pointed out (in 2008) that the interaction corrections to the optical conductivity are suppressed by roughly two orders of magnitude despite the largeness of the coupling constant. This spectacular prediction led to an earlier vigorous debate at workshops and seminars and in publications (Herbut, Juricic, Vafek, 2008, 2010) before being accepted by the theorists (Sheehy, Schmalian, 2009; Sodeman, Fogler, 2012), and in agreement with multiple experiments (Basov et al, Geim et al, Heinz et al, 2008). Among specific problems currently studied are: properties of collective plasmon modes in graphene, effects of resonant impurities on properties of graphene and topological insulators, the role of many-body effects on the optical properties of carbon nanotubes. We employ broad range of methods including quantum transport theory based on kinetic equations, diagrammatic technique, hydrodynamics of electron liquid, etc. Both analytical as well as numerical approaches are utilized. As far as the fundamental physics is concerned, our main effort is to study transport phenomena and effects of electron-electron interactions from a general perspective of elucidating features common to various chiral systems.

Recent progress

Nanotubes: Luttinger Liquid effects in the optical absorption

The tunneling density of states of the massless (linear) bands in metallic carbon nanotubes is well-known to have power-law energy dependence characteristic of Luttinger Liquid behavior. It is also established (by Balents, 2000), though not as well known, that the massive (gapped) subbands undergo a similar many-body renormalization. This is the result of coupling to multiple low-energy bosonic excitation (plasmons). For both kinds of particles the ensuing effect is the suppression of the density of states by electron-electron interactions. Motivated by the fact that optical measurements are relatively simpler than the tunneling experiments we addressed the question whether Luttinger Liquid behavior could be observed in optical transitions, FIG. 1. Surprisingly, the suppression of the density of states of both the massless and massive subbands is overcompensated by the enhancement due to vertex corrections, in case of the transverse polarization of photons, FIG 1b). The resulting absorption probability, being a simple step-function for non-interacting electrons develops a power-law frequency dependence,

$A(\omega) \sim (\omega - \Delta)^{-\gamma}$, where $\gamma \approx 0.2$ for typical nanotubes. In case of longitudinal photon polarization the vertex corrections exactly compensate the self-energy suppression and the many-body effects cancel to the leading order.

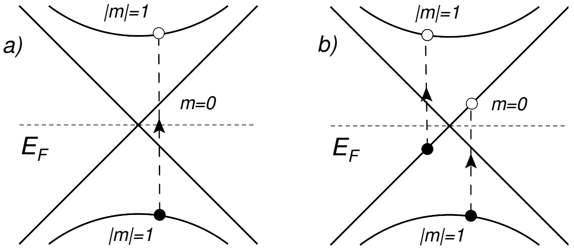


FIG. 1. Processes responsible for the optical absorption in metallic nanotubes. a) Polarization along the NT axis: only transitions with no change of the angular momentum are allowed, i.e. E_{11}. The transition is indicated by the dashed line. b) Polarization perpendicular to the NT axis, the change of angular momentum is required. The processes involving right-moving massless particles are indicated. At zero temperature the transitions E_{10} and E_{01} are contributing to the optical absorption.

Graphene: Plasmonics of p-n junctions

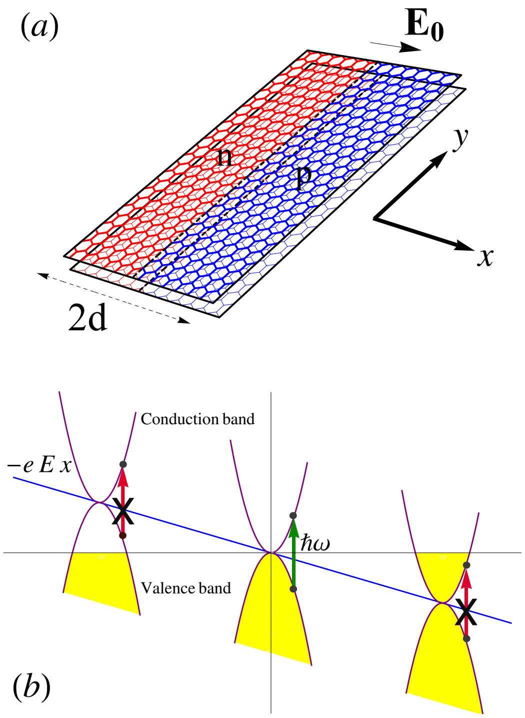
Spatial separation of electrons and holes in graphene gives rise to the existence of novel quasi-one-dimensional plasmon waves confined to the boundary region. Theory of such guided plasmon modes within the hydrodynamics of electron-hole liquid has been developed for both monolayer and bilayer graphene structures. For plasmon wavelengths smaller than the size of charged domains plasmon dispersion is found to be $\omega^2(q) \sim \sqrt{Eq}$ in case of a monolayer. Plasmons propagating in bilayer graphene reveal a much greater variety of their spectral properties, as both the ungapped as well as gapped (of particular interest to potential applications) cases have been studied. In particular, plasmons in ungapped bilayer graphene typically have a gap $\sim eE/m^{*}d \sim 2-3\ meV$. Frequency, velocity and direction of propagation of guided plasmon modes can potentially be controlled by both the direction and magnitude of the external electric field $\vec{E}$. Among the most promising applications of plasmons in p-n junctions we envisage the possibility of a plasmon transistor. In particular, by simply switching the electric field on and off across the flake propagation of plasmons can be facilitated or prevented. We have further studied additional gapless magnetoplasmon excitations in the presence of magnetic field.

Graphene: Resonant impurities

The limit of infinitely strong inpurities (unitary limit) in graphene is known to lead to qualitatively new effects compared with conventional metallic systems.. One of them is the long-range, $\sim (r \ln r)^{-1}$, interaction between adatoms on graphene. We considered another realization of the unitary limit, a finite-size impurity, whose depth is tuned in such a way that the wavelength induced by the imourity becomes of the order of the size of the defect. In particular, we calculated the density of graphene electrons induced by the defect both for undoped (intrinsic) and doped graphene, where Firdel oscillations develop. Far from the resonance, as long as the scattering length is much smaller than the distance $l << r$ the density decreases as r^{-3} from the impurity. At the resonance $l >> r$ the behavior changes to r^{-2}. Finally, very close to the resonance when the ratio of the scattering length to the radius of the defect R becomes logarithmically large, $\ln(l/R) >> 1$, the induced density becomes logarithmically suppressed, $r^{-2}/\ln(l/R)$.

Planned activities: 2012-2013

Nanotubes: The above described many-body enhancement of the optical absorption is only the first step towards developing a comprehensive theory that could be offered to experimentalists for verification. The corresponding probability has been calculated with respect to the *local* electric field. What is measured in experiments, however, is the response to the *external* field. The two fields for the transverse polarization of light are related by the depolarization factors. In systems of higher dimensions the relation between the two are routinely found from Random Phase approximation. Naïvely, thinging within RPA would lead to a power-law *suppression* (with the same exponent γ) with respect to the external field. It is obvious however, that the RPA, by missing the correlations between different polarization loops, fails to account properly for many-body effects in the massive subbands. Developing a proper description of the correlation effects is one of our immediate projects.



Bilayer graphene flake is placed in electric field that separates *p* and *n* regions. Guided plasmons propagate along the dashed line and decay in the perpendicular. b) Schematic picture of the electron band structure: in equilibrium the sum of the electrostatic potential and kinetic energy of electrons (at the Fermi level) is constant. Vertical arrows indicate possibility of optical absorption with a given frequency: while possible near the center of the flake (green arrow), such transitions are forbidden (red arrows) when both initial and final states are empty or occupied.

In a separate but closely related project we are going to study the interplay between LL behavior of the gapless and gapped subbands in the formation of excitons in metallic nanotubes for the longitudinal *polarization* of photons. Though the many-body effects cancel in the leading approximation, taking into account the finite spatial separation of electron-hole pairs leads to interaction corrections that should modify exciton binding energy. While the existence of excitons in metallic nanotubes has been established experimentally by T. Heinz's group no comprehensive theory including correlation effects has been developed so far.

Graphene: a) he existing theory for strong (resonant) impurity centers in graphene manifestly fails to take into account interaction effects. On the other hand, the exciting predictions of long-range coupling of resonant impurities warrant investigation whether the effects predicted survive when the interaction effect are considered. The resonant impurity is typically treated within the Fano-Anderson hybridization model. The role of interactions is anticipated to be two-fold. First, the usual Hubbard coupling for localized states needs to be taken into account. Second, the itinerant electron density induced by the impurity produces long-range Coulomb fields weakly screened in an undoped graphene that could be expected to affect the long-range interaction between adatoms.

b) The resonant impurity effects in graphene originate in the vanishing of the density of states that leads to the infinite lifetime of the localized state with $\varepsilon = 0$. This is a situation when the Hubbard interaction could result in the appearance of a well localized spin-½ state. The resonant coupling between two impurities could then be expected to result in the effective (Casimir-like) long-range interaction *between spins*, with interesting consequences for magnetic impurity ordering.

c) In 2008 the PI published a paper addressing the singular behavior of the polarization operator of Dirac fermions $\Pi(\omega, q)$ near the threshold of electron-hole excitation, $\omega = qv$. The conclusion was achieved that the vertex corrections (representing the exciton-type interaction in the final state) in fact are dominant over the bubble-type RPA corrections, which is a consequence of the largely unscreened nature of the Coulomb interaction in graphene. The pioneering 2008 work did not take into account the electron-electron interaction-induced curvature of Dirac spectrum. Over the course of the last two years the experimental advances made it possible to study absorption in graphene at finite wave-vectors and thus made more detailed investigations of the polarization function $\Pi(\omega, q)$ of acute interest. We are going to reexamine this problem, this time taking effects of spectrum curvature into account in order to make relevant experimental predictions.

Recent publications

1. V.V. Mkhitaryan, and E.G. Mishchenko, *Resonant finite-size Impurities in graphene, unitary limit and Friedel oscillations*, arXiv:1205.3558, submitted to Phys. Rev B.

2. P.G. Silvestrov, P.W. Brouwer, and E.G. Mishchenko, *On the structure of surface states in topological insulators*, arXiv: 1111.3650,submitted to Phys. Rev B.

3. N.M. Hassan, V.V. Mkhitaryan, and E.G. Mishchenko, *One-dimensional plasmons confined in bilayer graphene p-n junctions*, accepted to Phys. Rev. B **85** 125411 (2012).

4. E.G. Mishchenko, and O.A. Starykh, *Intersubband Edge Singularity in Metallic Nanotubes*", Phys. Rev. Lett. **107**, 116804 (2011).

5. W. Chen, A.V. Andreev, E.G. Mishchenko, and L.I. Glazman, *Decay of a plasmon into neutral modes in a carbon nanotube,* Phys. Rev. B **82**, 115444 (2010).

6. V.V. Mkhitaryan and M.E. Raikh, Disorder-induced magnetooscillations in bilayer graphene at high bias, Phys. Rev. B **83**, 045406 (2011).

7. E.G. Mishchenko, A.V. Shytov, and P.G. Silvestrov, *Plasmons in graphene p-n junctions,* Phys. Rev. Lett. **104**, 156806 (2010).

Modeling the Self-Assembly of Ordered Nanoporous Materials

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Project Scope

This research program is about modeling the synthesis of ordered nanoporous materials. These materials are of enormous importance in modern technology with traditional applications in catalysis and separations for the chemical process industries and more recent applications in areas like biosensing and microelectronics. The materials science and engineering of these materials focuses on the development of materials that are tailored for specific applications through control of pore structure, size and shape as well as the chemistry of the material components. Through detailed modeling of the nanoscale assembly processes of these materials we seek to provide a greater understanding that can be used in improved control of the synthesis outcomes as well as guidance in the discovery of new materials.

Our focus is on two types of materials that both feature the formation of three-dimensional networks of polymerized silica. These are all-silica zeolite frameworks and ordered mesoporous silicas. In the first of these the network structure is crystalline with nanoscale order created by small structure-directing agents or templates. In the second the network structure is amorphous at the atomic length scale but ordered on the length scales in the range 2-10 nm through structure direction by larger surfactant molecules, block copolymers or both. These represent two of the most important routes for the controlled synthesis of ordered nanoporous materials. Our research program has two main elements: i) Modeling polymerization processes in 3-d network solids including zeolite frameworks and ii) Modeling ordered mesoporous materials synthesis by surfactants and block copolymers. Our research is based on the hypothesis that both of these kinds of systems can be understood in terms of a framework that focuses on modeling silica polymerization through the assembly of corner-sharing SiO_4 tetrahedral units. This is a difficult problem in condensed phase statistical mechanics. It involves assembly of low coordination number networks, addressing order at different length scales (zeolites vs. ordered mesoporous materials) and balancing the level of detail required in models with the feasibility of wide ranging computational studies. We have developed both lattice-based and off-lattice models for the assembly of corner-sharing tetrahedral and these models are providing a number of important insights into the nanoscale behavior of these systems.[1-5]

Recent Progress

Microporous crystalline ground state structures (zeolite analogs) of our lattice model of silica

We have made a detailed study of the types of ground states of our lattice-based model of silica polymerization. As might be anticipated from knowledge of real silica we have found a wide variety of crystalline ground states depending on the density that we choose. The primary computational tool in these studies is the parallel tempering Monte Carlo (PTMC) method, which allows us to cross the free energy barriers between structures with different connectivities. In this way we have found a rich array of crystalline nanoporous materials, from known chalcogenides to zeolite and clay-analogs. Figure 1 shows the evolution of PTMC from a random initial condition to a structure denoted as a "zeolite analog" in an 8 × 8 × 8 bcc lattice with $x = 0.75x_\beta = 0.04688$. The resulting structure contains two interpenetrating 12-ring channels, as shown in Figure 1c,d, and exhibits both allowed T-B-T angles of 109.5 and 180°.

This work creates important opportunities for future research, including analysis of crystallization pathways to determine critical nuclei for formation of zeolites and related nanoporous materials.

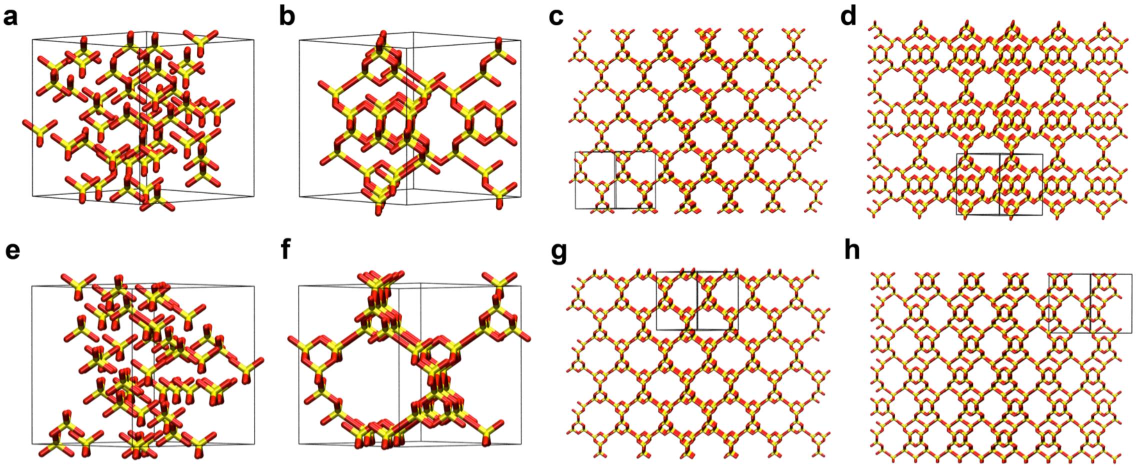

Figure 1. Self-assembly of crystalline microporous zeolite-analogs with two interpenetrating channels formed via PTMC in an 8 × 8 × 8 unit bcc lattice with x =0.04688.

Modeling assembly of mesoporous silica materials using surfactants as structure directing agents

We have combined the surfactant lattice model of Larson, together with our atomic tetrahedral lattice model of silica to make a model of the surfactant templating of ordered mesoporous silica, e.g. MCM-41. We wish to apply modeling to answer the following question. When experimentalists fabricate MCM-41, they generally find that the best approach involves a two-step synthesis where step 1 involves low temperature and high pH, while the second step requires higher temperature and lower pH.

Although this fact is well documented, there is little molecular-level understanding why this is necessary. Our simulations are revealing insights into this as illustrated in figure 2.

Figure 2a depicts the initial configuration with surfactant and silicate molecules randomly distributed in the system. When the canonical ensemble simulations were carried out, surfactant molecules tend to form micelles with hydrophobic tail groups gathering inside and hydrophilic head groups facing outside, and silicate species were strongly attracted to the head segments. Due to the strong interaction between silica and surfactant head, the system phase separates into a surfactant-silicate rich phase in equilibrium with a solvent phase. The dense phase was found to have mesoscale ordering, possessing a hexagonal array of pores occupied by tail segments, as shown in Figure 2b. The final configuration in Figure 2b was the starting point of "step two" where silica polymerization and silica deprotonation reactions were considered as occurs with a decrease solution pH and/or increase system temperature in the real synthesis. During this approach, silicate species continue to polymerize and condense. Snapshots taken before and after the condensation step are shown in Figures 2b and c

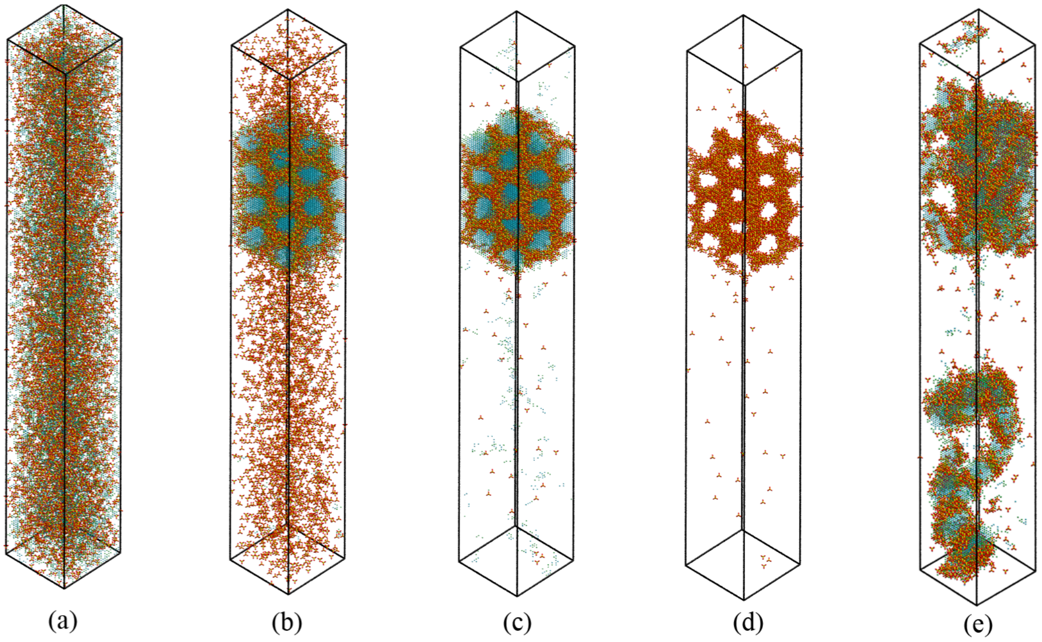

Figure 2. Simulation of the formation of ordered mesoporous silica materials, at T^* = 6.5, box size of 30×30×240. c_{H4T4} = 0.009375 and c_{Silica} = 0.015 (a) Initial configuration with 4,050 H_4T_4 and 6,480 ionic silica S_I randomly distributed in the simulation box. (b) Final configuration of step one. Snapshot taken in direction where hexagonal array of cylindrical pores are shown. MC simulations were carried out under conditions that silicate polymerization is negligible. (b) is also the starting configuration of step two. (c) Snapshot of final configuration of step two. (d) Only silicate species were shown from snapshot (c). (e) Instead of using the two-step synthesis method, a one-step synthesis scheme that allows simultaneous silicate polymerization, silica deprotonation and surfactant-assembly was adopted with a random initial configuration. A much more disordered structure is obtained.

respectively for comparison. Figure 2d shows only the silicate species, and this mimics the calcination procedure that removes the template molecules and makes the pore space available. Figure 2e shows what happens if the polymerization reaction and self-assembly are run at the same time and a much more disordered structure is obtained.

Future Plans

We will begin modeling the templating of the crystalline microporous structures in the lattice model to reveal new information about the nature of the formation process for microporous crystalline silica materials (zeolites and their analogs). Our starting point will be to design model templates that can be accommodated into the void spaces of the ground state structures discussed above. Having done that we will proceed to make Monte Carlo simulations initiated from disordered mixtures of silica and template to see if we can observe the assembly of the ordered microporous structures.

We will be making further studies of the formation of ordered mesoporous materials using the lattice model. So far we have focused on only one template and one mesoporous structure. We plan to study surfactants with longer chains to obtain materials with larger pore sizes and also to see if we can obtain other pore geometries such as the ordered bicontinuous pore spaces.

We will continue our studies of our off-lattice model [4, 5] at high pH and the formation of nanoparticles to capture the essential physics of the transition from gel-like structure at low pH to compact nanoparticles at higher pH. We will also extend of the off-lattice model to templating of ordered mesoporous silica materials and zeolites.

Publications

1. Jin, L., S.M. Auerbach, and P.A. Monson, *Modeling Nanoparticle Formation during Early Stages of Zeolite Growth: A Low-Coordination Lattice Model of Template Penetration.* Journal of Physical Chemistry C, 2010. **114**(34): p. 14393-14401.
2. Jin, L., S.M. Auerbach, and P.A. Monson, *Modeling three-dimensional network formation with an atomic lattice model: Application to silicic acid polymerization.* Journal of Chemical Physics, 2011. **134**(13): p. 134703.
3. Jin, L., S.M. Auerbach, and P.A. Monson, *Emergence of Zeolite Analogs and other Microporous Crystals in an Atomic Lattice Model of Silica and Related Materials.* Journal of Physical Chemistry Letters, 2012. **3**(6): p. 761-765.
4. Malani, A., S.M. Auerbach, and P.A. Monson, *Probing the Mechanism of Silica Polymerization at Ambient Temperatures using Monte Carlo Simulations.* Journal of Physical Chemistry Letters, 2010. **1**(21): p. 3219-3224.
5. Malani, A., S.M. Auerbach, and P.A. Monson, *Monte Carlo Simulations of Silica Polymerization and Network Formation.* Journal of Physical Chemistry C, 2011. **115**(32): p. 15988-16000.

Non-Equilibrium Physics at the Nanoscale

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Project Scope

This program focuses on (a) understanding the microscopic origin and the relevant physical quantities that determine non-equilibrium transport (both charge and excitonic) in nanoscopic quantum networks, (b) exploring the emergence of strong correlations at the nanoscale, and (c) combining the results of these projects to design nanoscale quantum structures with new functionalities that utilize the balance between quantum coherence and noise. Of particular interest for this program are systems where (a) correlation effects arise from strong interactions, such as nanoscopic Kondo lattices, (b) a complex bandstructure allows for the emergence of novel quantum phenomena, as is the case in graphene, and (c) topologically non-trivial bandstructures are induced by interactions, such as in topological insulators. The question of how non-equilibrium transport occurs in these systems at the nanoscopic level, is not only of fundamental interest for our understanding of quantum phenomena at the nano-, meso and macroscale, but also of great importance for the further development of nano- and molecular electronics as well as for the continued miniaturization of electronic devices and the fabrication of artificial quantum structures.

Recent Progress

Current Eigenmodes, Imaging and Dephasing in Nanoscopic Quantum Networks

The PI recently demonstrated how the flow of current through a nanoscopic quantum network is determined by the interplay between the electronic structure, geometry, and topology of the quantum network, the leads' location and width, as well as interactions and the resulting dephasing effects [PRB **85**, 195459 (2012)]. In particular, this study provided a microscopic relation between local currents and the global electronic structure of the network, thus opening new venues for qualitatively changing and manipulating the spatial current paths through a network via gating [Figs. 1(a) and (b)], through constrictions [Fig. 1(c)], or by changing the lead positions in cylindrical networks [Fig. 1(d)]. Moreover, by considering an electron-phonon interaction, the PI demonstrated how the current patterns in a network evolve with increasing dephasing rate from those of the ballistic (quantum) limit to those of a classical resistor network. These results provided important insight into the microscopic origin of charge transport at the nanoscale.

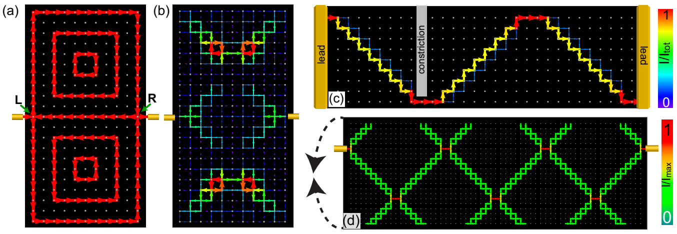

Figure 1: Manipulating current paths via gating (a),(b), through constrictions (c), or lead position (d).

The question naturally arises of how such current patterns in nanoscopic networks can be imaged with atomic resolution. To this end, the PI recently proposed a new method, based on scanning tunneling microscopy (STM) [preprint, submitted to PRL]. Investigating different network geometries and topologies, the PI demonstrated that by measuring the current flowing from an STM tip into one of the leads, I_L, attached to the network as a function of tip position, $\mathbf{T}$, one can obtain an atomically resolved spatial image of current paths in the network. An example for the success of this method is shown in Fig. 2 where the spatial current paths [Fig. 2(a)] and the imaged current pattern [Fig. 2(b)] are presented for a more complex network containing constrictions and circulating current loops.

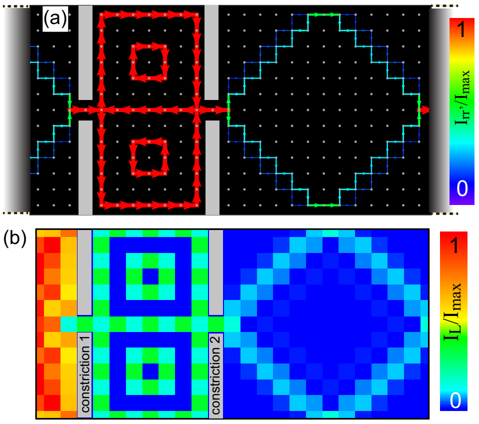

Figure 2: Spatial current paths (a), and imaged current (b).

The proposed imaging method thus provides a promising new approach for exploring charge transport in nanoscopic systems.

Transport and Localization in Nanoscopic Graphene Lattices (NGLs)

Graphene has attracted significant interest due to its electronic structure and the resulting unconventional properties. Recent experimental advances have made it possible to create nanoscopic graphene lattices (NGL) [see Fig. 3(a)]. The PI demonstrated that the unconventional electronic structure of graphene leads to complex and distinctive spatial current patterns [see Figs. 3(b) - (e)]. Moreover, due to the presence of inequivalent edges in NGLs [see Fig. 3(a)], their transport properties when (narrow) leads are attached to the *zig-zag* (Z) edges are qualitatively different from those when leads are attached to the *armchair* (A) edges. This asymmetry can be maximized by gating the NGL to the $E = 0$ state (the so-called *Dirac points*), which is localized along the *zig-zag* edges. As a result, charge transport perpendicular to the *zig-zag* edges is exponentially suppressed with increasing distance between the edges. Moreover, the proposed STM-based method discussed above can also be successfully applied to image current patterns in graphene with atomic resolution, (thus demonstrating the broad impact of this new method), as follows from a comparison of the spatial current pattern shown in Fig. 3(e) and the related STM current, I_L in Fig. 3(f). These results demonstrate that graphene is ideally suited to study unconventional transport properties at the nanoscopic level.

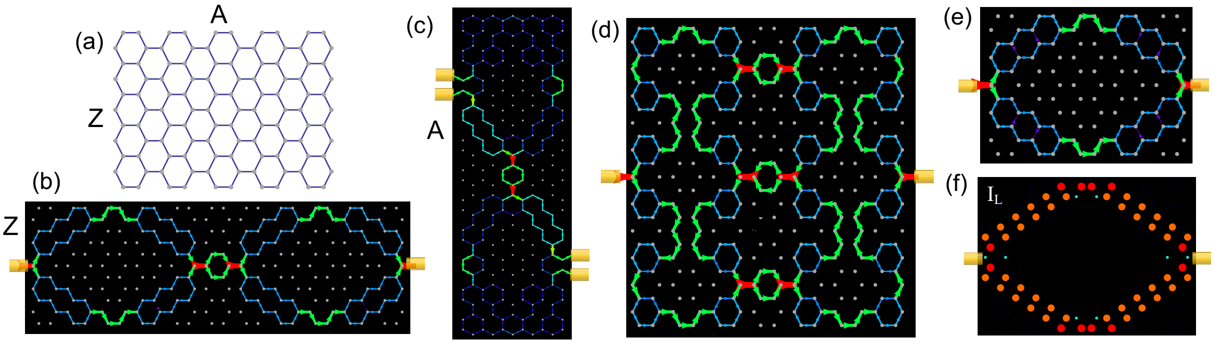

Figure 3: (a) Nanoscopic graphene lattice. (b) - (e) spatial current patterns, and (c) STM current, I_L, in NGLs.

Future Plans

Correlation Effects and Transport in Nanoscopic Kondo Lattices

The question of how strong correlation effects influence charge transport is of fundamental importance for our understanding of many strongly correlated systems. As a first step in addressing this question, the PI is currently studying how the onset of Kondo screening affects the current flow through a nanoscopic Kondo lattice. To this end, two methods developed in the PI's group were combined: a path-integral method to study Kondo screening in finite size systems, so-called Kondo droplets, and the Keldysh Greens function method to study transport in nanoscopic systems. This approach has proven to be quite successful: preliminary results shown in Fig. 4 have demonstrated that the spatial current patterns change significantly with the onset of strong correlations. While above the Kondo temperature, T_K, the current pattern is diffuse [see Fig. 4(a)], the onset of Kondo screening and the ensuing correlation effects lead to a well defined current paths well below T_K, as shown in Fig. 4(b).

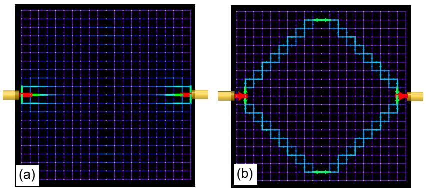

Figure 4: Spatial current pattern above (a) and below (b) T_K.

The successful implementation of this approach enables the PI to explore how defects modify the local transport properties ("how does a current flow around a defect?") of strongly correlated systems in general, and of nanoscopic Kondo droplets in particular. This study will provide insight into the microscopic origin of many unconventional and puzzling transport properties of strongly correlated electron systems with quenched disorder.

Pseudomagnetic Fields, Veselago Lenses, and Localization in NGLs

Among the many unconventional properties of graphene is the possibility to create pseudomagnetic fields through the application of strain and to observe the resulting Landau quantization without breaking of the time-reversal symmetry. While the effects of these pseudomagnetic fields on the local density of states is identical to that of externally applied (real) magnetic fields, it is presently unclear whether this analogy also holds for charge transport through strained graphene lattices; a question the PI intends to address. Another exciting property of graphene is the possibility to build a Veselago lens from *p*-*n* junctions. The PI plans to study how such a Veselago lens will affect the charge transport, and in particular the spatial current patterns in nanoscopic graphene lattices. Finally, preliminary studies by the PI's group have shown that the introduction of defects in NGLs leads to localization effects. However, it was found that the resulting localization lengths can vary over orders of magnitude depending on the position of the defect with respect to the underlying spatial current path (which by itself can be changed through gating). These preliminary results open an interesting new approach to exploring and manipulating localization effects in graphene.

Transport at the Nanoscale in Topological Insulators

Topological insulators (TIs) have attracted significant interest due to their topologically nontrivial electronic bandstructure arising from spin-orbit coupling, resulting in an insulating bulk and a conducting surface. At the present, however, it is unclear how a current will flow across the surface, or to what extent it will penetrate into the bulk, when it is injected/extracted by leads that are much smaller than the size of the TI. In particular, based on the results described above, it is expected that the total conductance, as well as the spatial current patterns will sensitively depend on the relative position of the attached leads, as well as their position with respect to edges. Moreover, the use of spin-polarized leads where the relative polarization axis can be varied, is likely to lead to interesting spin-filter effects. The PI intends to explore these exciting possibilities.

Excitonic Energy Transport in Biological Systems

Over the last few years, it has been argued that energy transport in biological systems, such as the Fenna-Matthews-Olson (FMO) complex, exhibits many properties usually associated with quantum mechanical rather than classical networks. To explore this idea further, the PI has begun a collaboration with G. Engel (University of Chicago) whose group is studying energy transport in FMO complexes using Fourier transform electronic spectroscopy. In contrast to the cases discussed above, the energy transport in FMO complexes is excitonic (i.e, bosonic) in nature. The PI's group is therefore currently developing a bosonic, non-equilibrium Greens function method that will enable him to investigate (a) to what extent energy transport in biological systems in quantum mechanical, and (b) how it is determined by the interplay between (naturally occurring) disorder and external noise (arising from the coupling to phonons). Of particular interest is here the question of how much noise is optimal in order to render energy transport robust against localization effects on one hand, but to ensure the highest possible efficiency (i.e., conductance) on the other hand.

Publications 2009 - 2012

1. *Hidden Order Transition in URu_2Si_2 and the Emergence of a Coherent Kondo Lattice*, T. Yuan, J. Figgins, and D.K. Morr, arXiv:1101.2636, accepted for publication in Phys. Rev. B.
2. *Current Eigenmodes and Dephasing in Nanoscopic Quantum Networks*, T. Can, H. Dai, and D.K. Morr, Phys. Rev. B **85**, 195459 (2012).
3. *Defects in Heavy-Fermion Materials: Unveiling Strong Correlations in Real Space*, J. Figgins and D.K. Morr, Phys. Rev. Lett. **107**, 066401 (2011).
4. *Multiband Superconductivity in Spin Density Wave Metals*, J.-P. Ismer, I. Eremin, E. Rossi, D.K. Morr, and G. Blumberg, Phys. Rev. Lett. **105**, 037003 (2010).
5. *Differential Conductance and Quantum Interference in Kondo Systems*, J. Figgins and D.K. Morr, Phys. Rev. Lett. **104**, 187202 (2010).
6. *Contrasting Nodal and Anti-Nodal Behavior in the Cuprates Via Multiple Gap Spectroscopies*, D. Wulin, C.-C. Chien, D.K. Morr, and K. Levin, Phys. Rev. B **81**, 100504(R) (2010) (Rapid Communication).
7. *Vertex Corrections for Impurity Scattering near Ferromagnetic Quantum Critical Points*, E. Rossi and D.K. Morr, Phys. Rev. B, **81**, 054443 (2010).
8. *Quasiparticle interference in temperature dependent-STM as a probe of superconducting coherence*, D. Wulin, Y. He, C.-C. Chien, D.K. Morr, and K. Levin, Physica C **470** S904 (2010).
9. *Model for the temperature dependence of the quasiparticle interference pattern in the measured scanning tunneling spectra of underdoped cuprate superconductors*, D. Wulin, Y. He, C.-C. Chien, D.K. Morr, and K. Levin, Phys. Rev. B **80**, 134504 (2009).
10. *Charge Transport and Quantum Phase Transitions in Singlet Superconductor - Ferromagnet - Singlet Superconductor Junctions*, B. Kastening, D.K. Morr, L. Alff, and K. Bennemann, Phys. Rev. B **79**, 144508 (2009).

Project Title: Studies of the Marginally Jammed Solid
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Project Scope:
A collection of idealized spheres can jam into a disordered solid when it is compressed at zero temperature and zero shear stress. Our work has shown that this jamming transition is singular in that there is a diverging length scale that appears at the transition. This length scale is due to the fact that the number of inter-particle contacts at the transition is exactly the minimum number needed for mechanical stability. In the manner of an ordinary critical point, this singularity controls the harmonic as well as the anharmonic properties of the solid in the vicinity of the transition. Our project addresses the following questions: (1) How does the system behave when pushed beyond the harmonic regime so that anharmonic effects become important? Our preliminary results show that the most anharmonic vibrational normal modes are at low-frequency where they are quasi-localized. These modes are exquisitely sensitive to stress or temperature because they have low energy barriers to particle rearrangements. Can these modes be used to predict where local failure might occur? Can we predict from the harmonic spectrum or the anharmonic response how close a system is to the edge of failure? At the jamming transition, anharmonic effects diverge. How do they evolve as the system is compressed above that transition? (2) What is the effect of temperature? Could the anharmonic quasi-localized modes be responsible for phenomena associated with the glass state, such as the excess number of excitations, or dynamical heterogeneities that appear as the glass transition is approached? In particular, how is the jamming transition related to the glass transition? (3) How do generalizations of the model, such as non-spherical particle shapes, attractive interactions and three-body interactions affect the picture developed for idealized spheres?

We have been able to generalize many of the results for idealized spheres to more realistic systems. Several laboratories, including our own, are providing experimental tests to these ideas. We believe that these fundamental studies of jamming will not only provide theoretical insight to general packing problems, but also reveal the underlying cause of some of the longstanding experimental phenomena found in disordered solids.

Recent progress:
Heat transport in model jammed solids:

We calculated numerically the normal modes of vibrations in three-dimensional jammed packings of soft spheres as a function of the packing fraction and obtain the energy diffusivity, a spectral measure of transport that controls sound propagation and thermal conductivity. The crossover frequency between weak and strong phonon scattering is controlled by the coordination and shifts to zero as the system is decompressed toward the critical packing fraction at which rigidity is lost. We present a scaling analysis that relates the packing fraction dependence of the crossover frequency to the anomalous scaling of the shear modulus with compression. Below the crossover, the diffusivity displays a power-law divergence with inverse frequency consistent with Rayleigh law, which suggests that the vibrational modes are primarily transverse waves, weakly scattered by disorder. Above it, a large number of modes appear whose diffusivity plateaus at a nearly constant value before dropping to zero above the localization frequency. The thermal conductivity of a marginally jammed solid just above the rigidity threshold was calculated and related to the one measured experimentally at room temperature for most glasses.

Anharmonicity and quasi-localization of the excess low-frequency vibrations in jammed solids:

A starting point for understanding any solid is a calculation of its harmonic vibrational excitations. However, many important properties require an understanding of anharmonic effects as well. For example, in a crystal, heat transport and thermal expansion are governed by anharmonic coupling of the modes. Anharmonic effects become even more essential when one considers how a solid, be it crystalline or amorphous, disintegrates and loses rigidity. Such behavior requires the system to depart from the harmonic regime as it continually moves over potential-energy barriers to explore different configurations. We studied harmonic and anharmonic properties of the vibrational modes in 3-dimensional jammed packings of frictionless spheres interacting via repulsive, finite-range potentials. A crossover frequency is apparent in the density of states, the diffusivity and the participation ratio of the normal modes of vibration. At this frequency, which shifts to zero at the jamming threshold, the vibrational modes have a very small participation ratio implying that the modes are quasi-localized. The lowest-frequency modes are the most anharmonic, with the strongest response to pressure and the lowest-energy barriers to mechanical failure.

Mapping the slowdown of the dynamics of soft spheres onto hard sphere behavior:

Relaxation in a liquid proceeds by numerous pathways that each depend on temperature and pressure. It has remained an enduring challenge to delineate different modes of relaxation and to bring them into a common framework where they can be treated on a common footing. To reach such a goal, it is necessary to understand what combinations of variables control liquid dynamics in different regimes of temperature and pressure. We have shown that dynamics of soft repulsive spheres near their glass transition can be described in terms of the dynamics of hard spheres by introducing an effective hard sphere diameter that is determined via the Andersen-Weeks-Chandler approximation. We have shown that this approximation, which is known to describe static properties of liquids remarkably well, also describes a dynamical quantity, the relaxation time. These results indicate that the dynamics of soft spheres depend on an effective free volume in a universal way.

Experimental investigation of the onset of jamming in a thermal 3D system: Observation and characterization of the vestige of the jamming transition

We studied the dependence of the pair-correlation function, g(r), and particle mobility on packing fraction in a dense three-dimensional packing of soft colloids made of poly N-isopropyl acrylamide (pNIPAM), a thermo-sensitive gel. We find that g(r) for our samples is qualitatively like that of a liquid at all packing fractions. There is a peak in g_1, the height of the first peak of g(r), as a function of packing fraction. This peak is identified as the thermal remnant of the T=0 divergence found at the jamming transition in simulations of soft frictionless spheres at zero-temperature. Near where there is a peak in g_1 the particles become arrested on the time scale of the experiment.

Generic transient memory formation in disordered systems with noise:

Using the computation facilities provided by our DOE grant, we have studied a class of systems that combine information storage and memory loss in a single, uniform process. In the short term, these systems form concurrent memories of multiple external driving parameters. However, with no change in the driving, the systems gradually eliminate this information, selecting only one or two input values to be preserved at long times. With the addition of noise, all memories can be retained indefinitely. We have identified a class of systems with this behavior, giving as an example a model of non-Brownian suspensions, close to but below the jamming threshold density, under cyclic shear. We demonstrate that this is *generic*; a commonly observed phenomenon, not previously interpreted in terms of memory formation, has similar behavior to the multiple-pulse-duration memory in charge-density waves.

Future plans:

We are currently studying the nature of rearrangements under mechanical load, focusing on how they depend on the conditions under which load is applied and their connection to the low-frequency density of vibrational states. This will allow a better understanding of plastic flow in disorder solids as well as a direct comparison with the low-temperature properties of glasses where there is also an excess number of low-energy excitations.

We wish to continue our study of anharmonic effects near the jamming threshold. In particular we are interested in see how the stability of the amorphous solid is influenced by anharmonicity.

We are interested in seeing how plane waves affect the normal modes of vibration in a jammed system. This will be achieved by looking at the entire system as a crystal with a very large unit cell. The plane waves will then coexist with quasilocalized modes in the same frequency range.

We will continue to simulate the affect of small temperatures and small applied shear stresses on a model system that is close to the transition at Point J. This has to do with the shear modulus mentioned above but we also will continue to study how the relaxation time varies with temperature and pressure near the onset of jamming. We are interested in studying the affect of shear stress on the first peak in g(r) to see if it behaves in the same way as it does due to an increase in the pressure. In the case of pressure, this was observed in experiment as well as simulation. We would like to see if the effect of shear can also be seen in experiment.

We are studying whether it is possible to see echoes caused by the anharmonicity of the normal modes. Echoes, which are caused by phase collapse of many distinct oscillators, have been seen in two-level systems. They appear as spin echoes or photon echoes. Low-temperature properties of glasses have been interpreted in terms of two level systems and such systems should also produce echoes. However, they have not been seen in a system where the only excitations are the normal modes. We have seen indications that phonon echoes can be produced in our simulations of jammed systems. If so, this would offer an alternative explanation of some aspects of the low-temperature properties of glasses.

We are continuing our work to study the three dimensional structure and excitations of the colloidal system p-NIPAM. As mentioned above, this system undergoes a thermal jamming transition. While studies of this system have been undertaken in two dimensional geometries, we are attempting to study the more challenging experimental geometry in three dimensions to look for the density and shape of the normal modes.

A list of papers resulting from DOE sponsored research since 2009:

1. "Energy transport in jammed sphere packings," N. Xu, V. Vitelli, M. Wyart, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. **102**, 038001 (2009).

2. “Normal modes in model jammed systems in three dimensions,” L. E. Silbert, A. J. Liu and S. R. Nagel, Phys. Rev. E **79**, 021308 (2009).

3. “Thermal vestige of the zero-temperature jamming transition, ”Z. Zhang, N. Xu, D. T. N. Chen, P. Yunker, A. M. Alsayed, K. B. Aptowicz, P. Habdas, A. J. Liu, S. R. Nagel and A. G. Yodh, Nature **459**, 230 (2009).

4. “Excitations of ellipsoid packings near jamming,” Z. Zeravcic, N. Xu, A. J. Liu, S. R. Nagel and W. van Saarloos, Europhys. Lett. **87**, 26001 (2009).

5. “Equivalence of glass transition and colloidal glass transition in the hard-sphere limit,” N. Xu, T. K. Haxton, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. **103**, 245701 (2009).

6. “Heat transport in model jammed solids,” V. Vitelli, N. Xu, M. Wyart, A. J. Liu, S. R. Nagel, *Phys. Rev. E* **81**, 021301 1-14 (2010).

7. “Anharmonicity and quasi-localization of the excess low-frequency vibrations in jammed solids,” N. Xu, V. Vitelli, A. J. Liu, and S. R. Nagel, *Europhys. Lett.* **90**, 56001 1-6 (2010).

8. “The jamming transition and the marginally jammed solid,” A. J. Liu and S. R. Nagel, *Annual Reviews of Cond. Mat. Phys.* **1**, 347-369 (2010).

9. “Granular and Jammed Materials,” A. J. Liu and S. R. Nagel *Soft Matter*, **6**, 2869-2870 (2010); editorial for focus issue on Jamming. Guest editors: A. J. Liu and S. R. Nagel.

10. “The jamming scenario — an introduction and outlook,” A. J. Liu, S. R. Nagel, W. van Saarloos, and M. Wyart in *Dynamic heterogeneities in glasses, colloids, and granular media*, edited by L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, W. van Saarloos, accepted (Oxford University Press, 2011).

11. `“Generic transient memory formation in disordered systems with noise,” N. C. Keim and S. R. Nagel *Phys. Rev. Lett.* **107**, 010603 (2011).

12. “Mapping the slowdown of the dynamics of soft spheres onto hard sphere behavior,” M. Schmiedeberg, T. K. Haxton, S. R. Nagel, and A. J. Liu, *Europhys. Letts.* **96**, 36010 (2011).

13. “Mapping the glassy dynamics of soft spheres onto hard-sphere behavior,” M. Schmiedeberg, T. K. Haxton, S. R. Nagel and A. J. Liu, Europhys. Lett. **96**, 36010 (2011).

14. “Finite-size scaling at the jamming transition,” C. P. Goodrich, A. J. Liu and S. R. Nagel, Phys. Rev. Lett. (in press, 2012).

15. “Observation and Characterization of the Vestige of the Jamming Transition in a Thermal 3D System,” T. A. Caswell, Zexin Zhang, M. L. Gardel, and S. R. Nage1, submitted (2012). arXiv:1206.6802

Condensed Matter Theory

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Project Scope

Condensed matter theory research programs in the Materials Science Division at Argonne are currently carried out in the areas of superconductivity, spectroscopy, magnetism, and mesoscopics, with emphasis on synergistic interactions with various experimental programs within MSD, Argonne, and beyond. Condensed matter theory research contacts the materials research program at Argonne through a mix of individual theoretical studies, and collaborative studies with experimental groups. These frequently involve detailed modeling of complex materials and phenomena for which new theoretical methods and concepts are developed as needed.

Recent Progress

We studied the effect of a single magnetic impurity on the transport properties of helical edge states in spin-Hall devices. We found that such an impurity does not affect the electrical conductance, but suppresses the thermal conductance of the system [13].

We expressed the conductance of uniform quantum wires in terms of the equilibration rate of the electron system. These results apply for any strength of the electron-electron interactions and any length of the wire [10, 12].

We explored the thermal transport in quantum wires at weak interaction strength. We found that in relatively short wires the interactions between electrons reduce the thermal conductance while the electrical conductance remains quantized [11].

We calculated the Nernst effect for underdoped cuprates based on pair fluctuations, and found that the observed temperature dependence could be reproduced if the influence of the pseudogap on suppressing the current vertices is taken into account [8].

We developed a new theory for the hidden order phase of heavy fermion URu_2Si_2 based on a novel spin liquid state, and found that several observed properties, including the breaking of the tetragonal symmetry of the spin susceptibility, could be accounted for [6].

We mapped out the electronic phase diagram of cuprates using photoemission data, and showed that the doping dependence of the various phase lines was consistent with that predicted for a doped Mott insulator [4].

We elucidated the presence of a spin nematic phase for undoped iron pnictides above their magnetic ordering temperature using inelastic neutron scattering, and found that the data could be modeled by assuming an anisotropic in-plane exchange interaction [3].

We explained the doping dependence of the spin resonance seen in inelastic neutron scattering data in iron pnictides from the change of hole and electron Fermi surfaces with doping, in particular describing both its energy and momentum dependence [2].

We found that cuprates were on the borderline between stripe and checkerboard charge ordering using a Ginzburg-Landau theory with coefficients extracted from the electronic dispersion determined from photoemission data [arXiv:1102.5443].

Future Plans

Low-energy properties of interacting electron systems are commonly described by the Luttinger liquid theory. One of the limitations of this approach is its inability to account for the processes of backscattering of electrons that are responsible for the equilibration of the system. We will extend the theory to account for such processes and evaluate the equilibration rate in terms of the parameters of the excitation spectrum of the system. This result will have important implications for the transport properties of quantum wires.

In an interacting one-dimensional electron system, the particle excitations decay even at zero temperature whereas the holes remain stable. We will explore the decay of holes at non-zero but small temperatures by accounting for their scattering by the thermally excited quasiparticles. This will be accomplished by treating holes as mobile impurities in a Luttinger liquid. We will then generalize our results to the case of a foreign particle added to the system.

At strong interactions an electron system forms the so-called Wigner crystal with excitations similar to the phonons in an ordinary crystal. In one dimension, the Wigner crystal differs from the conventional Luttinger liquid theory in that the spectrum of phonons is not entirely linear. We will take advantage of this non-linearity to study the scattering of phonons and the relaxation of their distribution function. We expect that this will enable us to study the thermal conductance of strongly interacting quantum wires.

Recent x-ray dichroism results on monoclinic copper oxide indicate the presence of an unusual symmetry breaking in the commensurate antiferromagnetic phase that is reminiscent of orbital currents. We will explore this possibility by calculating the resonant x-ray diffraction pattern expected for such orbital currents in copper oxide, including the effect of anapoles and magnetic quadrupoles. We will then extend this approach to address data on underdoped cuprates.

Recent neutron, STM, and ARPES data on the charge density wave material $NbSe_2$ indicate the presence of unusual spectroscopic features reminiscent of cuprates, including the possibility of a pseudogap. We will address such data by calculating spectroscopic features assuming either a single Q or triple Q state, and then consider the influence of fluctuations above the ordering temperature.

In many heavy fermion quantum critical systems, transport data indicate a linear in temperature resistivity. Theories for such materials can account for a linear T inverse lifetime for single particle states, but find that the transport lifetime should involve a higher power in temperature. We wish to address this issue within the context of a Kondo breakdown scenario, where we speculate that the localized nature of the f electrons conspires to keep the transport lifetime the same as the single particle one.

Spectroscopic data on underdoped cuprates differ dramatically depending on the group reporting them. We believe that these differences are due to how the samples are prepared. We plan to analyze the effects of various dopants, including calcium, lanthanum, and dysprosium, and see how photoemission spectra differ as one goes from one class of materials to another, and correlate this with differences in structural and magnetic properties.

We will explore the sensitivity of charge ordering in cuprates to variations in the electronic structure by calculating the phase diagram within a Ginzburg-Landau approach, using different assumed tight binding dispersions for the electronic structure. We will then extend this methodology to charge density wave systems like $NbSe_2$.

Publications (2011-2012)

1. S. Di Matteo and M. R. Norman, "Orbital currents, anapoles, and magnetic quadrupoles in CuO", Phys. Rev. B 85, 235143 (2012).

2. J.-P. Castellan, S. Rosenkranz, E. A. Goremychkin, D.Y. Chung, I. S. Todorov, M. G. Kanatzidis, I. Eremin, J. Knolle, A.V. Chubukov, S. Maiti, M. R. Norman, F. Weber, H. Claus, T. Guidi, R. I. Bewley and R. Osborn, "Effect of Fermi Surface Nesting on Resonant Spin Excitations in $Ba_{1-x}K_xFe_2As_2$", Phys. Rev. Lett. 107, 177003 (2011).

3. L. W. Harriger, H. Q. Luo, M. S. Liu, C. Frost, J. P. Hu, M. R. Norman and P. Dai, "Nematic spin fluid in the tetragonal phase of $BaFe_2As_2$", Phys. Rev. B 84, 054544 (2011).

4. U. Chatterjee, D. Ai, J. Zhao, S. Rosenkranz, A. Kaminski, H. Raffy, Z. Z. Li, K. Kadowaki, M. Randeria, M. R. Norman and J. C. Campuzano, "Electronic phase diagram of high-temperature copper oxide superconductors", Proc. Natl. Acad. Sci. 108, 9346 (2011).

5. Y. Sassa, M. Radovic, M. Mansson, E. Razzoli, X. Y. Cui, S. Pailhes, S. Guerrero, M. Shi, P. R. Willmott, F. Miletto Granozio, J. Mesot, M. R. Norman, and L. Patthey, "Ortho-II band folding in $YBa_2Cu_3O_{7-\delta}$ films revealed by angle-resolved photoemission", Phys. Rev. B 83, 140511(R) (2011).

6. C. Pepin, M. R. Norman, S. Burdin and A. Ferraz, “Modulated Spin Liquid: A New Paradigm for URu_2Si_2”, Phys. Rev. Lett. 106, 106601 (2011).

7. S. R. Julian and M. R. Norman, “Genetics and g-factors”, Nat. Phys. 7, 191 (2011).

8. A. Levchenko, M. R. Norman and A. A. Varlamov, “Nernst effect from fluctuating pairs in the pseudogap phase of the cuprates”, Phys. Rev. B 83, 020506(R) (2011).

9. K. A. Matveev, A. V. Andreev and M. Pustilnik, “Rate of equilibration of a one-dimensional Wigner crystal”, Physica B 407, 1898 (2012).

10. K. A. Matveev and A. V. Andreev, “Equilibration of a spinless Luttinger liquid”, Phys. Rev. B 85, 041102 (2012).

11. A. Levchenko, T. Micklitz, Z. Ristivojevic, and K. A. Matveev, “Interaction effects on thermal transport in quantum wires”, Phys. Rev. B 84, 115447 (2011).

12. K. A. Matveev and A. V. Andreev, “Equilibration of Luttinger Liquid and Conductance of Quantum Wires”, Phys. Rev. Lett. 107, 056402 (2011).

13. Y. Tanaka, A. Furusaki and K. A. Matveev, “Conductance of a Helical Edge Liquid Coupled to a Magnetic Impurity”, Phys. Rev. Lett. 106, 236402 (2011).

14. A. A. Golubov and A. E. Koshelev, “Thermal conductivity in the mixed state of a superconductor at low magnetic fields”, Phys. Rev. B 83, 094521 (2011).

15. A. E. Koshelev, A. I. Buzdin, I. Kakeya, T. Yamamoto, and K. Kadowaki, “Fluctuating pancake vortices revealed by dissipation of the Josephson vortex lattice”, Phys. Rev. B 83, 224515 (2011).

16. L. N. Bulaevskii and A. E. Koshelev, “Intrinsic Josephson effect in layered superconductors”, in *100 Years of Superconductivity*, eds. H. Rogalla and P. H. Kes (Chapman & Hall, 2011).

17. J. Lin and A. J. Millis, “Optical and Hall conductivities of a thermally disordered two-dimensional spin-density wave: Two-particle response in the pseudogap regime of electron-doped high-T_c superconductors”, Phys. Rev. B 83, 125108 (2011).

18. A. Levchenko, Z. Ristivojevic, and T. Micklitz, “Interaction-induced corrections to conductance and thermopower in quantum wires”, Phys. Rev. B 83, 041303 (2011).

19. T. Micklitz and A. Levchenko, “Thermalization of Nonequilibrium Electrons in Quantum Wires”, Phys. Rev. Lett. 106, 196402 (2011).

Theory of Oxide Nanostructures: Polarity, Dimensionality, and Strong Interactions.

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1 Project Scope

This research project focuses on layered oxides, mostly pertaining to transition metal oxides, with specific attention to effects of low dimensionality and strong interactions. Novel electronic phases arising in oxide heterostructures are intriguing not only from a fundamental point of view, but are anticipated to be important for future device applications (very thin 2DEGs, polarized carriers, etc.). A prominent example is the two-dimensional electron gas realized at the interface between the two simple band insulators $LaAlO_3$ (LAO) and $SrTiO_3$ (STO). Due to the valence mismatch (layers of differing polarity), the interface will have either excess electrons or holes, depending on the STO termination layer, and it is this question of how local charge neutrality is accommodated that lies at the foundation of the scientific questions. A number of unexpected phenomena occur, first of all the two dimensional electron gas (2DEG) observed by all groups but depending greatly on growth parameters, and extending to magnetism and superconductivity, and even their coexistence. A large variation especially in conduction behavior has attracted close attention, and is now understood to some degree by taking into account three aspects: the likely presence of oxygen vacancies produced by the deposition procedure, lattice deformations (including cation disorder) and an electronic reconstruction at the interface. Close connections of theoretical modeling with experimental groups is important for clarifying issues. Theoretical issues range from the effects of strong interactions – both on-site Coulomb repulsion on the transition metal ions and long range Coulomb interactions across a dielectric slab – to the importance of ionic displacements giving large polarization effects, and on to the impacts of orbital occupation and carrier density.

2 Recent Progress

Our progress lies in three areas, all deriving from the “strongly interacting layered oxides” theme of this project but leading to separate, distinctive new physics.

2.1 A semi-Dirac, semi-Weyl, semi-half metal in an oxide nanostructure

Throughout this grant period our group has worked to illuminate the origin of, and the expected properties of, this unique type of quasiparticle system discovered computationally at the end of the previous grant that ties in with three highly active topics in condensed matter physics: graphene science, oxide nanostructures, and topological character. After working on oxide polar interfaces (LAO/STO) for some time, we asked whether non-polar interfaces between oxides held the possibility for surprises. Studying VO_2/TiO_2 multilayers, we discovered computationally a new, so far unique, type of 2D point ‘Fermi surface’ system: linear (Weyl) dispersion $\pm v k_y$ in one direction, quadratic (Dirac) dispersion $k_x^2/2m^*$ in the perpendicular direction:

$$\varepsilon_k = \pm\sqrt{(\frac{k_x^2}{2m^*})^2 + (v k_y)^2} = \pm\varepsilon_o\sqrt{K_x^4 + K_y^2}; \quad K_j \equiv \frac{k_j}{2m^* v}; \quad \varepsilon_o = 2m^* v^2. \tag{1}$$

Such a system, which we dubbed semi-Dirac for simplicity, lies midway between graphene and conventional zero-gap semiconductors in many respects. Unlike both, however, it displays extreme anisotropy in its electronic structure and and low-energy properties. Alas, unlike the point of essence in graphene, this point is non-topological, but at least it is non-topological in a non-trivial manner: the Berry curvature $\nabla \times \vec{A}_k$ corresponds to the sum of two oppositely directed topological points which however coincide in k-space, which although non-zero has a total effect that vanishes by symmetry.

More on linear bands. The quasilinear bands in the topologically trivial skutterudite narrow gap insulator $CoSb_3$ were studied under adiabatic, symmetry-conserving displacement of the Sb sublattice. In this cubic, time-reversal and inversion symmetric system, a transition from trivial insulator to topological insulator occurs through a point Fermi surface critical point in which massless (Weyl) bands appear; moreover, they are degenerate with massive bands. Spin-orbit coupling coupled with tetragonal strain opens the gap required to give the topological insulator. The mineral skutterudite ($CoAs_3$) and $CoSb_3$ are near the critical point in their natural state.

2.2 Overlayers on STO and its relation to electronic reconstruction

A wealth of intriguing properties emerge in the seemingly simple system composed of the band insulators $LaAlO_3$ and $SrTiO_3$ such as a quasi two dimensional electron gas, superconductivity and magnetism. We have explored the strong dependence of the electronic properties on the surface and interface termination, the finite film thickness and confinement effects, lattice polarization and defects. A further aspect that that has been studied is how the electronic behavior and functionality can be tuned by a $SrTiO_3$ capping layer, by adsorbates, and by metallic contacts. First principles calculations revealed that adding a metallic overlayer on $LaAlO_3/SrTiO_3(001)$ eliminates the electric field within the polar $LaAlO_3$ film and thus suppresses the thickness-dependent insulator-to-metal transition observed in uncovered films. Independent of the $LaAlO_3$ thickness both the surface and the interface are metallic, with an enhanced interface carrier density relative to $LaAlO_3/SrTiO_3(001)$ after the metallization transition. Moreover, a monolayer thick metallic Ti-contact exhibits a magnetic moment and for a thin $SrTiO_3$-substrate induces a spin-polarized 2D electron gas at the n-type interface due to confinement effects.

First-principles calculation was used to study the structural and electronic features of the low-dimensional oxide structure, $SrTiO_3/Sr_{1-x}La_xTiO_3$ ($x = 0.25$) superlattices, constructed by sub-monolayer low-dimensional La doping into $SrTiO_3$. We demonstrated a dimensionality crossover from three-dimensional (3D) to two-dimensional (2D) electronic behavior in this multilayer system. Two types of carriers, one confined to 2D and the other extended, are induced in the low-dimensional structure, leading to distinct tunable (3D 2D) transport characteristics that will enable the study of many properties (e.g., superconductivity) through this change in dimensionality.

2.3 Mott insulating behavior in a non-half-filled band nickelate

The recently synthesized layered nickelate $La_4Ni_3O_8$, with its cuprate-like NiO_2 trilayer, seemingly requires a 3Ni ($d^{8.67}$) $\rightarrow$ Ni1 (d^8)+2Ni2 (d^9) charge order, together with strong correlation effects, to account for its insulating behavior. Using density functional methods including strong intra-atomic repulsion (Hubbard U), no such charge-ordered insulating state could be found. Instead, we obtained an insulating state via a new mechanism: *without charge order*, Mott insulating behavior arises based on quantum coupled, spin-aligned *molecular* Ni2-Ni1-Ni2 d_{z^2} states across the NiO_2 trilayer (rather than being based on atomic states). Antiferromagnetic ordering within layers is necessary to narrow the bandwidth and allow d_{z^2} coupling to become dominant. The weak and frustrated magnetic coupling between cells may account for the small spin entropy that is removed at the Néel transition at 105 K and the lack of any diffraction peak at the Néel point.

Three low-valence layered nickelates with general formula $La_3Ni_2O_{7-\delta}$ ($\delta = 0.0, 0.5, 1$) have been studied by ab initio techniques. Both the insulating and the metallic limits were analyzed, together with the compound at the Mott transition ($\delta = 0.5$; Ni^{2+}) that shows insulating behavior, with all Ni atoms in a S = 1 high-spin state. The compound in the $\delta = 1$ limit ($La_3Ni_2O_6$), with mean formal valence $Ni^{1.5+}$ and hence nominally metallic, nevertheless shows a correlated molecular insulating state, produced by the quantum confinement of the NiO_2 bilayers and the presence of mainly $d(z^2)$ bands (bonding-antibonding split) around the gap. The metallic compound shows a larger bandwidth of the e_g states that can sustain the experimentally observed paramagnetic metallic properties. The evolution of the in-plane antiferromagnetic coupling with the oxygen content was analyzed, providing similarities of this series of compounds to the layered superconducting cuprates.

Our ab initio calculations predicted a metal-insulator, high- to low-spin transition at zero temperature to occur in $La_4Ni_3O_8$ at moderate pressures, driven by the spin-state transition. The spin-state transition that is observed at 105 K at ambient pressure from a low-temperature high-spin state to a high-temperature low-spin state had been observed to be shifted to lower temperatures as pressure is applied. From our calculations we find that a smaller unit cell volume favors the metallic low-spin state, which becomes more stable at 5 GPa. Experimental verification of this spin-state transition in our predicted pressure range has just been reported. Similar physics appears in the related compound $La_3Ni_2O_6$, but on a different energy scale, which may account for why the transition has not been observed in this material.

3 Planned Activities

Our grant expires in ∼6 months and decisions on extensions or new directions of research are in rapid development but not yet fixed. For the remainder of this grant period:

- we will complete the current work on the low energy behavior of a semi-Dirac system by student S. Banerjee, with a Phys. Rev. B paper to be completed and published. The aspects he has studied include: Hall coefficient, Faraday rotation, cyclotron frequencies and orbits, plasmon dispersion and its angular dependence, spin and orbital susceptibilities, and Klein tunneling. Study of quantum chaos in a semi-Dirac system is in progress.

- the extensive work on the peculiar layered nickelates $La_{n+1}Ni_nO_{2n}$, with collaborator V. Pardo, has stimulated experimental work and our prediction of a spin-state transition at ∼ 5 GPa has been verified. Student Y. Quan has obtained unexpected information relating directly to the 'charge ordering' transition occurring in the bulk rare earth (R) nickelates $\mathcal{R}NiO_3$: differences in $3d$ occupation can be identified objectively (without any volume integration), and several "charge order" transitions do not involve *any* rearrangement in $3d$ charge. It is for us a priority to follow up on this, building a correct understanding of the microscopic basis for these "charge-ordering" transitions which usually involve a structural change of symmetry and often are metal-insulator transitions as well.

- our studies of electronic reconstruction in polar nanolayers, and the effects of overlayers, especially metallic contact layers, have been making contact with experimental data. In this field, however, interpretation of essentially all of the data is clouded by defects, many of which release carriers but whose extent and character is unclear. We are considering a set of calculations involving intermixing of La and Sr at an LAO/STO interface that could clarify the effects of this kind of disorder or non-stoichiometry.

4 Publications

1. Avoiding the polarization catastrophe in $LaAlO_3$ overlayers in $SrTiO_3$ through polar distortion. R. Pentcheva and W. E. Pickett, Phys. Rev. Lett. **102**, 107602 (2009).
2. Half-metallic semiDirac point generated by quantum confinement in TiO_2/VO_2 nanostructures. V. Pardo and W. E. Pickett, Phys. Rev. Lett. **102**, 166803 (2009).
3. Tight-binding modeling and low-energy behavior of the semi-Dirac point. S. Banerjee, R. R. P. Singh, V. Pardo, and W. E. Pickett, Phys. Rev. Lett. **103**, 016402 (2009).
4. Metal-insulator transition through a semi-Dirac point in oxide nanostructures: VO_2 (001) layers confined within TiO_2. V. Pardo and W. E. Pickett, Phys. Rev. B **81**, 035111 (2010).
5. Role of Crystal Symmetry in the Magnetic Instabilities of β-YbAlB4 and α-$YbAlB_4$. D. A. Tompsett, Z. P. Yin, G. G. Lonzarich, and W. E. Pickett, Phys. Rev. B **82**, 235101 (2010).
6. Quantum Confinement Induced Molecular Mott Insulating State in $La_4Ni_3O_8$. V. Pardo and W. E. Pickett, Phys. Rev. Lett. **105**, 266402 (2010).
7. Dirac Point Degenerate with Massive Bands at a Topological Quantum Critical Point. J. C. Smith, S. Banerjee, V. Pardo, and W. E. Pickett, Phys. Rev. Lett. **106**, 056401 (2011).
8. Tuning Two-dimensional or Three-dimensional Electron Gases by Submonolayer La Doping of $SrTiO_3$. P. V. Ong, Jaichan Lee, and W. E. Pickett, Phys. Rev. B **83**, 193106 (2011).
9. Metal-Insulator Transition in Layered Nickelates $La_3Ni_2O_{7-\delta}$ ($\delta = 0.0, 0.5, 1.0$). V. Pardo and W. E. Pickett, Phys. Rev. B **83**, 245128 (2011).
10. Evaluation of Compensated Magnetism in La_2VCuO_6: Exploration of Charge States. V. Pardo and W. E. Pickett, Phys. Rev. B **84**, 115134 (2011).
11. Termination Control of Electronic Phases in Oxide Thin Films and Interfaces: $LaAlO_3/SrTiO_3(001)$. R. Pentcheva, R. Arras, K. Otte, V. G. Ruiz Lopez, and W. E. Pickett, Phil. Trans. Roy. Soc. A (2012) .
12. Tuning the Two-dimensional Electron Gas at the $LaAlO_3/SrTiO_3(001)$ Interface by Metallic Contacts. V. G. Ruiz Lopez, R. Arras, W. E. Pickett, and R. Pentcheva, Phys. Rev. B **85**, 125404 (2012).
13. Pressure-induced Metal-insulator and Spin-state Transition in Low-valence Layered Nickelates. V. Pardo and W. E. Pickett, Phys. Rev. B **85**, 045111 (2012).

Atomistic study of ultrafast dynamics in multifunctional materials in bulk and nanoforms

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Project Scope. The program focuses on the computational exploration of ultrafast dynamics in multifunctional materials such as ferroelectrics and multiferroics. The research effort is directed towards development and use of computational tools that allow the study of the intrinsic high-frequency dynamics of such materials at both macro- and nano- scales. In particular, we explore the interaction of ferroelectric materials with high-frequency excitations in order to achieve fundamental understanding of ultrafast dynamical processes including the energy conversion. Special emphasis is on the ultrafast dynamics in nanostructures, such as ultrathin films, nanowires, nanodots. The research utilizes high-performance computing including the Department of Energy super-computing resources.

Recent progress.

Ultrafast dynamics at the nanoscale: ulrathin films.

Nanosize objects are known to have properties that are very different from their bulk counterparts. For example, ferroelectric nanostructures exhibit a variety of dipole patterns and states that are prohibited in the bulk. Interestingly, nanoscale ferroelectric films and superlattices can develop nanostripes that are nanoscopic regions of “up” and “down” polarizations. While the static properties (such as nanodomain morphology at equilibrium) may follow the general trends and laws for ferroelectric domains, their dynamical properties deviate substantially. Such dynamical properties at nanoscale are of technological importance since they are at the heart of polarization switching (and, therefore, ultradense ferroelectric memory technology) and contribute to most of the materials responses such as dielectric and piezoelectric responses. Given the need for device miniaturization and strong deviation of ferroelectrics nanoscale dynamics from the dynamics of their macroscopic counterparts, the deep atomistic knowledge of ferroelectrics *nanodynamics* is highly desirable. In particular, one may wonder if and how the intrinsic dynamics of ferroelectric domains will change at the nanoscale.

Using first-principles-based computational technique we have studied the nanodynamics of ferroelectric ultrathin films made of Pb($Ti_{0.6}Zr_{0.4}$)O_3 ferroelectric alloy with thicknesses ranging from 2 to 20 nm. An example of the ground state nanostripe pattern is given in Fig.1. The area that separates the regions with opposite polarization is the nanowall. To study the oscillatory dynamics of these nanowalls we use non-equilibrium Molecular Dynamics (MD) and apply sub-switching *ac* electric field with frequencies 1 GHz - 4 THz along the film's out-of-plane direction at $T = 10$ K. Since the direction of the electric field alternates, so does the direction of the domain wall motion resulting in the oscillatory dynamics of the nanowall.

We first focus on the oscillatory dynamics in the thinnest film and trace the time evolution of the average nanowall's displacement from its equilibrium position ΔX. After the first few transient oscillations the dynamics reaches its steady state where the displacement follows the harmonic solution $\Delta X = X \sin(\omega t + \phi)$, indicating that the nanowall moves as an elastic object. Here X is the amplitude of the nanowall's displacement, ω is the *ac* field frequency, t is time, and ϕ is the phase-shift with respect to the electric field. By analyzing the nanowall's response to an electric field of different frequencies we obtain dependencies $X(\omega)$ and $\phi(\omega)$ given in Fig.1. Below 0.3 THz the domain response is independent of the frequency (Fig.1(a)) with the nanowalls oscillating in phase with the electric field (Fig.1(b)). Above 1.5 THz the nanowalls have difficulty following the electric field as indicated by the drastic decrease in the amplitude X and increase in phase-shift ϕ. Surprisingly, there are *two* peaks in the amplitude of nanowall's oscillations that occur at 0.7 THz (low-frequency peak) and at 3.2 THz (high-frequency peak). Existence of these peaks suggests that the nanowalls exhibit a resonance dynamics and must have a mass associated with them.

We developed a general theory of nanowall dynamics. When applied to our computational findings the theory revealed that indeed at the nanoscale the domain wall behaves as an elastic object and has a mass associated with it. The nanowall mass is size-dependent and gives rise to a unique size-driven transition from resonance to relaxational dynamics in ultrathin films. We also found an unusual dynamical coupling between nanodomains and mechanical deformations that could potentially be used in ultrasensitive electromechanical nanosensors.

Ultrafast dynamics at the nanoscale: ultrathin nanowires.

Polarization reversal in ferroelectrics has been a subject of intense interest for many years

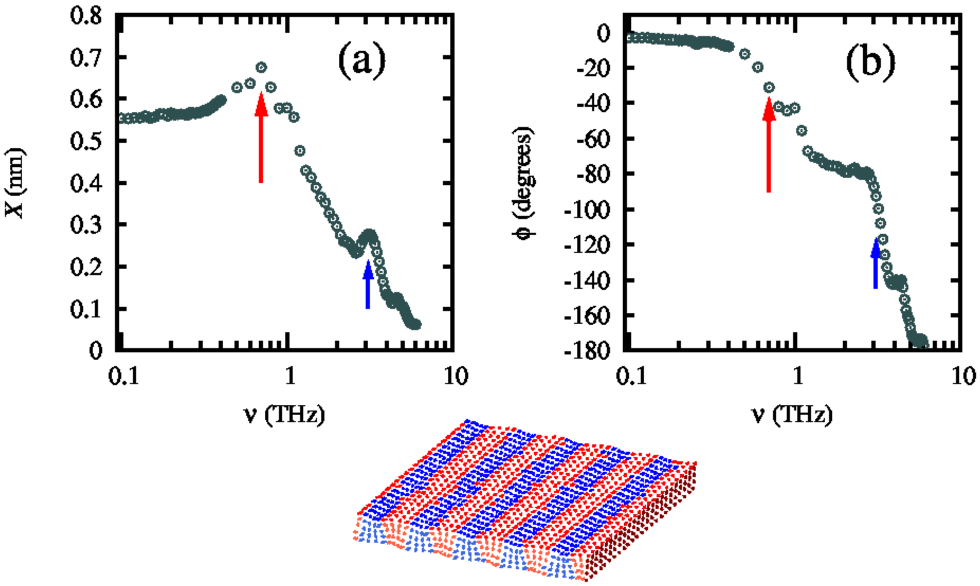

FIG. 1. Frequency dependent response of a nanowall to the electric field in a 0.2 nm thick film. The arrows indicate positions of the peaks. The nanostripe morphology is shown on the bottom.

owing to both its scientific appeal and practical utility. In the recent years the interest has increased even further thanks to the expectations of achieving ultrafast polarization reversal at the nanoscale. While most of the studies up to now are focused on the polarization reversal in ferroelectric thin films, we report the intrinsic dynamics of ultrafast polarization reversal in ferroelectric nanowires. Using atomistic first-principles-based simulations, we traced the time evolution of polarization under applied electric field to reveal the existence of two competing polarization reversal mechanisms: (i) domain-driven and (ii) homogeneous.

We used classical MD with the force-field derived from a first-principles-based effective Hamiltonian to investigate seven ferroelectric ultrathin nanowires made of $\mathrm{PbTi_{0.6}Zr_{0.4}O_3}$ ferroelectric alloy and with square cross sections with average diameters ranging from 3.2 to 8 nm. To study the dynamics of polarization reversal in such nanowires we subject them to *dc* electric field E applied in the direction opposite to the direction of polarization. Our simulations typically run for 15 ps.

We found that under lower electric fields the polarization reversal occurs via formation and propagation of coaxial nanodomain. The snapshots of domain structure in the nanowire cross section are given in Fig.2. However, as the applied field increases the polarization reversal occurs almost uniformly in the nanowire cross section indicating the activation of homogeneous polarization reversal mechanism. By carrying out the microscopic analysis of

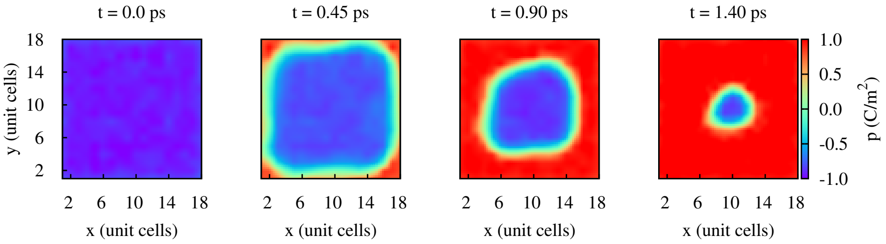

FIG. 2. Snapshots for the dipole patterns in the nanowire cross section obtained for $E = 2.8$ MV/cm. The red and blue colors indicate the areas with dipoles pointing “up” and “down”, respectively.

the dipoles reversal dynamics we derived the fundamental law that drives such dynamics and relates the polarization reversal rate t_{sw}^{-1} to the strength of the applied electric field E

$$t_{sw}^{-1}(E) = t_0^{-1}\sqrt{E - E_c}, \tag{1}$$

where t_0^{-1} is a constant and E_c is the coercive field. This law is in excellent agreement with both our computational findings and recent experimental reports in the literature.

Future plans

In the remaining year of the project we will continue with the studies of ultrafast dynamics in ferroelectrics and multiferroics at the nanoscale. We will focus on the non-equilibrium dynamics in such materials. We have recently identified new ways to use non-equilibrium conditions to generate and control electric fields within ferroelectric materials. This appears to be promising for potential photovoltaic applications where such internal fields can be used to decrease the carriers recombination rates. The work under the current project has also allowed to identify new research directions such as ultrafast dynamics in the presence of interfaces and extrinsic free carriers.

Publications

1. “Nanodynamics of ferroelectric ultrathin films”, Qingteng Zhang, R. Herchig and I. Ponomareva, Phys. Rev. Lett. **107**, 177601 (2011).
2. I. Ponomareva and S. Lisenkov, “Bridging the Macroscopic and Atomistic Descriptions of the Electrocaloric Effect”, Phys. Rev. Lett. **108**, 167604 (2012).
3. I. Ponomareva, A. Tagantsev, and L. Bellaiche, “Finite-temperature flexoelectricity in ferroelectric thin films from first principles”, Phys. Rev. B. **85**, 104101 (2012).

Theoretical and Computational Studies of Functional Nanoalloys and other Nanomaterials

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Project Scope

Recognizing that nanoalloys are advanced materials of immense scientific and technological interest, our work focuses on understanding structure-function relationship to enable the *long term goal of rational design of functional nanomaterials*. Our interest is in understanding factors that control the *magnetic* and *optical* properties of these materials. For the purpose we develop and apply appropriate techniques which require more accurate description of *excited and bound states, and other correlation effects* than afforded by density functional theory (DFT). To ensure dynamically stability of nanostructures we also determine their vibrational dynamics and *thermodynamic*s. Additionally, we probe non-equilibrium behavior of nanosystems, as in the presence of external fields. Through systematic study of characteristics for a set of selected materials and corroboration of their results with experimental data, we formulate rules and guidelines for predictive material design. The research stages include determination of: 1) the geometric and electronic structure of lowest energy structures using reliable schemes (e.g.DFT); 2) vibrational dynamics and thermodynamics through density functional perturbation theory (DFPT); 3) magnetic properties via our nano-DFT+DMFT approach; 5) optical response, using time dependent density functional theory (TDDFT) and its density matrix version as proposed by us for systems with bound states, multiple excitation and strong correlation effects. We also intend to develop a non-equilibrium nano DFT+DMFT for extracting non-equilibrium behavior of systems.

Recent Progress

Development of the nano-DFT+DMFT approach:
We have recently developed a Nano DFT + nonhomogeneous DMFT approach for reliable and efficient examination of electron-electron correlation effects using an Iterative Perturbative Theory (IPT) impurity solver and applied it to examine the magnetic properties of Fe and FePt nanoparticles (NPs) consisting of 3-27 atoms. In all cases inclusion of dynamical effects leads to a reduction of NP magnetization and better agreement with experiments (where available) than the DFT+U approach (see Table below). Ours is the first demonstration of suitability of the DFT+DMFT approach for nanosystems. As seen in Table 1, our approach (labeled DMFT) provides the best agreement with the calculated size dependent values of the magnetization.

NPs	DFT	DMFT	DFT+U	Experiment
Fe11	3.24	2.73(U=2.3)	3.29(U=2.3)	4.80
Fe13	3.23	2.61(U=2.3)	3.22(U=2.5)	2.55
Fe15	3.20	2.76(U=2.2)	3.15(U=2.2)	2.72
Fe17	3.06	2.87(U=2.3)	3.09(U=2.3)	2.86
Fe19	3.05	2.94(U=2.4)	3.07(U=2.4)	2.92

Table 1 Comparison of size dependent magnetic moment

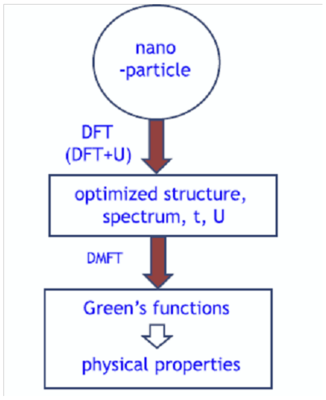


Fig. 1 Schematics of DFT+DMFT

Development of time-dependent density-matrix functional theory for ultrafast processes

We have formulated a time-dependent density-matrix functional theory (TDDMFT) approach to study ultrafast phenomena and higher-order correlation effects like biexcitons in various bulk systems and nanostructures. An interesting result is that non-zero biexcitonic binding energies may be obtained within the adiabatic approximation. To test the approach, we have calculated the biexcitonic binding energies using different exchange-correlation (XC) potentials for bulk CuCl, CuBr, CdS and ZnO, materials with rather large biexcitonic binding energies. We show that the excitonic, biexcitonic and other higher-order correlation effects are more pronounced when the XC kernel contains a Coulomb singularity. The role of non-adiabaticity of the XC potential in description of the correlation effects within the approach is analyzed.

Optical properties of transition metal-doped gold clusters

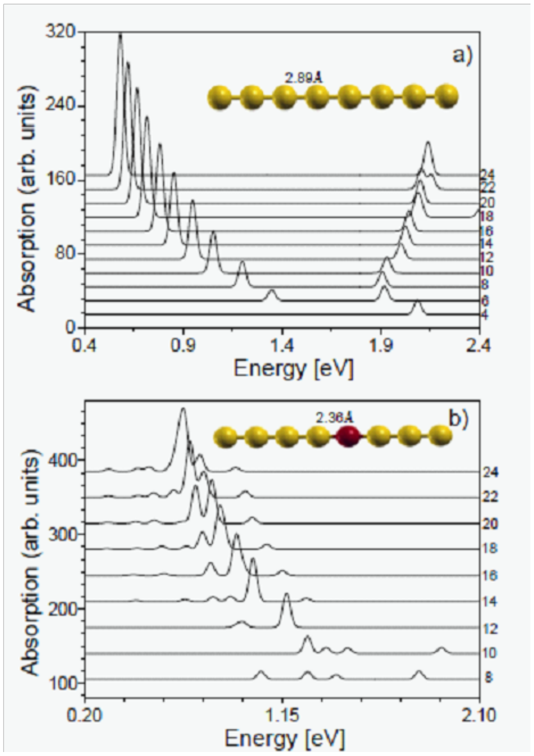
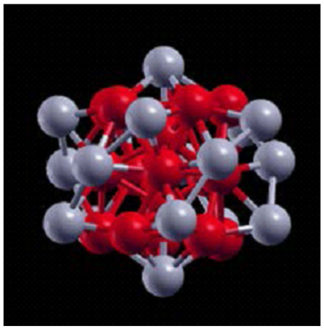


Fig.2. TDFFT results for the oscillator strength as a function of energy for: a) Au chains as a function of number of atoms (right y-axis). b) AuN-1Ni clusters (N at right top). The Au-Au distance of 2.89Å corresponds to the experimental results in the c

We have applied TDDFT to investigate the changes in the optical properties of small Au chains when doped by transition metal (Ni, Fe, Rh) atoms. We find that in the case of non-doped gold chains a collective plasmon mode forms when the number of atoms is larger than 10 (Fig.2a)). The plasmon energy approaches asymptotically a value of ~0.6eV as the number of atoms increases. The plasmon peak of the gold chains splits into two peaks when doped with some TM (Ni, Fe, Pd) atoms. We find that the additional peak is associated with a local plasmonic mode which corresponds to charge oscillations around the potential minimum related to the d-orbital states of the impurity atoms. The effect takes place when the number of TM atoms is much smaller than the number of Au atoms. This is the first demonstration of the constructive role of the TM atoms in the plasmonic response of the noble-TM clusters..

Anomalously soft and stiff modes of transition-metal nanoparticles

Applying DFPT to 34- and 38-atom AgCu, PtFe, and Cu NPs, we relate their enhanced low- and high-energy tails n the vibrational density of state (with respect to bulk) to the . radial breathing and non-radial tidal vibrations, analogous to the pulsations observed in variable stars. Additionally, we show that the features in the high frequency end can help identify whether a nanoparticles has core-shell or bulk-like structure, the former having more pronounced modes above the bulk band. We provide measures to relate geometric structure with EXAFS data while establishing that the concept of Debye temperature does not work for NPs, as the density of states are far from Debye (Fig.3).



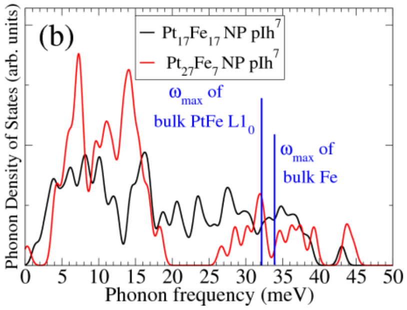


Fig. 3 The core shell NP has more modes above the bulk band

Future Plans

Nano-DFT+DMFT code with the Quantum Monte Carlo Impurity solvers

The accurate solver of the single-impurity problem is the most important issue in the DMFT, both for the extended systems and the nano-case. The single impurity problem in DMFT is finding the single-electron (Anderson impurity) Green’s function for the given site/orbital treating the rest of the electron system as a bath. At present, we use the Iterative Perturbation Theory (IPT) approximation for the solver. In this approximation the expression for the single-electron self-energy is a function of the second order (in the local Coulomb repulsion parameter) self-energy, chosen in such a way that the resulting self-energy satisfies correctly some known limiting cases (like the high-frequency and large-Coulomb repulsion limits). The main advantage of the approximation is its simplicity which leads to a rather high speed of the calculations. As we have shown in our calculations, it leads to a very accurate description of the magnetization of the Fe_{11}-Fe_{19} iron clusters, much better comparing to the DFT case. However, in general it would be very helpful to have a solver in which formally no approximation is made. One of the most often used is the (determinant) Quantum Monte Carlo solver, in which the exact evaluation of the path integrals is done in order to calculate the electron Green’s function. We plan to implement the QMC solver (with the Hirsch-Fye method) together with the IPT one into the Fireball code.

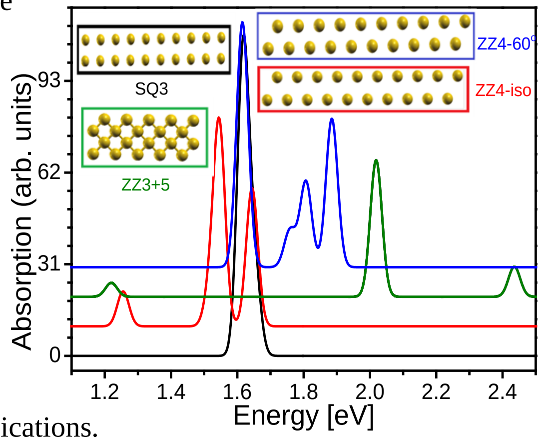
Magnetic properties of nanoparticles: application of Nano-DMFT+DFT

We will continue to investigate the structure-magnetism relationship for nanoalloys using DFT and the Nano-DMFT+DFT methods. Of particular interest will be Pt-Fe, Rh-Fe, and Rh-Co nanoalloys, to address the following issues.

- how magnetic properties of 3d TM NP change when doped with unfilled 4d- (Rh) and 5d-(Pt) shells.
- Existence of magnetism in the 4d-(Rh) and 5d-(Pt) atoms. In the bulk, these systems are non-magnetic, but small NP may demonstrate magnetism.
- Pt-Fe is of great interest because of expectation of magnetic anisotropy. Very little is so far know about features at the nanoscale for this important material.

Tuning the plasmon excitations in transition-metal doped arrays of noble-metal nanochains

Our preliminary results for the absorption spectrum of arrays of nano-scale pure Au chains shows that as the number of chains in the array increases the plasmon peak shifts to higher energies and appears in the visible range for an array of three gold chains, each consisting of 10 atoms. Doping with TM atoms also leads to the formation of additional plasmon peaks and is especially pronounced for Ni-doped chains. However, the response is very different when we have two chains in the array each doped with one TM atom in the middle. We trace the origin of the additional modes to the interplay between the collective and local plasmon oscillations of the chains. We also analyze the case of arrays consisting of chains of two different noble metal atoms (Au-Ag) and of arrays in which one chain is of noble metal atoms and the other of TM atoms. We find that the plasmon mode is suppressed when the second chain is composed of TM atoms. We need to compare the calculated optical absorption spectrum of the doped chains for several different types of TM atoms at different positions in the chains, and provide rationale for the trends. In addition we need to examine the effect of plasmon – exciton interaction in arrays of infinite Au chains. The latter will help determine the validity of the results for energy applications.



Publications from DOE Grant: DE-FG02-07ER46354 (2009 – present)

1. F. Behafarid , L. K. Ono, S. Mostafa, J. R. Croy, G. Shafai, S. Hong, T. S. Rahman, S. R. Bare and B. Roldan Cuenya, "Electronic properties and charge transfer phenomena in Pt nanoparticles on γ-Al2O3: size, shape, support, and adsorbate effects," Phys. Chem. Chem. Phys., 2012, Advance Article DOI: 10.1039/C2CP41928A
2. V. Turkowski, A. Kabir, N. Nayyar, and T. S. Rahman, Dynamical Mean-Field Theory for Molecules and Nanostructures, J. Chem. Phys. 136, 114108 (2012).
3. S. Kahle, Z. Deng,N. Malinowski, C. Tonnoir,A. Forment Aliaga,N. Thontasen, G. Rinke, D. Le, V. Turkowski,T. S. Rahman, S. Rauschenbach,M. Ternes, and K. Kern, "Addressing the Quantum Magnetism of Individual Manganese-12-Acetate Molecular Magnets Anchored at Surfaces," NanoLett. 12, 518 (2012).
4. V. Turkowski, S. Babu, D. Le, M. K. Haldar, A. Wagh, Z. Hu, A. S. Karakoti, A. J. Gesquiere, B. Law, S. Mallik, T. S. Rahman, M. N. Leuenberger, and S. Seal "Linker-induced anomalous emission of organic molecule-conjugated metal oxide nanoparticles," ACS Nano **6**, 4854 (2012).
5. G. Shafai, M. Alcantara Ortigoza, and T. S. Rahman, "Vibrations of Au_{13} and $FeAu_{12}$ nanoparticles and the limits of the Debye temperature concept, J. Phys.: Condens. Matt. **24**, 104026 (2012).
6. H. Yildirim, A. Kara, and T. S. Rahman," Tailoring the Electronic Structure by Alloying: the Ag_nCu_{34-n} Nanoparticle Family," J. Phys. Chem. C **116**, 281 (2012).
7. G. Nandipati, A. Kara, S. I. Shah, T. S. Rahman, "3-dimensional pattern recognition scheme for off-lattice kinetic Monte Carlo simulations," J. Comp. Phys. 231, 3548 (2012).
8. S. Hong, M. Alcántra Ortigoza, T. S. Rahman, E. Z. Ciftlikli, and B. J. Hinch, "Stress balance in nanopatterned N/Cu(001) surfaces," Phys. Rev. B **84,** 165413 (2011).
9. T. S. Rahman, "Vibrations at Surfaces," J. Phys.: Condens. Matter 23 (2011) 480301.
10. B. Roldan Cuenya, M. Alcantara Ortigoza, L. K. Ono, F. Behafarid, S. Mostafa, J. R. Croy, K. Paredis, G. Shafai, T. S. Rahman, L. Li, Z. Zhang, and J. C. Yang, "Thermodynamic properties of Pt nanoparticles: Size, shape, support, and adsorbate effects," Phys. Rev B 84, 005400 (2011).
11. A. Karim, A. Kara, O. Trushin, and T. S. Rahman, "The crossover from collective motion to periphery diffusion for 2D adatom-islands on Cu(111)," J. Phys. Condens. Matt. (Fast Track) 23, 462201 (2011) (also selected for inclusion in IOP Select http://Select.iop.org).
12. S. I. Shah, G. Nandipati, A. Kara and T. S Rahman, "Extended pattern recognition scheme for self-learning kinetic Monte Carlo simulations," J. Phys. Condens. Matt. (in press)
13. S. Hong, G. Shafai, M. Bertino, and T. S. Rahman, "Toward an Understanding of Ligand Selectivity in Nanocluster Synthesis" J. Phy. Chem. C 115, 14478 (2011)
14. G. Nandipati, A. Kara, S. I. Shah, and T. S. Rahman, "Island Size Selectivity during 2D Coarsening of Ag islands on Ag (111) Surface, "J. Phys. Condens. Matt.(Fast Track) **23**, 262001 (2011).
15. R. I. Gonzalez, G. Garcia, R. Ramirez, M. Kiwi, J. A. Valdivia, T. S. Rahman, "Iron-gold nanoclusters: properties and characteristics from molecular dynamics simulations,' Phys. Rev. B **83**. 155425 (2011).
16. V. Turkowski, C.A. Ullrich, T.S. Rahman, and M.N. Leuenberger, "Time-dependent density-matrix functional theory for biexcitonic phenomena," Phys. Rev. B **82**, 205208 (2010)
17. V. Turkowski, A. Kabir, N. Nayyar, and T.S. Rahman, "DFT+DMFT approach for Nanosystems," J. Phys. Condens. Matt (Fast Track) **22**, 462202 (2010).
18. H. Yildirim, A. Kara, T. S. Rahman, R. Heid, and K.P. Bohnen, "Surface vibrational thermodynamics from ab initio calculations for fcc(100)," Surf. Sci. 604, 308 (2010).
19. E.Z. Ciftlikli, L.V. Goncharova, B.J. Hinch, M. Alcántra Ortigoza, S. Hong, and T.S. Rahman, "Vibrational Dynamics of a *c(2x2)* phase Induced by nitrogen adsorption on Cu(001)," Phys. Rev. B **81**, 115465 (2010).
20. H. Yildirim, A. Kara, T. S. Rahman, R. Heid, and K.P. Bohnen, "Surface vibrational thermodynamics from *ab initio* calculations for fcc(100)," Surf. Sci. 604, 308 (2010).

21. H. Yildirim, A. Kara, and T. S. Rahman, “Structure, dynamics and thermodynamics of Ag-Cu nanoalloys,” J. Phys. Cond. Matt. **21,** 084220 (2009).
22. G. Shafai, S. Hong, and T. S. Rahman, “Effect of ligands on the geometric and electronic structure of Au_{13} clusters,” J. Phys. Chem. C **113**, 12072 (2009).
23. H. Yildirim, A. Kara, and T. S. Rahman, “Diffusion of 7-atom Cu and Ag clusters on Cu(111): insights from several theoretical techniques,” to be submitted
24. H. Yildirim and T. S. Rahman, “The effect of lattice strain on adatom diffusion barriers on terraces and step edges ,”submitted to Phys. Rev. Lett.; preprint available at http://physics.ucf.edu/~talat/
25. N. Nayyar, V. Turkowski, and T.S. Rahman, “Transition metal impurity-induced generation of plasmonic collective modes in small gold clusters,” submitted to Phys. Rev. Lett (3rd review)
26. M. Alcántara-Ortigoza, R. Heid, K. P. Bohnen, and T. S. Rahman, “Star-pulsation-like vibrations: the anomalously soft and stiff modes of transition-metal nanoparticles,” submitted to ACS Nano (2012).
27. M. Alcántara-Ortigoza, R. Heid, K. P. Bohnen, and T. S. Rahman, “Ab initio lattice dynamics of Bi(111),” to be submitted to Phys. Rev. B (manuscript available).
28. A, Kabir, V. Turkowski, and T.S. Rahman, “A DFT+Nonhomogeneous DMFT approach for Finite Systems,” to be submitted (preprint available).
29. K. Kuhnke, V. Turkowski, A. Kabakchiev, T. Lutz, T. S. Rahman, and K. Kern, “Stark shift in the luminescence of individual pentacene nanocrystals reveals exciton mixing,” submitted to PRL.

Theoretical investigations of single particle spectroscopies of novel materials

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Project Scope:

The goal of this project is to gain insight into the properties of strongly correlated quantum materials and to theoretically model experimental probes of single-particle spectral functions like angle-resolved photoemission spectroscopy (ARPES). While the main focus of this project is on theoretical and computational modeling of complex materials, a part of it consists of collaborations with experimental groups on analysis of data.

Recent Progress:

1. Electronic structure of d-wave vortex liquid in underdoped high-Tc cuprates:

The nature of the electronic state in underdoped cuprates remains a mystery, despite many years of effort. The observations of quantum oscillations in high magnetic fields H imply the existence of well-defined quasi-particles, but with a smaller Fermi surface (FS) than expected from the Luttinger count. Various order parameters have been suggested as leading to a Fermi surface reconstruction with small electron pockets that would account for the observed quantum oscillations. However, existing theories do not address the following questions.

- How can we explain the nontrivial H-dependence of specific heat coefficient γ, which finds the 1/H-periodic oscillations riding on top of a $H^{1/2}$ background?
- Why is the specific heat γ strongly suppressed, by about a factor of five at a field H= 50T, relative to the normal state γ?
- What role does the vortex liquid state play in the quantum oscillation phenomena?
- How can we reconcile the near-nodal Fermi arcs and antinodal pseudogap observed in H=0, high-T ARPES experiments with the electronic excitations probed by quantum oscillations?

Our main theoretical progress in the last year has been in addressing all of the above questions, in addition to incorporating the FS reconstruction by competing order parameters. We model the vortex liquid by specifying its gauge-invariant superconducting (SC) order parameter correlation function, which decays in real-space like a Gaussian on the scale of the magnetic length ℓ and in time as an exponential with a frequency scale Γ describing damping due to vortex motion.

We then investigate the electronic structure of this d-wave vortex liquid state using a diagrammatic approach in the regime where the cyclotron radius $R_c >> \ell >>$ coherence length >> a, the lattice spacing. We find that the ARPES spectral function has qualitatively different behavior depending on the timescale of SC fluctuations, as shown in Fig. 1. For the "static" case, with $(\Gamma, T) < T_c$, there is a pseudogap near the antinodes and a Fermi arc near the nodes, just as in the ARPES experiments. On the other hand, when the dynamics of the SC fluctuations is important, with $\Gamma > T$, we find quasiparticles all around the FS. It is in the latter case, that we expect – and find, as described below -- quantum oscillations.

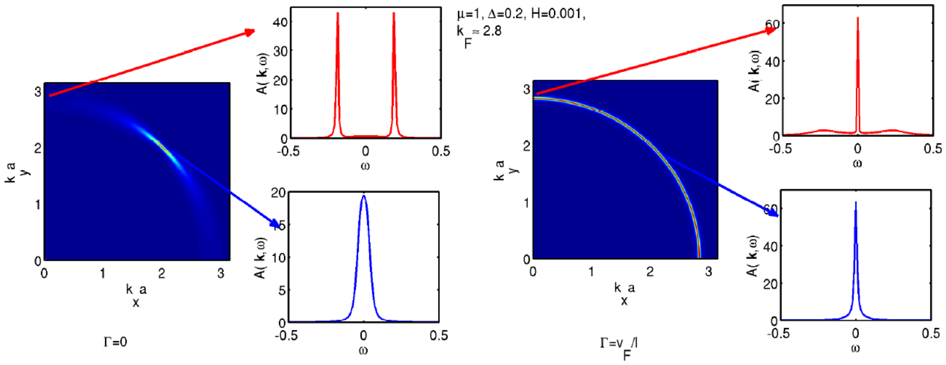

Figure 1: ARPES spectral functions. Static case with pseudogap and Fermi arc on the left contrasted with the full Fermi surface found for the dynamic case on the right.

We next compute the electronic density of states (DOS) at the chemical potential as a function of the magnetic field H. The field dependence of the self energy is quite nontrivial and unlike that of conventional Fermi liquids studied earlier, so we validate the usual **k**-space based semi-classical approach by a more elaborate calculation in the Landau level (LL) basis as shown in Fig. 2.

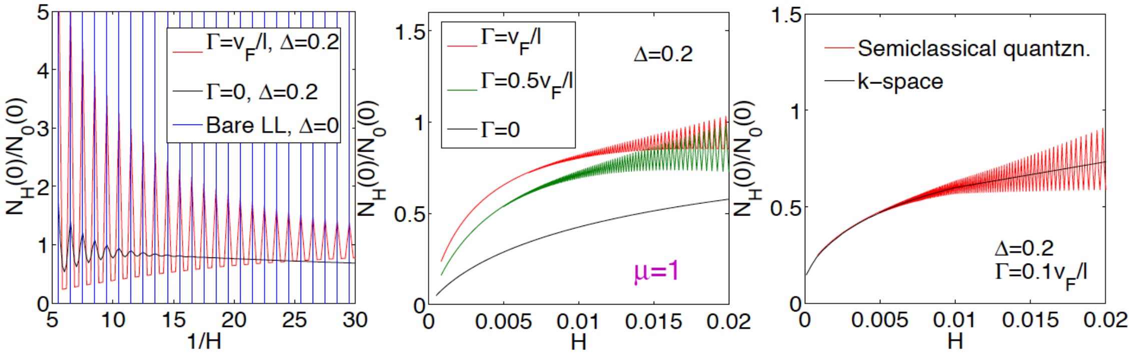

Figure 2: DOS N(0) for d-wave vortex liquid based on a Landau Level and semi-classical calculation for a parabolic dispersion. Note that the 1/H-periodic quantum oscillation rides on top of a strongly H-dependent background that goes like $H^{1/2}$ at small fields.

We see that quantum oscillations in the “static” case are only seen at very high fields, where the pseudogap is completely destroyed. On the other hand, in the dynamic case, the oscillations persist down to fields much smaller than H_{c2}. For low fields $\mu/\omega_c \gg 1$, we find the $H^{1/2}$-dependences of the electronic density of states, consistent with that observed in the specific heat measurement [S. C. Riggs et al., Nature Phys. **7**, 332 (2010)]. Ours is the first calculation in the literature that shows a smooth interpolation between this low-field behavior with quantum oscillations, as shown in Fig. 2.

The unusual self-energy effects of the d-wave vortex liquid that are responsible for the strong suppression of the DOS relative to the normal state are found not to alter the quantum oscillation frequency, which is still determined by the are of k-space orbits. To get a realistic description of the quantum oscillation experiments, we have to include both the self-energy effects of the SC fluctuations in the vortex liquid and the FS reconstruction due to competing orders. Here we show one illustration of this by considering the nematic plus Q = (π/2,0) ordering [H. Yao, D.-H. Lee and S. Kivelson, Phys. Rev. B **84** 012507 (2011)]. As shown in Fig.3, this reconstructs the large ARPES FS into small electron pockets and open orbits. We include the SC fluctuations by modifying the dispersion with vortex-liquid self-energy and semiclassically quantize the results to obtain the quantum oscillations show in the right panel of Fig. 3.

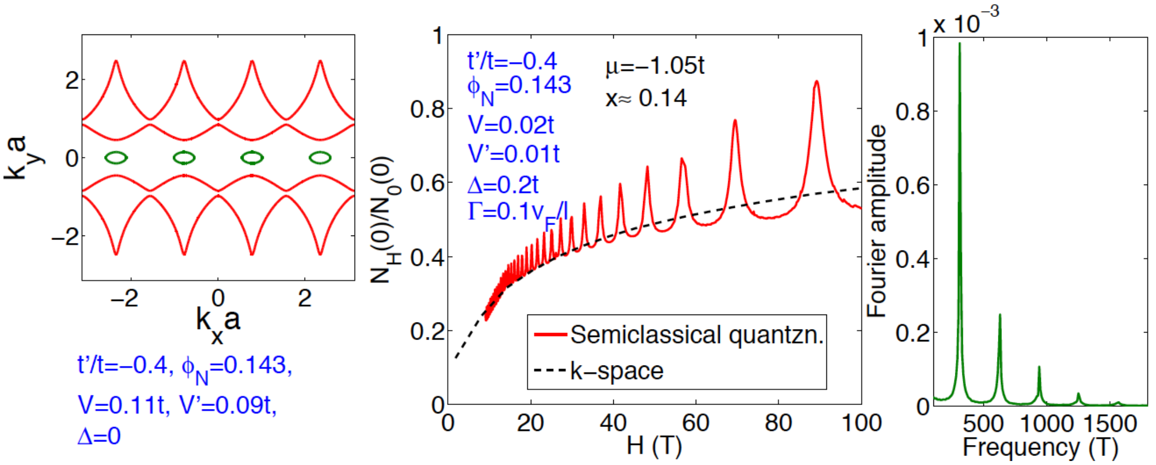

Figure 3: Left: Fermi surface reconstruction by competing order. Right panels: Quantum oscillation in the DOS with a strong field-dependent suppression that goes like $H^{1/2}$ at small fields.

We thus find that the combination of short-range SC fluctuations in the d-wave vortex liquid state together with a FS reconstructed by a competing order yields excellent agreement with quantum oscillation experiments: small electron pockets and hugely suppressed DOS relative to normal state, with $H^{1/2}$ asymptotic behavior.

2. ARPES studies of high-Tc cuprates:

A dramatic change in energy gap anisotropy upon reducing carrier concentration has often been observed in the high Tc cuprates. A simple d-wave gap in optimally doped materials evolves with underdoping into a “two-gap” behavior, with different **k**-dependences in different regions of momentum space. It is tempting to associate the large antinodal gap, which persists even above Tc in underdoped materials, with a second order parameter distinct from d-wave superconductivity. In collaboration with the angle-resolved photoemission spectroscopy (ARPES) group of J.C. Campuzano and M. R. Norman at Argonne National Labs, we have been analyzing various families of underdoped Bi2212 samples to gain insight into what seem to be apparent differences between various results reported in the literature.

We show that the two-gap behavior, and the concomitant destruction of well-defined electronic excitations, are *not* universal features of HTSC, and depend sensitively on how the underdoped materials are prepared. Depending on degree of cation substitution, essential for making highly underdoped single crystals, we find that the two-gap behavior sets in at different levels of underdoping. In contrast, many characteristics of HTSC like the superconducting dome (Tc versus doping), sharp nodal quasiparticles, antinodal gap that decreases monotonically with doping, and the pseudogap, are present in all samples, irrespective of whether they exhibit two-gap behavior or not. Our results imply that universal aspects of high Tc superconductivity are insensitive to differences in the electronic states in the antinodal region of the Brillouin zone.

Future Plans:

We plan to work on a variety of problems described below.

(1) We are broadening the class of materials that we look at to go beyond high Tc cuprates. We will investigate the connection between electronic properties and the lattice degrees of freedom. Specifically, we are looking at oxide interfaces, manganites, and charge density wave (CDW) materials.

(2) We plan to work on the formalism of pump-probe photoemission spectroscopy. We plan to investigate if there are any useful sum rules that we can derive and plan to apply our formalism to simple models of correlated materials.

(3) We will continue our collaboration with the Argonne ARPES group led by J. C. Campuzano and with M. R. Norman. Specifically, we are working on two problems. The first is related to ARPES, STM and X-ray data on CDW materials. The second problem is on the relation of ARPES intensity autocorrelations, a technique that we had introduced a few years ago, to gain further insight into the pseudo gap in underdoped cuprates.

Publications

[1] S. Banerjee, S. Zhang and M. Randeria, *"Quantum oscillations in vortex liquids"*, Bulletin of the American Physical Society, abstract Q23.00015, (2012).

[2] J. Zhao, U. Chatterjee, D. Ai, D. G. Hinks, H. Zheng, G. Gu, S. Rosenkranz, H. Claus, M. R. Norman, M. Randeria and J. C. Campuzano, *"One gap, two gaps, and universality in high temperature superconductors"*, submitted to Phys. Rev. Letters.

I. FIRST-PRINCIPLES INVESTIGATIONS OF THE PHYSICS OF NEW SEMICONDUCTING FERROELECTRICS FOR SOLAR LIGHT ABSORPTION AND CARRIER SEPARATION

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II. PROJECT SCOPE

Since the 1950s, when the bulk photovoltaic effect (BPVE) was discovered and the efficiency of intrinsic polarization for separating photoexcited carriers was first noted, ferroelectric materials have been investigated for photovoltaic and photocatalytic applications. Their practical use was hampered by the fact that large spontaneous polarization is usually found in highly ionic materials, typically oxides. The large electronegativity difference between the O atoms and the metal cations fosters high polarization, but also gives rise to a strong ionic component of bonding and a large band gap. This makes almost all ferroelectric materials unable to absorb solar energy in the visible range, where most of the energy in the solar spectrum lies. Incomplete understanding of BPVE and its relationship to atomic composition and structure, as well as insufficient understanding of the solid state physics and chemistry that give rise to ferroelectricity prevented design of new materials that combine a narrow band gap and robust carrier separation via the BPVE.

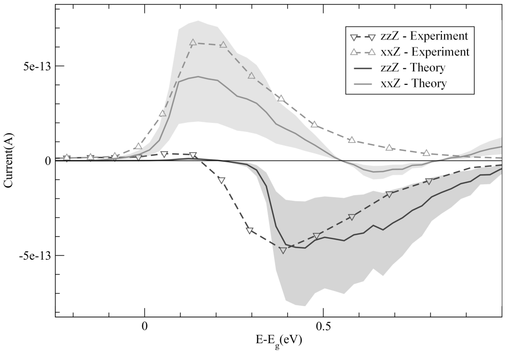

FIG. 1: The experimental BPVE current for $BaTiO_3$ is plotted versus incident photon energy, as is the first principles computed shift current response, for electric fields along $\hat{x}$ (σ_{xxZ}) and along $\hat{z}$ (σ_{zzZ}). The gray bands are error bars for the theory calculations based on uncertainty in the experimentally reported light intensity. The strong agreement demonstrates that the shift current mechanism quantitatively explains the observed BPVE in ferroelectrics. [1]

Recently, there has been an upsurge of interest in ferroelectric-based photovoltaic materials. This has been in part due to the increasing need for clean, renewable energy, and in part due to the advances made in the past three decades in the physical understanding of ferroelectric materials. New experimental techniques have been pioneered to manipulate the ferroelectric properties of materials, extending even to the induction of ferroelectricity in materials that are normally not ferroelectric, by the careful control of atomic arrangement, strain and morphology. Theoretical methods have played a key role in elucidating the physics and chemistry of ferroelectrics. Now, due to advances in methodology and computational power, theorists are able to accurately predict the structure and properties of new, unsynthesized materials. In the work reported here, we have used computational and theoretical methods to advance the understanding of the physics of photovoltaic ferroelectrics by first-principles studies of BPVE in ferroelectrics, and to design new low-band gap materials that efficiently separate carriers, through changing the band gap of current highly polar materials.

III. RECENT PROGRESS

III.A. The shift current mechanism for the BPVE

Various physical mechanisms have been proposed to explain the BPVE. We presented [1] the first convincing evidence that the shift current is responsible for the BPVE by calculating shift current response from first principles and comparing it with experimental shift current measurements. We calculated the bulk photovoltaic response of the ferroelectrics $BaTiO_3$ and $PbTiO_3$ from first principles by applying shift current theory to the electronic structure from density functional theory. The first principles results for $BaTiO_3$ reproduce experimental photocurrent direction and magnitude as a function of light frequency, as well as the dependence of current on light polarization, demonstrating that shift current is the dominant mechanism of the bulk photovoltaic effect in $BaTiO_3$.

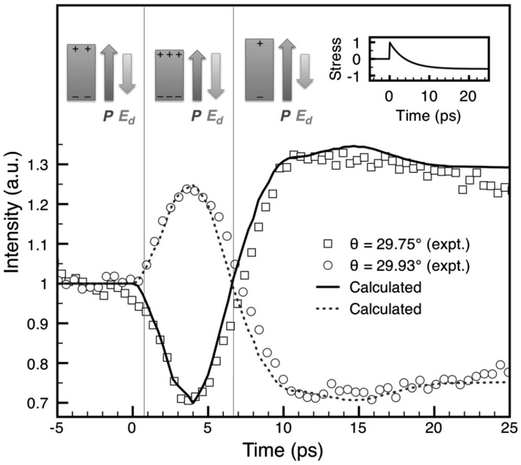

FIG. 2: (top) Time resolved x-ray diffraction reveals that after illumination, ferroelectric $PbTiO_3$ rapidly contracts and then expands, before returning to the equilibrium structure. Theoretical modeling showed that coherent carriers generated by the BPVE cause the contraction. Once these carriers reach the sample boundaries, they decohere and then screen the ferroelectric depolarizing field, expanding the sample. [2]

Additionally, we have analyzed the relationship between response and material properties in detail. The photocurrent does not depend simply or strongly on the magnitude of material polarization, as has been previously assumed; instead, electronic states with delocalized, covalent bonding that is highly asymmetric along the current direction are required for strong shift current enhancements. The complexity of the response dependence on both external and material parameters suggests applications not only in solar energy conversion, but photocatalysis and sensor and switch type devices as well.

We collaborated with an international experimental team to show [2] that light drives large-amplitude structural changes in thin films of the prototypical ferroelectric $PbTiO_3$ via direct coupling to its intrinsic photovoltaic response. Using time-resolved x-ray scattering to visualize atomic displacements on femtosecond time scales, photoinduced changes in the unit-cell tetragonality are observed. These are driven by the motion of photogenerated free charges within the ferroelectric and can be simply explained by a model including both shift and screening currents, associated with the displacement of electrons first antiparallel to and then parallel to the ferroelectric polarization direction.

III.B. Computational materials design of new ferroelectric solid solutions

An important goal of this project is the identification of new semiconducting ferroelectrics. Previously, it was thought that high polarization is incompatible with low band gap. Our previous work on $PbTiO_3$ doped with Ni, Pd, or Pt demonstrated the feasibility of fabricating new single-phase semiconducting ferroelectrics. During this grant period, we examined correlations between tetragonality, polarization, and ionic displacement [3] in order to develop new alloying strategies leading to new ferroelectrics. We modeled [4, 5] the solid solution of $BaTiO_3$, $BaCeO_3$, and $BaPdO_2$ in order to invent Pb-free semiconductor ferroelectrics using the vacancy-transition metal paradigm for band gap lowering and polarization enhancement pioneered in our previous work. We also examined tin-based [6] perovskites as a way to eliminate Pb in ferroelectrics, focusing on the $SnAl_{1/2}Nb_{1/2}O_3$ (SAN) material. We predict that SAN is very close to a morphotropic phase boundary, giving it a high piezoelectric coefficient, as high as $Pb(Zr,Ti)O_3$.

III.C. Correlating electronic band gap with oxide composition and cation arrangement

In view of the opportunities offered by shift current based photovoltaics, we undertook a study of how band gap relates to oxide composition. As others have noted as well, oxide band gaps do not change linearly with composition the way they do in compound semiconductors. In fact, we find [7, 8] that for perovskites, particular cation arrangements lead to local ionic and covalent bonding that can raise or lower the conduction and valence band edges significantly. As part of these studies, we systematically investigated the application of post-DFT methods to demonstrate their applicability for calculating band gaps in perovskites with transition metal cations [7–10]. We find that for low band gap and metallic oxides, post-DFT methods can reduce the overall accuracy of the density of states, even while improving the band gap itself.

III.D. The electronic structure of topological insulators

The topological insulating phase results from inversion of the band gap due to spin-orbit coupling at an odd number of time-reversal symmetric points. In Bi_2Se_3, this inversion occurs at the Γ point. For bulk Bi_2Se_3, we have analyzed [11] the effect of arbitrary strain on the Γ point band gap using density functional theory. By computing the band structure both with and without spin-orbit interactions, we consider the effects of strain on the gap via Coulombic interaction and spin-orbit interaction separately. While compressive strain acts to decrease the Coulombic gap, it also increases the strength of the spin-orbit interaction, increasing the inverted gap. Comparison with Bi_2Te_3 supports the conclusion that effects on both Coulombic and spin-orbit interactions are critical to understanding the behavior of topological insulators under strain, and we propose that the topological insulating phase can be effectively manipulated by inducing strain through chemical substitution.

IV. PLANNED ACTIVITIES 2012–2013

During the coming year, we plan to examine the shift current mechanism for BPVE for some of the semiconducting ferroelectric compositions that we have proposed, in order to assess their feasibility as solar materials. We will also examine how shift current behavior is modified in cation-alloyed perovskite oxides and those with oxygen vacancies. We will extend our use of beyond-DFT approaches for band gap calculations, focusing on methodological development to enhance the efficiency of *GW* calculations for complex materials. We have started a project to examine the different terms that enter the final shift current expression. Two different momentum-dependent functions are multiplied to give the final shift current. Alignment of the Brillouin zone peaks of these functions would give a remarkable enhancement to the shift current. We will therefore search for bonding motifs and structures that exhibit such an alignment. Finally, we intend to explore the application of similar photovoltaic mechanisms to magnetic systems.

V. PUBLICATIONS

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[1] S. M. Young and A. M. Rappe, "First principles calculation of the shift current photovoltaic effect in ferroelectrics," *Phys. Rev. Lett.* **in press** (2012).

[2] D. Daranciang, M. J. Highland, H. Wen, S. M. Young, N. C. Brandt, H. Y. Hwang, M. Vattilana, M. Nicoul, F. Quirin, J. Goodfellow, T. Qi, I. Grinberg, D. M. Fritz, M. Cammarata, D. Zhu, H. T. Lemke, D. A. Walko, E. M. Dufresne, Y. Li, J. Larsson, D. A. Reis, K. Sokolowski-Tinten, K. A. Nelson, A. M. Rappe, P. H. Fuoss, G. B. Stephenson, and A. M. Lindenberg, "Ultrafast photovoltaic response in ferroelectric nanolayers," *Phys. Rev. Lett.* **108**, 087601–1–6 (2012).

[3] T. Qi, I. Grinberg, and A. M. Rappe, "Correlations between tetragonality, polarization, and ionic displacement in $PbTiO_3$-derived ferroelectric perovskite solid solutions," *Phys. Rev. B* **82**, 134113–1–5 (2010).

[4] J. W. Bennett, I. Grinberg, P. K. Davies, and A. M. Rappe, "Pb-free semiconductor ferroelectrics: A theoretical study of Pd-substituted $Ba(Ti_{1-x}Ce_x)O_3$ solid solutions," *Phys. Rev. B* **82**, 184106–1–5 (2010).

[5] T. Qi, I. Grinberg, J. W. Bennett, Y.-H. Shin, A. M. Rappe, K.-L. Yeh, and K. A. Nelson, "Studies of Perovskite Materials for High-Performance Storage Media, Piezoelectric, and Solar Energy Conversion Devices," *2010 DoD HPCMP Users Group Conference* pp. 249–58 (2010).

[6] J. W. Bennett, I. Grinberg, P. K. Davies, and A. M. Rappe, "Pb-free ferroelectrics investigated with density functional theory: $SnAl_{1/2}Nb_{1/2}O_3$ perovskites," *Phys. Rev. B* **83**, 144112–1–6 (2011).

[7] G. Y. Gou, J. W. Bennett, H. Takenaka, and A. M. Rappe, "Post density functional theoretical studies of highly polar semiconductive $Pb(Ti_{1-x}Ni_x)O_{3-x}$ solid solutions: Effects of cation arrangement on band gap," *Phys. Rev. B* **83**, 205115–1–7 (2011).

[8] T. Qi, I. Grinberg, and A. M. Rappe, "Band-gap engineering via local environment in complex oxides," *Phys. Rev. B.* **83**, 224108–1–6 (2011).

[9] G. Y. Gou, I. Grinberg, A. M. Rappe, and J. M. Rondinelli, "Lattice normal modes and electronic properties of the correlated metal $LaNiO_3$," *Phys. Rev. B* **84**, 144101–1–13 (2011).

[10] T. Qi, M. T. Curnan, S. Kim, J. W. Bennett, I. Grinberg, and A. M. Rappe, "First-principles study of band gap engineering via oxygen vacancy doping in perovskite $ABB'O_3$ solid solutions," *Phys. Rev. B* **84**, 245206–1–6 (2011).

[11] S. M. Young, S. Chowdhury, E. J. Walter, E. J. Mele, C. L. Kane, and A. M. Rappe, "Theoretical investigation of the evolution of the topological phase of Bi_2Se_3 under mechanical strain," *Phys. Rev. B* **84**, 085106–1–4 (2011).

Extending the reach of computational-theoretical methods to materials at the energy frontier

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ABSTRACT

This program is designed to overcome materials theory challenges that are both at the frontier of basic research and beyond current theoretical and computational capabilities. Our overarching goal is to significantly improve our description and understanding of electronic correlations, magnetic interactions and spin-orbit coupling in an *ab initio* framework. This advance is key for the design of new materials for clean energy. Our goal is to describe the physical, chemical and electronic properties of materials with accuracy comparable to experimental characterization and in large physically-relevant systems. This program includes both accurate *ab initio* approaches and methods based on simpler models. Models will allow us to test new methods and extend *ab initio* results to larger systems. A priority is to develop, improve and implement in high-performance supercomputers new theories that go well beyond the current approaches. Many relevant properties of semiconductors, polymers, correlated, oxides and magnets are currently beyond the accuracy obtainable with the state-of-the-art approaches based on Density Functional Theory (DFT). Accordingly, we aim to provide an alternative route using the highly-accurate Quantum Monte Carlo (QMC) and/or improve DFT approximations (e.g. for finite temperature). A significant fraction of the theoretical research in materials is currently based on DFT approximations. In the short term, the results provided by our research will quantify the errors of these widely-used approximations. When even higher performance/high-capacity computers become readily available to a larger group of researchers, we aim to provide an alternative QMC-based approach to reach the required accuracy for energy applications.

The dream of theoretically predicting the properties of new materials before they are synthetized has been a long-standing goal of theoretical research. This elusive goal is increasingly urgent due to major advances in synthesis and fabrication techniques. While there are several popular methods used for high-fidelity computation (some massively used, e.g. DFT), they are based on approximations that limit their accuracy in many materials systems. Improved accuracy is important for example for nano-structured materials where physical properties become increasingly dominated by interfaces and reduced dimensionality. Control at the nano-scale opens up an exponential number of possibilities, taking advantages of the combinations that can be made with different materials. Each combination has the potential to be a useful discovery. However, it is impractical to explore all these possibilities by trial-and-error experiments. Therefore, we need a theoretical approach that can produce results with the accuracy required in real materials problems; without accuracy it is very difficult to design a material or guide experiment. However, in efforts to improve accuracy, it is also important to retain system size. Since both larger size and better accuracy increase computational cost, it is critical to improve the accuracy of methods that can eventually reach larger sizes.

In condensed matter theory, better accuracy is required in a plethora of cases: catalysts, energy storage materials, solar energy materials and functional materials. In other systems, where disorder is dominant, such as high-performance permanent magnets and high-entropy alloys, there is a pressing need to reach larger sizes with less expensive methods based on DFT. Most of the effort of this project is to develop high accuracy *ab initio* methods. However, a *qualitative* understanding of materials properties is undeniably helpful. Eventually, since models can reach larger sizes, we also want to determine with an accurate many-body calculation based solely on quantum mechanics, which models are valid for different material systems.

Theories to deal accurately with many-body correlations in an ab initio context: The adequate treatment of correlation and exchange are critical elements missing in accurate predictions of energy barriers for catalysis, optical gaps for solar energy and atomic transport in most materials of current interest for both energy and fundamental science. QMC methods are statistical techniques that can tackle electronic correlations in an *ab initio* framework taking full advantage of parallel supercomputers with a large number of processors. By solving the many-body Schrödinger equation through a stochastic projection, QMC avoids approximations in mean-field methods and has much better scalability than quantum chemical (QC) methods, enabling scientific discovery across a broad spectrum of disciplines. In the last decade, QMC has taken advantage of advances in hardware and software in evolving high-performance computer (HPC) architectures. Recently, one of the Co-PIs of this project J. Kim, has developed QMCPACK, an open-source QMC package for HPC [Kim 2010]. QMCPACK employs cutting-edge programming models and software engineering practices.

The QMC calculations of homogeneous electron gas by Ceperley and Alder laid the foundation for the approximations of DFT. QMC has played since an important role as a benchmark method. Most of the bulk QMC calculations to date have employed the simplest trial wavefunctions, namely single-Slater-Jastrow wavefunctions, but were able to capture a large fraction of the correlation and successfully predict electronic and structural properties of weakly binding to strongly correlated bulk systems Various methods to correct finite-size errors allow now QMC to use a simulation cell of a modest supercell of N=100-1000 electrons and to extrapolate the properties at the thermodynamic limits. All these improvements have opened up the possibility of improving fermion nodes of bulk systems.

The nodal error in QMC is one of the important technical challenges limiting applications of QMC. Finding wave-functions with good nodes has been a very demanding task both in human and computer time. We have developed a “self-healing diffusion Monte Carlo" (SHDMC) technique [Reboredo 2009a] that can find these nodes starting from random without human intervention. The method has been extended to the calculations of excited states [Reboredo 2009b], systems with charge flow (in periodic boundary conditions) and magnetic fields. Our "proof-of-principle" results [Bajdich 2010a] show that the study of much larger systems with SHDMC is possible. We using SHDMC and other methods to optimize the wave-function developed by Umrigar and others for (a) doing applications in realistic systems that are scientifically and technologically relevant; and (b) generating models that incorporate correlations in larger systems. QMCPACK, facilitates rapid deployments of new QMC capabilities on HPC systems for broad applications. It is designed to provide a framework for development of new QMC methods and algorithms like SHDMC. Accordingly, we aim to explore how far we can reach with this new approach in the description of new materials going well beyond the state of the art which is based on DFT.

Potential improvement of DFT calculations with QMC input:. DFT will remain an indispensable tool to study larger systems. A significant amount of research in the electronic structure community has been focused on the development of better DFT approximations. Benchmark data from QMC calculations can help this effort [Bajdich 2011].

Approaching a complete mutideterminat basis: QMCPACK already implements the most advanced QMC algorithms including i) variants of the linear optimization method [Toulouse 2008] that can both optimize the correlation-function parameters and the expansion coefficients of multi determinants; and ii) a new accelerating algorithm in computing multi determinants [Clark 2011].

Applications to real solids: We are choosing systems where we expect to find significant many-body effects but at the same time systems that present a manageable challenge. Studies in graphene, nano-ribons and carbon nano-tubes can potentially benefit the experimental programs [ERKCM43 (N. Gallego)], [ERKCS81 (D. Geohegan)] and [ERKCS89 (S. Pennycook]. As we make progress, we will tackle more ambitious problems of fundamental and technological significance. In the short term we plan to support experimental work in ORNL in semiconductors oxides and carbon compounds. These calculations will exploit synergies with the research Center for Defect physics [ERKCS99, (Stocks)] at ORNL which is focused on structural materials (metals) and will benefit the experimental programs performed in [ERKCS80 (H. Christen)] and the proposed research in [ERKCS87 (H. Weitering)].

Calculation of magnetic properties at finite temperature: In many condensed mater systems QMC calculations are impractical, thus approximated methods based on DFT are required. A particularly challenging case is the study of magnetic excitations at finite temperature, since there are no QMC benchmark calculations of the electron gas between the high temperature limit and zero temperature. Therefore, the development of *ab initio* theoretical techniques for describing the finite temperature properties of materials is an extremely challenging problem. The calculation of the full temperature/pressure magnetic phase diagram of complex multicomponent systems remains beyond the reach of existing techniques. However, recent progress that exploits novel theoretical, algorithmic and computational methods has advanced the state of the art to the point where direct *ab initio* simulation of the finite temperature properties of magnetic materials appears possible [Eisenbach 2011a, Nicholson 2011]. In this project the primary focus is on predictive statistics from first principles, thus advancing our capabilities to investigate magnetic materials at finite temperatures from first principles.

Theoretical and Computational Developments: Several statistical techniques have been designed to specifically deal with the problem of exploring complex free energy landscapes. Of particular interest here is the Wang-Landau Monte Carlo method [Wang 1995, Landau 2004]. In the Wang-Landau method a random walk is performed explicitly in the space of collective variables and the simulated system evolves in such a way that it avoids areas of phase space that have already been visited. This method provides an intelligent way to overcome the time-scale dilemma by using massively parallel computers. The Wang-Landau method is straightforwardly parallelized to thousands of walkers. The *ab initio* Wang-Landau sampling based methods are potentially extremely powerful. Here we propose to advance the state of the art on two fronts. Firstly, the development of new theoretical and algorithmic approaches that greatly accelerate statistical results even with current computing resources. Secondly, exploitation of improvements in computing power (exascale) that will result from expected developments in hardware architecture that will result in increased parallelism and performance, thereby enabling the treatment of more complex materials systems. While it is expected that the available computing resources will continue to grow, thus enabling us to make first principles based statistical physics more feasible, it is also clear that the computational paradigms are likely to undergo significant changes. Hence we are collaborating with the NCCS to modify our workhorse LSMS code to perform optimally on hybrid compute nodes that combine CPUs and GPUs as they are widely adopted in high performance computing.

Applications to Materials for Energy: While the possible areas of application of the methods described above are vast – magnetic states in nanoparticles or wires (raceways) for information storage, magneto-caloric and magneto-elastic properties, magneto-transport properties, hard magnets and structural alloys containing the magnetic 3d-elements Cr, Mn, Fe, Co and Ni – in the following we focus on a single case where synergies with experimental synthesis and characterization efforts with the broader BES-DMSE research portfolio at ORNL [ERKC73, (G. Ice)] [ERKCM06 (C. Liang)]].

High Entropy Alloys: (HEA) represent a new class of structural materials with potential for applications. One of the most interesting aspects of theses materials is that they exist at all. High entropy alloys typically comprise of four, five or even more elements but yet have simple crystal structures such as FCC or BCC. Given the number of possibilities for so many different elements to decompose into phases involving sub-sets of these components, it is extremely surprising that these alloys exist as apparent solid solutions on simple lattices. Of course, the term High Entropy Alloys was given to these unusual systems based on the conjecture that they are *entropically* stabilized as a result of the ever increasing entropy of mixing of alloys systems comprising more and more component species[1] HEA are currently the subject of experimental study within the BES-DMSE Materials Science program at ORNL to confirm that they indeed form single-phase solid-solution materials, to characterize their atomic and microstructure, measure their

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[1] The ideal entropy of mixing (S_M=k_BSum$_{i=1,N}$ $c_i \ln c_i$) is a maximum at equiatomic compositions and increases as the number of components increases.

mechanical properties and, more recently, measure other physical properties that can shed light on their unexpected stability ([ERKCM06, E. George] and [ERKCS73, G. Ice]). Of the systems that have been confirmed to form solid solutions [Bei, 2012], the FCC-structure, four component CrFeCoNi and five component CrMnFeCoNi systems, are worthy of particular attention in that they are comprised of most, or all, of the *3d*-transition metal elements that are magnetic. Thus understanding the role of magnetism and temperature in stabilizing these systems comes to the fore. In such multicomponent 3d-transiion metal alloys the magnetic state is likely to be extremely complex, strongly coupled to the compositional state (short-ranged order etc.) and correspondingly difficult to characterize experimentally leaving a clear role for *ab initio* theory to provide the needed input both to suggest key experiments and to aid in their interpretation.

Direct Calculations of S(q) and S(q, □): Neutron scattering is potentially the cleanest and most direct probe of the magnetic structure and dynamics of magnetic materials. The large cell order-N electronic structure and Wang Landau finite temperature statistical sampling methods outlined above have the potential to increase the information about the underlying atomic and magnetic correlations that can be extracted from neutron scattering experiments on complex systems. This coupled with new experimental capabilities at the SNS, offers exciting new possibilities. The use of Wang-Landau sampling offers the further possibility to obtain the full temperature dependence of the static correlations namely S(q,T) and thereby make direct and detailed contact with corresponding neutron scattering experiments [ERKCM73 (G. Ice)].

Selected References

[Bajdich 2010a] Bajdich M., Tiago M. L., Hood R. Q., Kent P. R. C., and, Reboredo F. A., “Systematic Reduction of Sign Errors in Many-Body Calculations of Atoms and Molecules”, *Phys. Rev. Lett.* **104**, 193001 (2010).

[Bajdich 2010b] Bajdich M,, Reboredo F. A, and Kent P. R. C. “Quantum Monte Carlo calculations of dihydrogen binding energetics on Ca cations: An assessment of errors in density functionals for weakly bonded*“, Phys. Rev. B* **82**, 081405 (2010).

[Clark 2011] B. K. Clark, M. A. Morales, J. McMinis, J. Kim and G. E. Scuseria, “Computing the energy of a water molecule using multideterminants: A simple, efficient algorithm”, *J. Chem. Phys*., **135** 244105 (2011)

Eisenbach, 2011a] M. Eisenbach, D. M. Nicholson, A. Rusanu, G. Brown, “First principles calculation of finite temperature magnetism in Fe and Fe_3C,” *J. Appl. Phys.* **107**, 07E138 (2011).

[Eisenbach, 2011b] M. Eisenbach, “Future Proofing WL-LSMS: Preparing for First Principles Thermodynamics Calculations on Accelerator and Multicore Architectures,” CUG 2011 Proceedings (2011).

[Kim 2010] J. Kim, K. Esler, J. McMinis and D. M. Ceperley, Proceedings of the 2010 Scientific Discovery through Advanced Computing (SciDac) Conference, Chattanooga, Tennessee, July 11-15, (2010), Oak Ridge National Laboratory.

[Reboredo 2009a] F. A. Reboredo, R. Q. Hood, and P. R. C. Kent, “Self-healing diffusion quantum Monte Carlo algorithms: Direct reduction of the fermion sign error in electronic structure calculations,” *Phys. Rev. B* **79**, 195117 (2009)

[Reboredo 2009b] Reboredo, F.A., “Systematic reduction of sign errors in many-body problems: generalization of self-healing diffusion Monte Carlo to excited states,” *Phys. Rev. B* **80**, 125110 (2009).

[Tiago 2008] Murilo L. Tiago, P. R. C. Kent, Randolph Q. Hood, and Fernando A. Reboredo, “Neutral and charged excitations in carbon fullerenes from first-principles many-body theories,” *J. Chem. Phys*. **129**, 084311 (2008).

[Toulouse 2008] J. Toulouse and C. J. Umrigar, “Full optimization of Jastrow–Slater wave functions with application to the first-row atoms and homonuclear diatomic molecules,” *J. Chem. Phys*., **128**, 174101 (2008).

[Wang 1995] Y. Wang, G. M. Stocks, W. A. Shelton, D. M. C. Nicholson, Z. Szotek and W. M. Temmerman, “Order-N Multiple Scattering Approach to Electronic Structure Calculations”, *Phys. Rev. Lett*. **75**, 2867 (1995).

Next Generation Photon and Electron Spectroscopy Theory: Advances in RSGF and GW/BSE Approaches

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Project scope

The primary goal of our DOE BES Grant is to develop improved theoretical techniques for quantitative calculations of photon and electron spectroscopies over a broad spectrum, spanning UV-VIS to x-ray energies. Our effort includes advanced computational techniques and codes based on extensions of our successful and well known real space Green's function (RSGF) codes FEFF. Our previous developments have been widely cited, and were recently recognized by the 2011 Advanced Photon Source Arthur H. Compton Award. Our current approach involves two levels of attack: 1) Efficient, parameter-free RSGF approaches; and 2) First-principles methods based on the GW/Bethe-Salpeter Equation (BSE). Both build on recent developments in the theory of excited states and response functions. Achieving these goals requires a quantitative treatment of many body effects beyond the independent electron approximation. For 1) we proposed to add new capabilities to FEFF, while for 2) we proposed techniques that augment our BSE codes, working partly in collaboration with NIST scientists. Linking different codes and making them compatible can be extremely valuable, since the combination of methods 1) and 2) yields a hybrid approach that exceeds the capabilities of either alone. Here we report significant progress toward these goals with several major advances.

Recent progress

Real Space Green's Approach

A. Many-body Corrections in X-ray Spectra

One of our goals has been to improve on the quasi-particle approximation through the inclusion of Hubbard model corrections and satellites in calculations of XAS. For example, we have implemented the Hubbard model using a rotationally invariant LDA+U formalism [1]. Rather than fitting to experiment, theoretical values of the Hubbard parameter U have been estimated using the constrained RPA method. Our treatment also includes a many-pole GW self-energy (MPSE) model which accounts for the interaction of the photo-electron with excitations such as plasmons. This leads to an efficient approach to account for correlation effects on localized and delocalized electrons, and their influence on x-ray spectra. Using this extension we have calculated the projected density of states (lDOS) as well as x-ray absorption (XAS) and emission spectra (XES) of several materials, yielding reasonable agreement with experiment. For comparison, Figure 1 below shows our cRPA estimates for U with other theoretical cRPA and cLDA results.

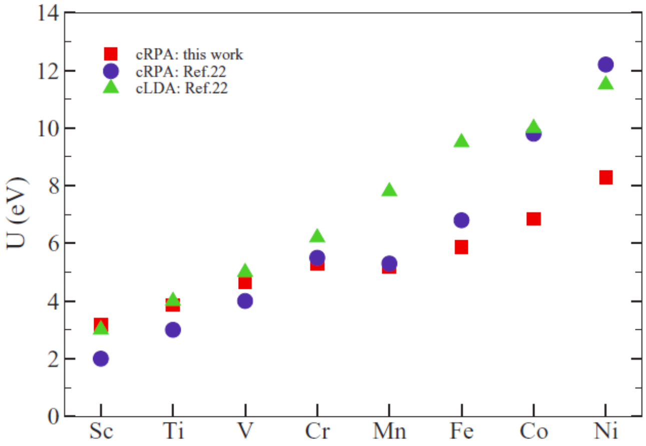

Figure. 1. Results of our cRPA calculations of *U* (red squares) for the 3*d* transition metals compared with the cRPA (blue circles) and cLDA (green triangles) calculations of Aryasetiawan.

We have also developed techniques for calculating corrections to the GW quasiparticle approximation based on cumulant expansion techniques and the quasi-boson approximation. This approach includes satellites in the spectral function, and yields spectra in excellent agreement with XPS experiment for Si and related materials [2].

B. Applications to x-ray spectra: RIXS and Compton profiles

X-ray spectra have proved to be extremely valuable for probing the excited state properties of materials, but their interpretation requires accurate theoretical methods. An important advance is the extension of our RSGF approach for calculations of resonant inelastic x-ray scattering (RIXS) [3], which typically have higher energy resolution than conventional XAS. This development was selected as a 2011 ESRF Scientific Highlight by the European Synchrotron Radiation Facility. Our method is based on the Kramers-Heisenberg formula and reasonable approximations which yield the RIXS cross section in terms of a convolution of effective x-ray absorption (XAS) and x-ray emission (XES) spectra. Core hole screening is included via a random-phase approximation to the dielectric function. Additional many-body features, including edge-singularity and satellite effects can also be included. Our method allows for calculations of both direct RIXS and high energy resolution fluorescence detected (HERFD) XAS over a large energy range, including pre-edge and main edge regions.

The method is applicable to a wide variety of materials with no constraint on symmetry. Calculated results have been compared to experiment for a variety of materials and edges, including core-core and core-valence RIXS of high Tc cuprates, lanthanides, and transition metal oxides. Extensions of our approach have also been developed to treat Compton scattering [4].

GW/BSE approach

A. Core-GW/BSE Code

A major achievement of our research was an extension of our GW/BSE codes for core-level x-ray spectra [5]. Dubbed OCEAN, the software is suitable for calculating near-edge x-ray spectroscopies, both dipole limited and at finite-momentum transfer, e.g., non-resonant inelastic x-ray scattering (NIXS). By explicitly including the photo-electron and the core hole and their interactions, the BSE approach can accurately describe L_{23} edge of transition metal spectra, historically a weakness for single-particle approaches. Additionally, building on density functional theory (DFT) and GW self-energy corrections, we obtain spectra in good agreement with experiment without adjustable parameters. The OCEAN code is band-structure based, but scales well to 100 electrons or 500 $Å^3$ units cells. As an example we show in Fig. 2 the vanadium L_{23} edge of metallic BCC V and insulating phase of VO_2. Vanadium dioxide is problematic in standard DFT, with the ground state incorrectly predicted to be conducting. By including self-consistent self-energy corrections, a band gap is opened in the ground state, and the resulting wave functions used to calculate the x-ray spectra. Notably the BSE approach does an excellent job of reproducing the L_3/L_2 ratio, which in transition metals often differs markedly from the statistical 2:1 ratio. Moreover, our approach can also include multiplet effects approximately, thus providing a unified treatment of both local correlation effects and extended states. This work has led to several other publications as well [6-7].

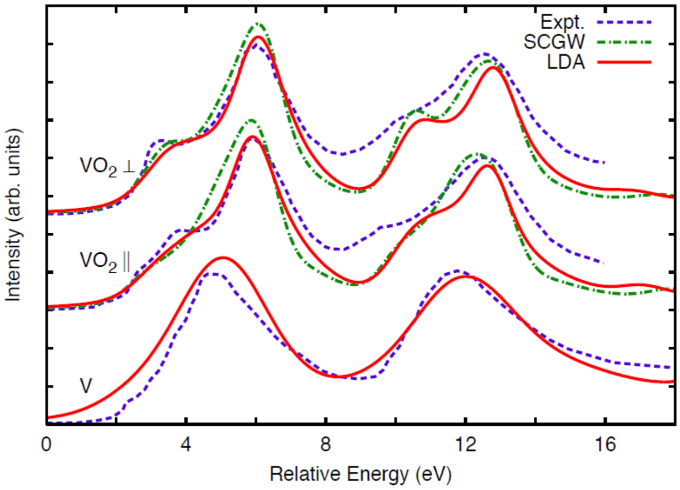

FIG 2. OCEAN calculations of the L_{23} spectra of V and VO_2.

Planned activities: 2012-2013

A priority for the next year is to develop extensions of our quasi-boson approach for treating satellites in XAS. In particular we plan to implement an approach of Lee, Gunnarsson and Hedin for treating charge-transfer satellites in correlated materials. A related topic is to treat contributions to the electron self-energy due to phonons, again within the quasi-boson, cumulant expansion approach.

A second priority is to extend the OCEAN code for larger systems. Originally the ABINIT electronic structure code was used as the DFT solver for the ground state and unoccupied Kohn-Sham state basis. However, recently we have begun adding support for Quantum Espresso (QE). The motivation is that QE is considerably faster, can handle larger system sizes, is more easily parallelized, and has significant user and developer communities. This improved version of OCEAN will allow users of OCEAN to select either ABINIT or QE as the DFT solver for core-BSE calculations.

Publications

1. *Hubbard model corrections in real-space x-ray spectroscopy theory,* Towfiq Ahmed, J.J. Kas and J. J. Rehr, Phys Rev B **85**, 165123 (2012).

2. *Valence Electron Photoemission Spectrum of Semiconductors: Ab Initio Description of Multiple Satellites*, Matteo Guzzo, Giovanna Lani, Francesco Sottile, Pina Romaniello, Matteo Gatti, Joshua J. Kas, John J. Rehr, Mathieu G. Silly, Fausto Sirotti, and Lucia Reining, Phys. Rev. Lett. **107**, 166401 (2011).

3. *Real-space Green's function approach to resonant inelastic x-ray scattering,* J. J. Kas, J. J. Rehr, J. A. Soininen, and P. Glatzel, Phys. Rev. B **83**, 235114 (2011).

4. *Real-space Green's function calculations of Compton profiles*, Brian A. Mattern, Gerald T. Seidler, Joshua J. Kas, Joseph I. Pacold, and John J. Rehr, Phys. Rev. B **85**, 115135 (2012).

5. *Bethe-Salpeter Equation Calculation of Core Excitation Spectra,* J. Vinson, E. L. Shirley, J. J. Rehr, and J. J. Kas, Phys. Rev. B **83**, 115106 (2011).

6. *X-ray absorption near-edge spectra of overdoped* $La_{2-x}Sr_xCuO_4$ *high-Tc superconductors*,Towfiq Ahmed, Tanmoy Das, J.J. Kas, Hsin Lin, B. Barbiellini, Fernando D. Vila, R.S. Markiewicz, A. Bansil, and J. J. Rehr, Phys. Rev. B **83**, 115117 (2011).

7. *Theoretical optical and x-ray spectra of liquid and solid* H_2O,J. Vinson, J. Kas, F. Vila, J. J. Rehr and E. L. Shirley, Phys. Rev. B 85, 045101 (2012).

Strong Correlations in Electron Systems

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I. Project Scope

The scope of this proposal is that of the theory of strongly correlated electronic materials. The proposal covers the theory of materials that contain elements from the lanthanide and actinide series and which show anomalous behavior due to the presence of strong interactions. One emphasis is placed on the effects of strong interactions on the the low-temperature quasi-particle dispersion relations near the Fermi-energy (such as the production of heavy masses or the formation of gaps), and their manifestations in spectroscopic probes (such as inelastic neutron scattering, ARPES etc.). Another emphasis is placed on the effects that the temperature-dependence of the quasiparticle spectra have on the phonon spectra and their relation to the temperature-dependent phonon anomalies observed in α-uranium and plutonium.

II. Recent Progress

An underscreened Anderson Model [9C] has been devised to describe the anomalies found in the ferromagnetic uranium-based compounds US, USe and UTe. The high temperature susceptibility of the materials shows evidence of spin $S = 1$ moments, while transport properties show the existence of a logarithmic temperature-dependence indicative of the Kondo effect. However, below the Kondo temperature, the system shows evidence of a set of partially compensated spin one-half moments that order ferromagnetically. The ordering in the uranium compounds contrasts sharply with the ordering in cerium compounds [1J], which show very much smaller values of the ordering temperatures and much reduced ordered magnetic moments. We have examined USb_2 theoretically and have described a kink that appears in the quasi-particle dispersion relation and which has been observed experimentally by the ARPES measurements of Durakiewicz *et al.* [2C,4C].

In a related study, we have shown that the Hund's rule coupling may produce a gapping of the Fermi-surface of the underscreened Anderson Lattice Model without producing either spin density wave ordering, orbital ordering or charge density wave ordering. The proposed phase shows a combined spin and orbital density wave that is difficult to detect experimentally [8J]. In the mean-field approximation, the proposed mechanism not only shows gaps at the Fermi-energy but also breaks spin-rotational invariance without producing ordered magnetic moments. The properties of this phase are fully consistent with the experimentally-determined properties of the “Hidden Ordered” phase of URu_2Si_2 measured thus far [5J,9C].

The effects of a temperature-dependent hybridization gap and strong electron-phonon coupling on the high-temperature phonon spectrum have been investigated [2J]. It has been shown that as the temperature increases, the hybridization gap is reduced via a polaronic mechanism [4J,7C]. For temperatures at which the reduced electronic gap is of the same order as the phonon energies[8C], the electronic excitations may resonate with the phonon excitations and can result not only in a softening of the zone-boundary optic phonons but may also produce a bifurcation of the phonon peak. This has been suggested as being responsible for the phonon anomalies observed in α-uranium and plutonium [2J]. An alternative suggestion for the origin of these anomalies, the formation of Intrinsically Localized Modes, has been investigated theoretically using a one-dimensional model first devised by Fermi, Pasta and Ulam [3J]. The quantized version of this anharmonic model suggests that, due to the anharmonic interactions, the phonon spectrum may contain multi-phonon bound states as well as the single-phonon peaks that are usually seen in inelastic scattering experiments [6J,7J]. In the one-dimensional model, any arbitrarily weak anharmonicity results in the production of bound states due to the effect of the real divergences found at the van Hove singularities. Although the predicted features are not fully consistent with the anomalies found in uranium by Manley *et al.*, it seems [6C] that an extension to three-dimensions might be consistent with anomalies observed by Manley *et al.* in the strongly anharmonic crystal NaI.

III. Planned Activities 2012-2013

In the next year of the project we intend to complete the theoretical investigation of the effects of mixed valence in the underscreened Anderson lattice and compare this with the ARPES measurements of Durakiewicz *et al.* on the uranium monochalcogenides. We also intend to continue the study of USb_2 in order to compare with recent ARPES results obtained by the Los Alamos photoemission group.

The relationship between the Hund’s rule mechanism proposed to describe the “Hidden Ordering” in URu_2Si_2 will be further examined. The effects of precursor fluctuations on the ARPES spectra will be examined, with the expectation that they may produce the effects suggested by Balatsky *et al.*. This study will also examine the nature of the Goldstone modes expected for the symmetry broken state and their overdamped extension in the normal state. Preliminary calculations show that, although the precursor fluctuations have large amplitudes, the amplitudes never diverge since the approach to a quantum critical point is arrested by the occurrence of a first-order transition. We shall investigate the approach to the quantum critical point with an eye on comparing our results with the first-order transition found in experiments of Jaime *et al.* on $\mathrm{URu_2Si_2}$ performed at Los Alamos in the High Magnetic Field Laboratory. We shall also investigate the magnetic anisotropy found in Shubnikov - de Haas experiments performed by Joe Thompson and co-workers in Los Alamos. Finally, we shall also examine whether the Hund's rule mechanism may be operative in transition metal compounds such as the ironpnictide high-temperature superconductors.

In the next year, we also expect to complete the generalization of the quantum Fermi-Pasta-Ulam model to higher dimensions so as to definitively answer the question as to whether Intrinsically Localized Modes can exist in three-dimensions at sufficiently high-temperatures, or whether these modes occur strictly in one-dimensional systems as a consequence of the divergent van-Hove singularities. High temperature ILMs could be expected in three-dimensional systems since the anharmonic interactions are enhanced by the Bose-Einstein distribution function. We expect to compare our results with the results found by Manley *et al.* in experiments on NaI.

Journal Publications

1. *The Transition from Heavy Fermion to Mixed Valence in* $Ce_{1-x}Y_xAl_3$*: A Quantitative Comparison with the Anderson Impurity Model.*
(with E.A. Goremychkin, R. Osborn, I.L. Sashin, B.D. Rainford, D.T. Adroja and J.M. Lawrence)
Physical Review Letters, 104, 176402 (2010).

2. *Phonon Anomalies in* α*-uranium.* (with Xiaodong Yang)
Physical Review B, 82, 094303 (2010).

3. *The Korteweg - de Vries Equation: Its place in the development of non-linear physics.*
Philosophical Magazine, 91, 997-1006 (2011).

4. *Temperature Dependence of Hybridization Gaps: Metallic Heavy-Fermion Systems.* (with Xiaodong Yang and Tomasz Durakiewicz)
Journal of Physics CM, 23, 094211 (2011).

5. *Anomalous Femtosecond Quasiparticle Dynamics of the Hidden-Order State in* URu_2Si_2. (with Georgi L. Dakovski, Yinwan Li, Steve M. Gilbertson, George Rodriguez, Alexander V. Balatsky, Jian-Xin Zhu, Krzysztof Gofryk, Eric D. Bauer, Paul H. Tobash, Antoinette Taylor, John L. Sarrao, Peter M. Oppeneer, John A. Mydosh, and Tomasz Durakiewicz)
Physical Review B, 84, 161103 (2011).

6. *Quantized Intrinsically Localized Modes of the Fermi-Pasta-Ulam Lattice.*
(with Sukalpa Basu)
Philosophical Magazine, 92, 134-144 (2012).

7. *Quantized Breather Excitations of the Fermi-Pasta-Ulam Lattices.*
Physical Review E, 85, 011129 (2012).

8. *Phase Transition arising from the Underscreened Anderson Lattice Model: A Candidate Concept for Explaining Hidden Order in URu_2Si_2.*
(with B. Coqblin and S.G. Magalhães)
Physical Review B, 85, 165116 (2012).

Conference Proceedings

1. *On the Role of Electronic Polarization in Continuous Structural Transitions.*
(with Xiaodong Yang, J.L. Smith, S.M. Shapiro and J.C. Lashley)
Physica Status Solidi B: 247, 580-582 (2010).

2. *Effect of Electronic Correlations on the Quasi-particle Dispersion of USb_2.*
(with Xiaodong Yang, Tomasz Durakiewicz, P.M. Oppeneer and S. Elgazzar)
Journal of Physics: Conference Series 200, 012164 (2010).

3. *Influence of Magnetic Fields on the Dielectric Response of Martensitic Materials.* (with Xiaodong Yang, K.A. Modic, R.A. Fisher, C.P. Opeil, T.R. Finlayson, J.C. Cooley, J.L. Smith, P.A. Goddard and J.C. Lashley)
Journal of Physics: Conference Series 200, 032062 (2010).

4. *Quest for Band Renormalization and Self-Energy in Correlated f electron Systems.* (with T. Durakiewicz, C.D. Batista, Yifeng Yang, P.M. Oppeneer, J.J. Joyce, E.D. Bauer and K.S. Graham)
Acta Physica Polonica, 117, 264-267 (2010).

5. *Quantum Fluctuations in Insulating Ferroelectrics.*
Chemical Physics, 375, 184-186, (2010).

6. *Intrinsically Localized Modes: Localization through Interaction.*
International Journal of Modern Physics: Conference Series, 11, 12-21 (2012).

7. *The High-Temperature Phonon Anomalies of α-uranium.*
Materials Research Society Proceedings, 1444, 894-913 (2012).

8. *Temperature-dependent Hybridization Gaps: A Cause of Phonon Anomalies in f Electron Systems?*
Journal of Physics: Conference Proceedings, 391, accepted (2012).

9. *The Underscreened Anderson Lattice : A Model for Uranium Compounds.*
(with B. Coqblin and S.G. Magalhães)
Journal of the Korean Physical Society, accepted (2012).

Fundamental Studies of Complex Oxides and Their Interfaces

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Project Scope

The scope of this project is to develop a theoretical description of the physics of the correlated oxides and their interfaces, starting from the density-functional studies of the electronic structure. Correlated oxides are of considerable current interest including materials such as the colossal magnetoresistive manganites, high-T_c cuprates, Luttinger liquid lithium oxide bronzes, magnetite with its peculiar Verwey metal-insulator transition, and the new spin-ice and quantum-spin-liquid oxides. Recently, high-quality oxide interfaces such as $LaAlO_3/SrTiO_3$ have been grown, leading to the promise of new physics and novel device applications. We discuss in this report three selected topics: (i) The origin and nature of the two-dimensional electron gas (2DEG) at the polar interfaces such as $LaAlO_3/SrTiO_3$ (ii) Control of orbital ordering with strain, which leads to the idea of 'orbitronics,' and (iii) The dynamical Jahn-Teller effect in graphene. Projects for the immediate future include the Rashba spin-orbit interaction at the oxide interfaces and a study of the interplay between the spin and orbital degrees of freedom in the frustrated triangular material $Ba_3CuSb_2O_9$ for possible quantum spin liquid behavior.

Recent Progress

2DEG at the Polar Interface $LaAlO_3$ / $SrTiO_3$

The LAO/STO interface has emerged as one of the prototypes for developing a basic understanding of the behavior of the electrons at the oxide interfaces because (i) it is uncluttered by magnetism as both materials are non-magnetic in the bulk and (ii) the ubiquitous "polar catastrophe" is also present in this interface. The polar catastrophe refers to the electrostatic Coulomb potential which grows unrestricted due to the alternate alignment of positively and negatively charge layers forcing some kind of "electronic reconstruction" to occur. Electron counting arguments suggest that the polar catastrophe would be resolved by the presence of half an electron per unit cell ($3.5 \times 10^{14} \text{cm}^{-2}$). However, careful transport measurements have found only a fraction of this density of about ~ 10^{13} cm^{-2}. To resolve this, we proposed two types of carriers at the interface based on a detailed density-functional (DFT) study. The electrons occupy multiple subbands at the interface with varying dispersions and localizations suggesting the presence of two types of carriers: One type is confined to a single interfacial layer and susceptible to localization due to Anderson type disorder or electron-phonon coupling and may not contribute to transport, while the second type with small masses and extended over several layers is expected to be conducting and what is seen in the experiments. This has been subsequently verified by other theoretical and experimental groups. Quite interestingly, the experiments find the presence of Kondo centers at the interface, even though there are no magnetic atoms present. A second piece of our work based on the Hubbard-Holstein model suggested that it might be due to the polaron formation at the interface. The Hubbard-Holstein model

$$H = \frac{1}{\epsilon} \sum_{ij}{}' M_{ij} q_i q_j - \sum_{\langle ij \rangle \sigma} t\, c_{i\sigma}^{\dagger} c_{j\sigma} + H.c. + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_i \left(\frac{1}{2} K Q_i^2 - g Q_i n_i \right),$$

contains the key competing interactions, viz., the polar potential, the electron kinetic energy, the Coulomb interaction, and the electron-phonon (Jahn-Teller) coupling. We showed that depending on the strengths of the competing interactions, the electrons could either (i) become strongly confined to the interface forming

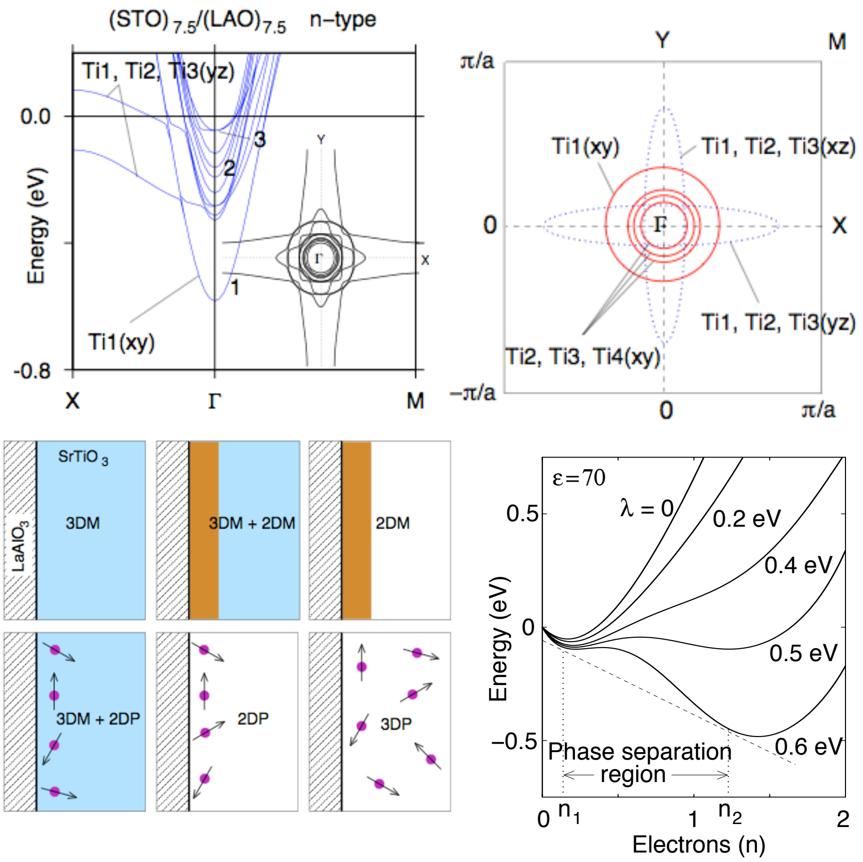

Fig. 1: Conduction subbands near Fermi energy for the LAO/STO interface (*top left*) and the idealized Fermi surface (*top right*). The three outermost orbits are susceptible to localization, while the three innermost orbits can participate in transport. Bottom left panel shows the various possible phases obtained from the Hubbard-Holstein model and the bottom right figure shows the Maxwell construction indicating a phase separation into a low-density metallic phase and a high-density polaronic phase, which might explain the experimentally observed Kondo centers at this interface.

a 2D metallic or an insulating phase, (ii) spread deeper into the bulk making a 3D phase, or (iii) become localized at individual sites forming a Jahn-Teller polaronic phase (Fig. 1). If the electron-phonon coupling strength $\lambda = g^2 / 2K$ is big enough, then the system could phase separate into a high-density ($n_2 \sim 1$ electron / site), insulating polaronic phase and a low-density metallic phase. In the polaronic phase, the electrons are localized at individual lattice sites, which are singly occupied owing to the on-site Coulomb interaction, producing thereby S=1/2 magnetic Kondo centers as experimentally observed. We have extended these studies to a magnetic polar interface and have predicted the formation of a spin-polarized 2DEG at the $SrMnO_3/LaMnO_3$ interface (Fig. 2).

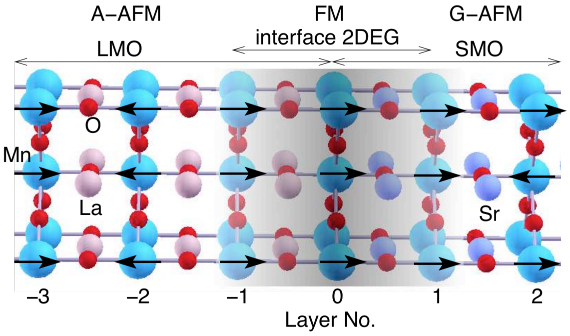

FIG. 2: The predicted formation of the spin-polarized 2DEG (shadowed region) at the magnetic polar interface between $SrMnO_3$ and $LaMnO_3$. Both bulks are antiferromagnetic, while the interface is ferromagnetic, where the spin-polarized 2DEG resides.

Effect of Strain on the interface Orbital Ordering and Magnetism --- The term "orbitronics" has been coined, where the conduction at the interface can be regulated by controlling orbital ordering by strain, which in turn may be controlled electrically by growing the superlattice on a piezoelectric substrate such as $BiFO_3$. We studied how strain affects orbital ordering and magnetism from density-functional methods and simple three-site many-body models solved by exact diagonalization. Fig. 3 describes the dependence of orbital ordering on strain in the $(LaMnO_3)_1$/($SrMnO_3)_1$ superlattice as obtained from our calculations. The orbital ordering goes from the planar x^2-y^2 like to z^2-1 like as one changes the strain from tensile to compressive. As a result, the transport along the c axis will change drastically as electron hopping is larger normal to the interface for the z^2-1 orbital order. What we see is that the orbital occupancies change continuously as a function of strain, indicating that one does not have to apply a drastic amount of strain for

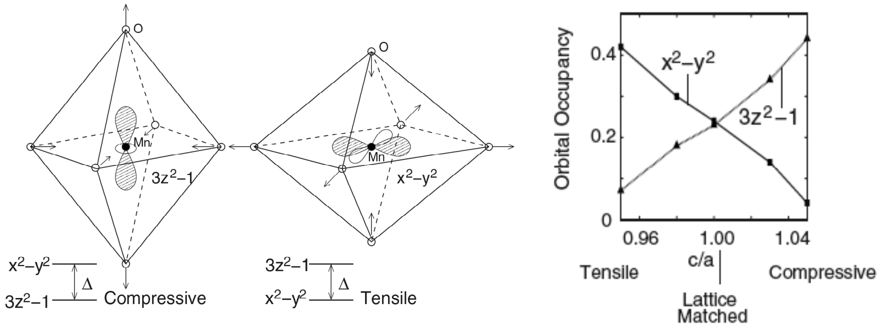

Fig. 3: Change of orbital order with strain as obtained from the DFT calculations for the (LMO)$_1$/(SMO)$_1$ superlattice. Orbital orientation and hence the transport can be controlled by strain or an electric field, leading to the notion of "orbitronics."

some change to occur. This suggests that the transport properties can be controlled electrically via the piezoelectric effect and this would indeed be a worthwhile phenomenon to explore experimentally.

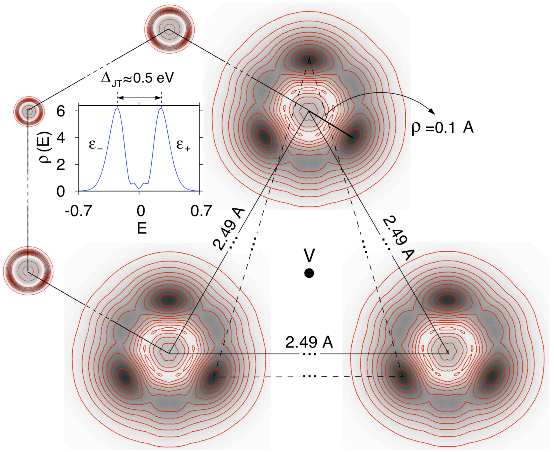

FIG. 4: Nuclear probability density showing the symmetric distortion of the carbon triangle surrounding the vacancy indicated by "V" owing to the dynamical Jahn-Teller effect. The inset shows the Jahn-Teller splitting of the electronic state computed within the adiabatic approximation.

Dynamical Jahn-Teller Effect in Graphene – The ideas developed during our work on the dynamical Jahn-Teller (JT) effect on magnetism in the oxides were extended to the current problem of graphene. In the static JT effect, there is a static distortion of the nuclear framework due to the electron-lattice coupling, where the nuclei are frozen in one of the several equivalent minima of the adiabatic potential surface. In contrast, in the dynamical JT effect, the tunneling barrier between the minima is low, which results in the tunneling of the nuclear wave function. For graphene, we showed that the substitutional vacancy forms a dynamical JT center by computing the adiabatic potential surface by density-functional methods, which has three minima due to the $E \otimes e$ JT coupling. The nuclei tunnel between these minima, leading to a large real-space delocalization of the carbon atoms next to the vacancy as shown in Fig. 4. We explained the energy structure of the combined electron-nuclear system in terms of the tight-binding hopping of the nuclei with a Berry phase factor due to the fictitious magnetic field introduced by the adiabatic motion of the electrons. This results in a JT splitting of the electron energy levels (inset of Fig. 4), even though the nuclei retain the symmetry of the honeycomb lattice.

Planned Activities: 2012-2013

Rashba Spin-Orbit coupling at the Oxide Interfaces: We are currently studying the Rashba spin-orbit coupling effects recently observed in the LAO/STO interface. The Rashba effect is well-known in semiconductors and it is a promising mechanism for the future spintronics devices. The effect has been seen recently for the oxide interfaces, but has many ill-understood features including the strong asymmetry of the Rashba parameter with the change of the sign of the electric field. The effect is expected to be different from the semiconductors because of the multiplicity of the d orbitals and also the magnitude of the effect is expected to be stronger. From our preliminary work, we find, quite interestingly, that within the d manifold, only the xz/yz bands show the Rashba effect, but not the xy bands, and furthermore, the xz/yz bands must be the lowest bands in energy and localized at the interfacial layer for any noticeable Rashba effect. These features lead to the prospect of manipulating the Rashba effect by electric field or strain. Our preliminary results show that indeed the electric field can alter the band structure quite drastically and produce a large Rashba effect, whereas none existed without the applied electric field.

Frustrated Spin-Ice Oxides: Recently, $Ba_3CuSb_2O_9$ (and its sister compound $Ba_3NiSb_2O_9$) has been proposed as a quantum spin liquid system due to its frustrated triangular lattice and the low S=1/2 of the Cu (d^9) ion. Frustration leads to a massively degenerate ground state, manifesting itself with a finite entropy at T=0, as is well-known from Pauling's pioneering work on the water ice and recently discovered in the spin-ice compound dysprosium titanate as well. A puzzling issue regarding $Ba_3CuSb_2O_9$ is that there is no Jahn-Teller distortion in the CuO_6 octahedron as would be expected for the d^9 system. In this project, we will understand the electronic structure and develop possible reasons for the absence of the Jahn-Teller interaction using DFT calculations. Based on this we will extract and solve minimal models for the electronic structure, studying the justification for the proposed Kugel-Khomskii Hamiltonian, which is only good in the large U/W limit. The proposed work will form the essential foundation for the understanding of the spin liquid behavior in this material and its sister compounds.

Publications

1. B. R. K. Nanda and S. Satpathy, "Electronic and Magnetic Structure of the $(LaMnO_3)_{2n}/(SrMnO_3)_n$ Superlattices," Phys. Rev. B 79, 054 428 (2009)
2. P. Larson and S. Satpathy, "Supercell studies of the Fermi surface changes in the electron-doped superconductor $LaFeAsO_{1-x}F_x$," Phys. Rev. B 79, 054502 (2009)
3. B. R. K. Nanda and S. Satpathy, "Strain and Electric Field Modulation of the Electronic Structure of Bilayer Graphene," Phys. Rev. B 80, 165430 (2009)
4. B. R. K. Nanda and S. Satpathy, "Polar catastrophe, electron leakage, and magnetic ordering at the $LaMnO_3/SrMnO_3$ interface," Phys. Rev. B 81, 224408 (2010)
5. B. R. K. Nanda and S. Satpathy, "Magnetic and Orbital Order in $LaMnO_3$ under Uniaxial Strain," Phys. Rev. B 81, 174 423 (2010)
6. B. R. K. Nanda and S. Satpathy, "Polar catastrophe and the spin polarized electron gas at the $LaMnO_3$/ $SrMnO_3$ interface," J. Vac. Sci. Technol. 28, c5A24 (2010)
7. B. R. K. Nanda and S. Satpathy, "Density Functional studies of $LaMnO_3$ under Uniaxial Strain," J. Magn. Mag. Materials 322, 3653 (2010)
8. S. Mishra and S. Satpathy, "Photoinduced magnetism in the ferromagnetic semiconductors," Int. J. Mod. Phys. B 24, 359 (2010)
9. B. R. K. Nanda and S. Satpathy, "Electronic Phases and Phase Separation in the Hubbard-Holstein Model of a Polar Interface," Phys. Rev. B 83, 195114 (2011)
10. M. Sherafati and S. Satpathy, "RKKY Interaction in Graphene from Lattice Green's Function," Phys. Rev. B 83, 165425 (2011)
11. M. Sherafati and S. Satpathy, "Impurity states on the honeycomb lattice using the Green's function method," Phys. Stat. Solidi (B) 248, 2056 (2011)
12. M. Sherafati and S. Satpathy, "Analytical Expression for the RKKY Interaction in Doped Graphene," Phys. Rev. B 84, 125 416 (2011)
13. M. Sherafati and S. Satpathy, "On the Ruderman-Kittel-Kasuya-Yosida interaction in graphene," Proc. of the Int. Workshop on Functional Materials, AIP (2012, in press) arXiv: 1202.2879
14. B. R. K. Nanda, M. Sherafati, Z. Popovic, and S. Satpathy, "Electronic structure of the substitutional vacancy in graphene: Density-Functional and Green's function studies," New J. Physics (2012, in press) arXiv:1105.1129
15. Z. S. Popovic, B. R. K. Nanda, and S. Satpathy, "Nuclear Tunneling and Dynamical Jahn-Teller Effect in Graphene with Vacancy," Phys. Rev. B (2012, in press) arXiv:1207.3075

Strongly Correlated Electrons

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Project scope

The research in this program is on aspects of heavy fermions, complex phase diagrams of transition metal oxides, one-dimensional quantum wires, and, in the context of ultracold atoms in a one-dimensional trap, the Fermi gas with attractive potential and arbitrary spin. Here I briefly report on three projects. (1) A discontinuous transition observed in the heavy fermion compound $\mathrm{CeIn_3}$ in high magnetic fields is shown to arise from a Lifshitz transition due to the interplay of the Landau quantization and interactions. (2) A theoretical explanation that electron spin resonance (ESR) can be observed in heavy fermion lattices with ferromagnetic correlations. Of particular interest is the case of the cubic compound $\mathrm{CeB_6}$ which has a Γ_8 ground quadruplet with antiferro-quadrupolar long-range order. (3) The phase diagram of interacting ultracold atoms confined to a one-dimensional optical trap is studied for arbitrary spin. The system displays phase separation along the trap and instabilities to superfluid phases with FFLO signatures.

Recent progress

(1) Discontinuous Lifshitz transition

A Lifshitz transition is a topological change of the Fermi surface. The two most common Lifshitz transitions studied are (i) the disruption of a neck of the Fermi surface into two parabolic pieces and (ii) the appearance or disappearance of a Fermi surface. I consider the second type, which can be induced in some compounds as a function of pressure or a magnetic field. As a consequence of the vanishing group velocity at the transition point, the van Hove singularity gives rise to power laws with half-integer exponents in the low temperatures properties. Hence, in 3D at the transition the occupation of the pocket should vary continuously with temperature as $T^{1/2}$.

Yamaji et al. (J. Magn. Magn. Mater. **310**, 838 (2007)) have shown that in 2D the presence of interactions can turn the Lifshitz transition discontinuous, in contrast to the continuous transition for noninteracting systems. Interactions alone are not expected to change the order of the transition in 3D. However, the Landau quantization in a strong magnetic field gives rise to 1D properties for the direction parallel to the magnetic field. Due to this reduction in dimensionality the interactions play a relevant role and give rise to a discontinuous Lifshitz transition.

A possible application for a Lifshitz transition in a correlated electron system in high magnetic fields is $\mathrm{CeIn_3}$. From quantum oscillations it was found that a set of hole pockets disappears for fields above 41 T (Harrison et al., Phys. Rev. Lett. **99**, 056401 (2007); Sebastian et al., PNAS **106**, 7741 (2009)). Skin depth measurements with a tunnel diode oscillation technique (Purcell et al., Phys. Rev. B **79**, 214428 (2009)) showed that this transition occurs at 45 T, displays hysteresis and becomes better defined at lower T. Extrapolated to $T \to 0$, the transition represents a jump in the conductivity to a less resistive state at higher fields.

Due to the 1D properties in the extreme Landau limit the vertex functions and the density correlation function have logarithmic singularities to all orders of perturbation in the Coulomb interaction. These logarithms have to be summed via a renormalization group (Schlottmann and Gerhardts, Z. Phys. B **34**, 363 (1979); Schlottmann, Phys. Rev. B **83**, 115133 (2011)). The renormalized density of states for the Lifshitz transition acquires an essential singularity for the vanishing 1D Fermi momentum, q_0. The band filling is given by an integral over this singularity, which is not integrable, so that the change in the number of particles when the band starts to get filled is discontinuous at $T = 0$. The magnitude of the jump cannot be determined in linear response. The Fermi points and the logarithms are smeared at finite T, so that the singularity is cut-off and the filling of the first Landau level is continuous as a function of q_0. The logarithm of the density of states as a function of q_0 is shown in the left panel of Fig. 1 for various T.

(2) ESR in heavy fermions

The common belief that an electron spin resonance (ESR) signal could not be observed in heavy-fermion compounds due to the broad linewidth proportional to the Kondo temperature was proven wrong, when an ESR signal was found in single crystals of $YbRh_2Si_2$, $YbIr_2Si_2$, CeRuPO, YbRh, and $YbCo_2Zn_{20}$. All of the above compounds are very anisotropic and have ferromagnetic correlations among the rare earth spins. Abrahams and Wölfle (Phys. Rev. B **78**, 104423 (2008)) obtained within the framework of the Anderson lattice that the heavy mass in conjunction with ferromagnetic fluctuations can lead to observable narrow resonances in heavy fermion compounds. Schlottmann (Phys. Rev. B **79**, 045104 (2009)) arrived at similar conclusions for the Kondo lattice exploiting the proportionality of the linewidth and the inverse susceptibility. This clearly shows the relevance of the ferromagnetic correlations: While the Kondo effect yields a broad (and hence not observable) ESR line, ferromagnetic correlations enhance the susceptibility and narrow the linewidth. The ferromagnetic correlations and the magnetic anisotropy play the central role.

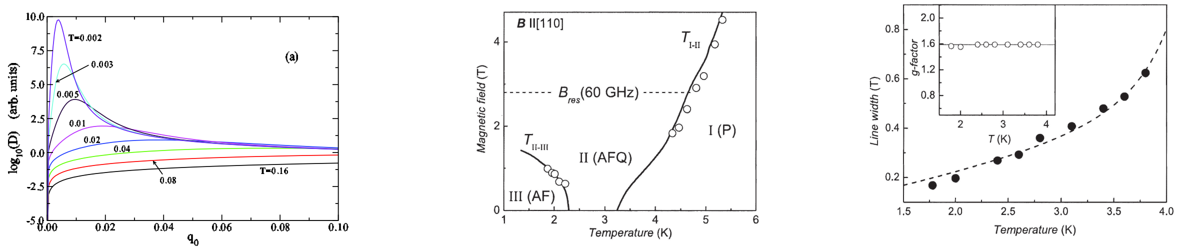

Figure 1: *Left panel:* Temperature and 1D Fermi momentum dependence of the logarithm of the density of states for the lowest Landau level. As $T \to 0$ the essential singularity emerges. *Middle panel:* Phase diagram of CeB_6. *Right panel:* Linewidth and g-factor of ESR line in CeB_6 (from Demishev et al, Phys. Rev. B **80**, 245106 (2009)).

Recently, Demishev et al (Phys. Rev. B **80**, 245106 (2009)) observed an ESR signal at 60 GHz in the antiferro-quadrupolar (AFQ) phase of the *cubic* compound CeB_6. The phase diagram of CeB_6 and the linewidth and g-factor of the resonance are shown in the middle and right panels of Fig. 1, respectively. The Ce^{3+} ions in CeB_6 have a Γ_8 ground-quartet which has simultaneously spin and quadrupolar content. The long-range order is driven by the quadrupolar degrees of freedom. There are several questions arising in the context of the observation of the ESR signal in CeB_6: (1) A Γ_8 quartet allows four transitions, why is only one observed? (2) The isotropy of a cubic compound does not favor ferromagnetic correlations, why is a resonance observed at all?

The AFQ order quenches two of the resonances, leaving two resonances, one corresponding to each sublattice. The coherence of $4f$-electrons in a lattice finally leads to *one* resonance with a g-factor equal to the half-sum of the g-values of the two sublattices. CeB_6 is the first heavy fermion compound where a collective ESR band resonance needs to be invoked. All other systems can be interpreted alternatively either as a resonance of local moments or the resonance of carriers in a heavy electron band.

The origin of the ferromagnetic correlations can be understood from the two-particle wave-functions, which is a product of three factors, one coordinate wave-function (even parity), one for the quadrupolar (odd parity) and one for the spin degrees of freedom (even parity). The spins are then necessarily

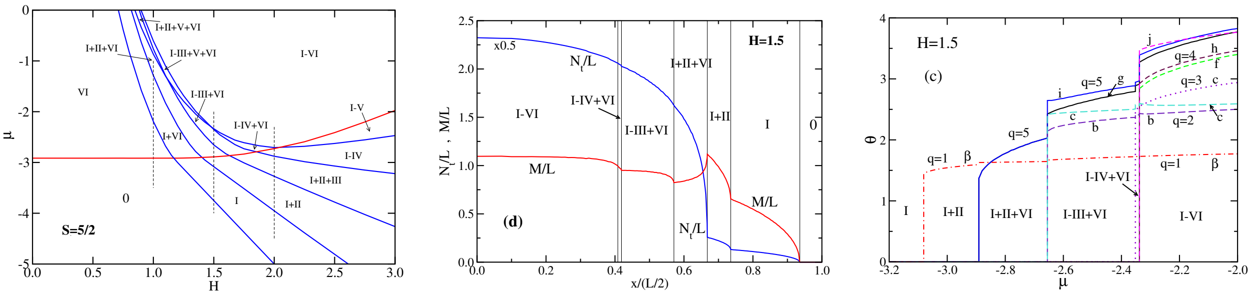

Figure 2: *Left panel:* Ground state phase diagram for a homogeneous fermion gas of spin $S = 5/2$ with unit interaction strength. The phase denoted with 0 (lower left corner) has no particles. The Roman numbers indicate the number of particles in the bound state. Regions with more than one Roman number are mixed phases with coexisting bound states. *Middle panel:* Profile of the total number of particles, N_t/L, (blue curve) and the magnetization density, M/L, (red curve) for $H = 1.5$ (see dashed vertical line in left panel) showing the phase separation due to varying confinement along the trap x. *Right panel:* Critical exponents of the superfluid response functions as a function of μ for $S = 5/2$ and $H = 1.5$.

in a triplet state and ferromagnetically correlated. On the lattice, since quadrupolar singlets cannot be satisfied for all nearest neighbor sites, the system becomes a quadrupolar resonant valence bond lattice. A magnetic field enhances the spin alignment and hence the AFQ and ferromagnetic correlations. This explains the increase of T_c with magnetic field seen in Fig. 1 (center panel). The susceptibility also increases with field in agreement with experiment and this enhancement of χ_0 narrows the ESR linewidth ($\propto 1/\chi_0$), rendering the signal observable.

(3) Phase separation and FFLO signatures in ultracold gas of atoms

Confinement of ultracold atoms to nearly 1D traps can be achieved in 2D optical lattices defining an array of tubes. The tubes can be regarded as isolated if the confinement by the laser beams is strong enough to suppress tunneling between tubes. The interaction between the fermions can be made attractive and its strength varied by fine-tuning the Feshbach-type resonance due to the scattering between atoms under transverse harmonic confinement. The interaction is local and can be approximated by a δ-function potential in space. The 1D gas of fermions of spin S with δ-function interaction is SU($2S+1$) symmetric and integrable. The solution via Bethe's *Ansatz* was obtained by Sutherland (Phys. Rev. Lett. **20**, 98 (1968)), Takahashi (Prog. Theor. Phys. **44**, 899 (1970)) and Schlottmann (J. Phys. Cond. Matter **5**, 5869 (1993) and **6**, 1359 (1994)). Tubes with ultracold gases of ^{40}K (spin 9/2), ^{43}Ca (spin 7/2), ^{87}Sr (spin 9/2), ^{173}Yb (spin 5/2), ^{9}Be (spin 3/2), ^{135}Ba (spin 3/2), ^{137}Ba (spin 3/2) and ^{53}Cr (spin 3/2) atoms provide a unique opportunity to study fermion systems with spin larger than 1/2.

The Bethe solution yields $N = 2S + 1$ basic states, namely bound states of $N, N-1, \cdots,$ two particles, and unbound particles. The ground state phase diagram will have many mixed phases, which can have up to N coexisting basic states, and is shown in the left panel of Fig. 2 for $S = 5/2$. The Roman numbers indicate the number of particles involved in a bound state. The phase diagram consists of six crossover lines given by the van Hove singularities of the bands corresponding to bound states of n particles. The red curve refers to clusters of six particles, which have a field independent potential. The remaining five (blue) lines refer to bound states with magnetic content.

The weak confinement along the tube is roughly harmonic and can be locally incorporated into the chemical potential. Consequently, these systems of fermions are only locally homogeneous and within the local density approximation display phase separation with the variation of the chemical potential along the tube of length L (see middle panel in Fig. 2).

In an array of tubes with weak Josephson tunneling long-range superfluid order may arise (dimensional crossover). The number of possible order parameters for superfluidity is very large. In order to decide which superfluid phase is the first to appear from the disordered (Luttinger liquid) phase when the temperature is reduced, the corresponding superfluidity response functions have to be computed making use of conformal field theory and the Bethe *Ansatz* solution. The equal time correlation functions are the product of a power law of the distance and an oscillating sinusoidal factor. The response with the smallest critical exponent is the most favorable for order. The exponents as a function of μ for $S = 5/2$ and $H = 1.5$ are shown in the right panel of Fig. 2. The most favorable first phase is denoted with β, which corresponds to a pairing of particles with spin component $S_z = 5/2$ and 3/2. The period of oscillations is determined by the spin imbalance and is reminiscent of the Fulde-Ferrell-Ovchinnikov-Larkin phase for superconductivity.

This calculation was carried out in collaboration with A.A. Zvyagin. It is the extension of Orso's work (Phys. Rev. Lett. **98**, 070402 (2007)) to spins higher than 1/2 and the generalization of the FFLO phase to arbitrary spin.

Planned activities

The projects presented above are essentially completed. The continuation of several other projects is planned. (1) Quantum criticality of heavy fermion compounds and the origin of the superconducting dome. (2) The central peak observed by neutron scattering in the dynamic susceptibility of heavy fermion compounds. (3) The origin of the magnetic anisotropy in ruthenates and iridates taking into account the orbital and spin degrees of freedom with spin-orbit coupling in an appropriate crystalline field reflecting the distortion, rotation and tilting of the octahedra.

Selected recent publications

[1] **P. Schlottmann**, Lifshitz transition with interactions in high magnetic fields, Phys. Rev. B **83**, 115133 (2011).

[2] **P. Schlottmann**, Magnetic field induced quantum criticality at a Lifshitz transition with interactions, J. Appl. Phys. **111**, 07E101 (2012).

[3] **P. Schlottmann**, Calculation of electric transport close to a Lifshitz transition in a high magnetic field, submitted.

[4] **P. Schlottmann**, Electron Spin Resonance in antiferro-quadrupolar ordered CeB_6, submitted.

[5] **P. Schlottmann** and A.A. Zvyagin, Fermi gas with attractive potential and arbitrary spin in a one-dimensional trap: Phase diagram for $S = 3/2$, $5/2$, $7/2$, and $9/2$, Phys. Rev. B **85**, 024535 (2012).

[6] **P. Schlottmann** and A.A. Zvyagin, Fermi gas with attractive potential and spin $S = 3/2$ in a 1D trap: Response functions for superfluidity and FFLO signatures, Phys. Rev. B **85**, 205129 (2012).

[7] **P. Schlottmann** and A.A. Zvyagin, Phase separation and FFLO phases in ultra-cold gas of $S = 5/2$ atoms with attractive potential in a one-dimensional trap, Modern Physics Letters B **147**, 1230009 (2012).

[8] D. Graf, R. Stillwell, T.P. Murphy, J.-H. Park, E.C. Palm, **P. Schlottmann**, R.D. McDonald, J.G. Analytis, I.R. Fisher, and S.W. Tozer, Pressure dependence of the $BaFe_2As_2$ Fermi surface within the spin density wave state, Phys. Rev. B **85**, 134503 (2012).

[9] J. Hwang, E.S. Choi, H.D. Zhou, J. Lu, and **P. Schlottmann**, Magneto-electric effect in $NdCrTiO_5$, Phys. Rev. B **85**, 014415 (2012).

[10] J. Hwang, E.S. Choi, H.D. Zhou, Y. Xin, J. Lu, and **P. Schlottmann**, Magnetic transitions and magnetodielectric effect in antiferromagnet $SrNdFeO_4$, Phys. Rev. B **85**, 224429 (2012).

[11] S. Yeo, K. Song, N. Hur, Z. Fisk, and **P. Schlottmann**, Effects of Eu doping on SmB_6 single crystals, Phys. Rev. B **85**, 115125 (2012).

[12] M. Ge, T.F. Qi, O.B. Korneta, L.E. DeLong, **P. Schlottmann**, W.P. Crummett, and G. Cao, Lattice-driven magnetoresistivity and metal-insulator transition in single-layered iridates, Phys. Rev. B **84**, 100402(R) (2011).

[13] J. Stankiewicz, M. Evangelisti, Z. Fisk, **P. Schlottmann**, and L.P. Gor'kov, Kondo physics in a rare earth ion with well localized 4f electrons, Phys. Rev. Lett. **108**, 257201 (2012).

Novel Charge and Spin Fractional Quantum Hall Effects and New Emerging Quantum Phases

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Project Scope

The research in this program involves developing theoretical (numerical) approaches to study the nature of new emerging quantum phases and associated novel transport and topological properties in several electron or boson systems. We focus on a few related topics in strongly correlated systems including: (a) The fractional quantum Hall effect (FQHE) in topological bands without a magnetic field; (b) The fractional quantum spin (or pseudospin) Hall effect (FQSHE) in topological bands without breaking time-reversal symmetry; (c) Quantum phase diagrams and quantum phase transitions through interaction engineering in complex systems like strained graphene and optical lattices. Due to the nature of strong correlations in all these systems, there are no well defined analytical theory, which can predict the quantum phases for realistic Hamiltonians involving competing interactions. We develop state of the art numerical approaches including exact diagonalization (ED) and density matrix renormalization group (DMRG) codes, which can access the ground state and low energy spectrum of different systems containing a large number of particles. At the same time, we design new measurements targeting the nature of the quantum phases including topological and transport properties, and work closely with other groups who develop analytic theory for such systems. By such joint effort, we make rigorous progress towards a better understanding of the topological matter and the emerging new quantum phases in strongly correlated systems.

Recent Progress

Fractional Chern Insulators: Emerging FQHE without Landau levels (LLs)

The FQHE is a remarkable new state of matter, where quasiparticles carry fractional charge. Such a state was associated with interacting systems under strong magnetic field or effective LLs. It is a very active direction in condensed matter to search for new realization of such a fractionalized state without a magnetic field. We have recently demonstrated that the interaction effect on various near-flat topological bands carrying nonzero Chern number can lead to both Abelian FQHE and Non-Abelian quantum Hall effects (NA-QHE)[1-3] with topological order and fractionalized quasiparticles. The emerging topological state is also being referred to as “Fractional Chern Insulator” as it is hosted by a class of Chern insulators known as Haldane model.

Shown in Fig. 1, we identify the NA-QHE state in the honeycomb lattice Haldane model with topological nontrivial flatband through extensive numerical studies for three-body hard-core bosons at filling number $\nu = 1$. Such a state is characterized by the three-fold quasi-degeneracy of ground states on a torus (Fig. 1d), a quantized Chern number[3], and a robust spectrum gap (Fig. 1e). Moreover, the spectrum for

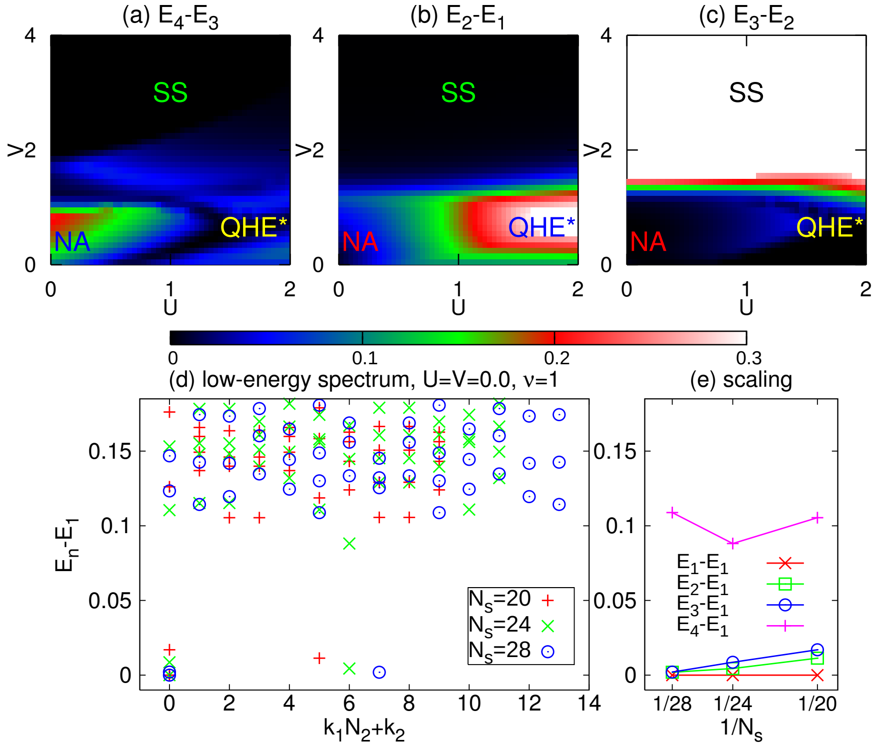

FIG. 1: (color online). (a-c) Intensity plots of spectrum gaps in U-V phase space for the 20-site lattice at filling number $\nu = 1$, where U and V are the nearest (NN) and next NN (NNN) interaction strengths between bosons. See [3] for detail. E_i $(i = 1, 4)$ denote the energies of the lowest four eigenstates. NA, QHE* and SS label the rough phase regions of NA-QHE, a possible quantum Hall phase (which may evolve with system sizes), and supersolid inferred from all three spectrum-gap plots and other calculations; (d) Low energy spectrum $E_n - E_1$ versus the momentum $k_1N_2 + k_2$ of the NA-QHE phase for three lattice sizes N_s = 20, 24 and 28; (e) Scaling plot of the spectrum gaps demonstrating robust gap and ground state three-fold degeneracy.

two-quasihole states also shows a finite energy gap, with the number of states in the lower energy sector satisfying the same counting rule as the Moore-Read Pfaffian state.

New Quantum Phases in Strained Graphene and Valley FQSHE

We model the strained graphene system as electrons in pseudo magnetic fields oriented in opposite directions in the two valleys. For strained graphene at neutrality[4], we predict that a spin or a valley polarized state is possible depending on the value of the onsite Coulomb interaction. At fractional filling, the unscreened Coulomb interaction leads to a valley polarized FQHE which spontaneously breaks time reversal symmetry. By tuning an attracting Hubbard interaction, a spin-polarized superconducting state emerges as shown in Fig.2a. We further consider tuning the short range part of interactions for spinless electrons relevant for artificial graphene systems, and demonstrate that exotic valley symmetric states, including a valley fractional topological insulator (FTI) as a FQSHE state, can be stabilized by such interaction engineering (see Fig.2b).

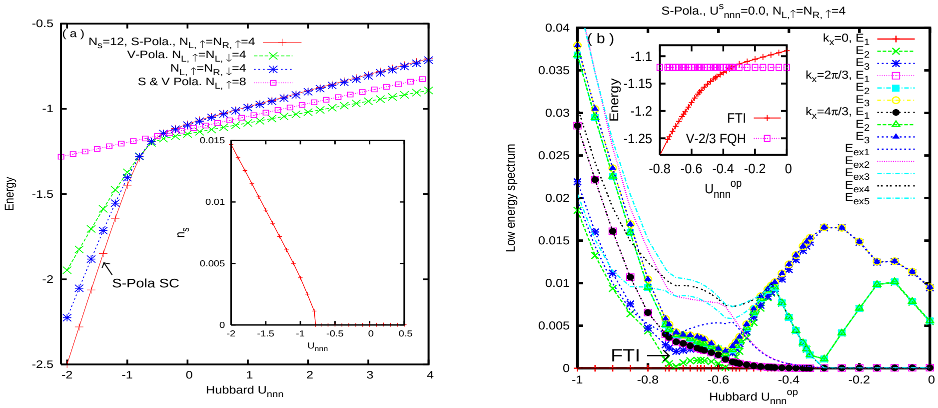

FIG. 2: (Color online). (a) The energy of different states at filling $\nu = -2+2/3$ of the strain induced LL as a function of NNN interaction U_{nnn}. With weak attraction or repulsion ($U_{nnn} > -0.8$), the ground state is valley polarized FQHE state. At $U_{nnn} < -0.8$ side, the valley unpolarized superconducting state with the spontaneous spin-polarization wins. (b) By tuning the opposite valley attraction U^{op}_{nnn}, in the region $-0.73 < U^{op}_{nnn} < -0.58$, the nine lowest energy states become close together and almost degenerated, thereby forming the groundstate manifold (GSM) of the valley FTI. The inset shows the groundstate energies of the valley polarized (V-2/3 FQH) and FTI states. See [4] for detail.

DMRG development for FQHE and topological systems with complex hopping

We have developed DMRG codes for FQHE and other systems with topological order. We are able to access 5/2 FQHE systems with 34 electrons, which is about twice the system size studied using ED method. We have also obtained full entanglement spectrum for the ground state, which can be used to determine the topological order of the system. We are currently obtaining interesting results for graphene electron systems regarding the competition between the real spin and pseudospin magnetism, SU2 and SU4 fractional states and quantum phase diagram. In the lowest LL (n=0), we find interesting new quantum states at filling 4/3, where both spin and pseudospin form singlet state, which may shed light for understanding experimental observations at fractional fillings of suspended graphene.

Future Plan

We will further study the challenging issues related to FQHE in topological bands. The universality of the wavefunction in real space at long distance has not been addressed. Can they be characterized by a flux binding picture? Is there the off-diagonal-long-range-order for such a state following the same universal behavior as the states in magnetic field? While we expect positive answer, it is essential to demonstrate that to fully establish the emerging of the FQHE without LLs. Furthermore, in searching for weaker FQHE of composite particles, strong finite size effect was observed and it remains unclear what is the microscopic conditions for realizing such states, which will be studied in details. By tuning interaction as well as the band structure, we will look into the development of the fractionalized states at larger system sizes using DMRG. In contrast to the continuum model in a magnetic field where the Chern number of a LL is always one, higher Chern numbers are possible for topological bands in lattice models.

The FQHE in such systems might do not have simple analogy in LL problems, which demands future study.

We will continue to search for new quantum phases in topological bands, bilayer systems, as well as graphene Dirac electron systems based on our newly developed DMRG codes for both torus systems (with around 40 particles) and cylinder systems (around 400 sites). We are developing numerical methods to detect the edge states, to characterize its motion when inserting flux and its edge transport of the FQHE systems. Furthermore, we will measure the topological entanglement entropy to determine the quantum dimension of quasiparticles and the topological order of the system. We will also use impurity to pin quasiparticles to study its braiding by adiabatically moving the quasi-particles around each other and to determine the resulting exchange matrix.

Publications

[1] D. N. Sheng, Z. C. Gu, K. Sun, and L. Sheng, "Fractional quantum Hall effect in the absence of Landau levels", Nature Communications **2**, 389 (2011).

[2] Yi-Fei Wang, Zheng-Cheng Gu, Chang-De Gong, and D. N. Sheng, "Fractional quantum Hall effect of hard-core Bosons in topological flat bands", Phys. Rev. Lett. **107**, 146803 (2011).

[3] Yi-Fei Wang, Hong Yao, Zheng-Cheng Gu, Chang-De Gong, and D. N. Sheng "Non-Abelian Quantum Hall Effect in Topological Flat Bands", Phys. Rev. Lett. **108**, 126805 (2012).

[4] P. Ghaemi, J. Cayssol, D. N. Sheng, and A. Vishwanath, "Fractional Topological Phases and Broken Time-Reversal Symmetry in Strained Graphene", Phys. Rev. Lett. **108**, 266801 (2012).

[5] Jize Zhao, D. N. Sheng, and F. D. M. Haldane, "Fractional quantum Hall states at 1/3 and 5/2 filling: Density-matrix renormalization group calculations", Phys. Rev. B **83**, 195135 (2011).

[6] Matthew S. Block, Ryan V. Mishmash, Ribhu K. Kaul, D. N. Sheng, Olexei I. Motrunich, Matthew P. A. Fisher, Exotic gapless Mott insulators of bosons on multi-leg ladders, Phys. Rev. Lett. **106**, 046402 (2011).

[7] Hao Wang, D. N. Sheng, and F. D. M. Haldane, "Particle-hole symmetry breaking and the $\nu = 5/2$ fractional quantum Hall effect", Phys. Rev. B **80**, 241311 (2009).

[8] Zhong Xu, L. Sheng, D. Y. Xing, Emil Prodan, and D. N. Sheng, "Topologically protected extended states in disordered quantum spin-Hall systems without time-reversal symmetry", Phys. Rev. B **85**, 075115 (2012).

[9] Y. Yang, Z. Xu, L. Sheng, B. Wang, D. Y. Xing, and D. N. Sheng, "Time reversal symmetry broken quantum spin Hall effect", Phys. Rev. Lett. **107**, 066602 (2011).

[10] R. Ma, L. Zhu, L. Sheng, M. Liu, and D. N. Sheng, "Thermoelectric and thermal transport in bilayer graphene systems", Phys. Rev. B **84**, 075420 (2011).

[11] H. Li, L. Sheng, D. N. Sheng, and D. Y. Xing, "Chern number of the thin films of the topological insulator Bi2Se3", Phys. Rev. B **82**, 165104 (2010).

[12] Lijun Zhu, R. Ma, L. Sheng, M. Liu, D. N. Sheng, "Universal Thermoelectric Effect of Dirac Fermions in Graphene", Phys. Rev. Lett. **104**, 076804 (2010).

Materials Theory

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Project Scope

This project uses state-of-the-art materials specific theoretical tools to develop understanding of materials. Working in conjunction with ORNL and external experimental efforts, we unravel the chemical and structural underpinnings of collective properties in specific materials, develop understanding of novel phenomena and materials, and devise new compounds with useful properties. The essential aspect is the use of methods that directly incorporate the chemical make-up and detailed structure of materials and so enable direct connections with experiments. Impacts of this work include microscopic understanding of materials properties, such as ferroelectricity, magnetism and the stability of oxide dispersion strengthened alloys, new concepts for functional hetero-structures, and the elucidation of chemical and physical trends leading to the discovery of new advanced materials. The main scientific thrust is exploration of the key physical phenomena in advanced functional materials, including magnetic materials, ferroelectrics, energy storage interfaces and materials with unusual characteristics, such as uncommon bonding patterns. The overarching goal behind this is materials discovery.

Recent Progress

An important aspect of our work is close collaboration with experiment on a wide variety of materials. These include Fe-based superconductors, various oxides, chalcogenides, and intermetallics. We also do work on spare materials, including carbons and functionalized surfaces. Two of our main thrusts are in magnetism and oxides. Some of our recent work in those areas is highlighted below.

Magnetism: The combination of theory and experiment is a powerful tool for understanding magnetism and magnetic interactions in solids. We collaborated with synthesis and neutron scattering groups studying technetium compounds leading to the discover that the 4d oxide **$SrTcO_3$** [1] has a magnetic ordering temperature above 1000 K, which is among the highest values known in any oxide and contradicts conventional wisdom that magnetism is necessarily weak in 4d oxides. The result was explained by our calculations showing an interplay of moment formation and exceptionally strong covalency. In the marcasite structure compound, **$CrSb_2$** [2] we found a low dimensional electronic structure and magnetic interactions in spite of the three dimensional bonding of the compound. Collaboration with synthesis and neutron scattering groups showed indeed one dimensional magnetic behavior and a very remarkable anisotropic thermal conductivity associated with magnons. In **$Ca_3Ru_2O_7$** [3] we used electronic structure calculations to prove that the drastic change in magnetic order from effectively ferromagnetic to G-type antiferromagnetic observed experimentally with very low level Ti alloying was associated with a Mott transition, and as such that this ruthenates is a borderline material. We used theory in relation to experiment to show that **$NaCoO_2$** [4] becomes close to a ferromagnetic metallic state upon hydration, implying that the superconductivity of this material when hydrated is of triplet character. We showed [5] in contrast to expectations that the triangular lattice delafossite,

$PdCrO_2$ is neither two dimensional nor well described by a short range Heisenberg model, even though it does have a non-collinear 120 degree ground state magnetic structure. We found that this material has a strong interplay between its metallic properties and its magnetic order.

Ferroelectrics and Dielectrics: First principles calculations provide an excellent tool for understanding the structure of oxides, which is central to their physical properties, for example dielectric and ferroelectric behavior, as well as the defects that are important in oxide the functionality of many oxides. We investigated the ABO_3 perovskite alloy **$(Bi,Sr)(Zn,Nb)O_3$** and discovered that this phase exhibits remarkably strong ferroelectricity with polarization comparable to $PbTiO_3$ even with only 50% of the *A*-sites occupied by the stereochemically active ion [6]. This provides a new direction for Pb-free ferroelectrics. A central challenge is the identification of oxide ferroelectrics with band gaps in the visible. We found two approaches for this. In collaboration with experiment we showed that site specific Co substitution in **$Bi_4Ti_3O_{12}$** and explained this behavior. [7] We also showed that alternate layer stackings designed to create charge imbalance can be effectively used without loss of ferroelectricity in this material. [8] We used first principles calculations to explore different polar interfaces, and discovered that the use of certain niobates can yield high mobility 2-dimensional interface electron gasses (**2-DEG**s) with carrier densities higher than the highest reported in titanates. [9] We found that **$BiFeO_3$** has a very strong optical anisotropy in the infrared and that this anisotropy is of a type that will yield exceptionally strong coupling in room temperature plasmonic device geometries. We using hybrid functional calculations to elucidate the chemical behavior of H-related defects in **Cu_2O** correcting showing very different behavior than had been previously claimed. We discovered that N bonds exceptionally well with O in **ZrO_2**, forming a nitrosyl structure defect. This provides a way of explaining the effect of N on the corrosion performance of Zircaloy fuel rod cladding [11]. Finally, we used finite electric field calculations to show that dielectric energy storage and hardness are connected in oxides. [12]

Future Plans

Our future work has two aspects. The first is, as discussed above, using first principles methods to understand properties of materials, usually in conjunction with experimental efforts. Questions that we will address are: How do interesting and useful properties arise? How can we modify materials to achieve and control properties and function? What are the chemical and structural motifs that lead to interesting and useful properties? In what materials should we expect the unexpected (e.g. where are there intense competitions between ground states that may lead to novel behavior)?

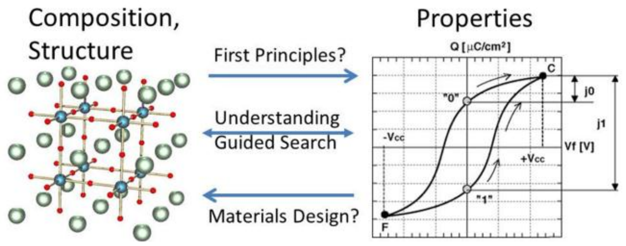

Figure 1. First principles calculations in materials discovery. For some properties, e.g. ferroelectricity, direct predictions can be made, while for others such as unconventional superconductivity this is not the case. Even in such cases theory can play a valuable role by providing microscopic understanding and in exploring trends. “Guided Search” is the use of understanding, trends and prediction for materials discovery.

The second aspect of our future work, which we elaborate on below, is the use of theory to aid materials discovery. The use of computational studies to discover novel materials with enhanced properties is a hot topic and approaches have been proposed and in some cases successfully used for this purpose. The approach we use is called “guided search” (Figure 1). This is an iterative approach involving both theory and experiment.

Guided search does not attempt the direct design of materials based on desired properties, but rather proceeds by developing understanding (in conjunction with experiment), establishing trends, and to exploring the space of materials for interesting properties or to suggest good targets for experimental synthesis. Our specific future materials targets are as follows:

High Energy Product Ferromagnets: Magnetic materials play central roles in energy technologies including in particular ferromagnets for motors and generators. For example, the electric traction motor in a hybrid passenger car typically contains ~5-10 kg of ferromagnetic $Nd_2Fe_{14}B$, typically alloyed with Dy. This is a material that was discovered over 25 years ago. Remarkably, in spite of the importance of ferromagnets in technology, there has been very little progress in the last 20 years and in particular $Nd_2Fe_{14}B$ remains the best practical ferromagnet currently known. We plan to explore novel transition metal ternary and multinary compounds seeking new approaches for producing high energy produces. Our initial work will aim at identified chemistries where one can have high ferromagnetic Curie temperatures in combination with high magnetic anisotropy. The strategy for obtaining high Curie temperature is to have a large fraction of ferromagnetic 3d element, while that for high anisotropy is to have a heavy element, such as a 5d transition metal whose moment is coupled to that of the 3d element perhaps through a hybridization involving a ligand.

Ferroelectrics and Piezoelectrics: Polar oxides play central roles in modern technologies, ranging from ceramic capacitors to the high resolution three dimensional medical ultrasounds that were enabled by recent developments in piezocrystals. Better polar materials may open up entirely new applications. Entirely new systems have been made ferroelectric and highly enhanced properties have been found in thin films and superlattices over the last several years, even though the basic phenomena, such as perovskite ferroelectricity, have been known and studied for many decades. The key is that epitaxial constraints create structures that have non-ideal bond lengths. These then favor lattice instabilities, which are often polar in nature. The basis of most practical polar oxides is the perovskite structure. This structure has two competing metal-oxygen (M-O) bond lengths that in general cannot be satisfied without lattice distortions (note that other aspects, e.g. lone pair physics are also important). Unfortunately, key functionalities, especially piezoelectricity, are suppressed in constrained films, while bulk perovskites with too large mismatch do not form. The challenge that we address is to use understanding developed over the last decade to bring the enhanced properties found in thin films into bulk materials. Specifically, we will explore the use of chemical disorder in combination with lone pair physics to produce strong local frustration in bulk synthesizable polar oxides. The goal is to develop insight into the interplay between local bond dissatisfaction, local structural distortions and collective polar behavior. This follows our work discussed above on Bi-containing perovskite alloys.

Intercalation Compounds: The anodes of advanced batteries, which are based on materials like Li intercalated carbons, are just one example of energy materials where a proper treatment of van der Waals is essential to obtain reliable predictions of properties. We have heavily involved in the development and testing of a new class of density functional that enables reliable predictions in such materials. Other critical energy problems where such functionals are needed include molecular adsorption for catalysis and CO_2 capture and chemical separations. We plan to study intercalation into layered materials such as graphite to obtain quantitative understanding of the dynamics and kinetics. We will combine accurate first principles calculations with non-local functionals and new efficient approaches for determining pressure and temperature dependent adsorption densities to explore H_2 and CO_2 uptake in an array of layered materials, such as h-BN and graphite. A second direction will be to examine the intercalation of Li ion in nanoporous graphite structures of relevance to Li battery anodes. Recent experimental results show that such structures may lead to improved kinetics. We want to understand the microscopic origins of this effect in detail and how it can be optimized, either through modifying the size of the pores or for example other strategies. Our goal is to find new materials that improve uptake and kinetics.

Transparent Conductors: A solar cell generally needs electrode materials that are both transparent to the visible light and highly conductive. Finding the right materials involves engineering of the electronic structure and defect properties for targeted material properties. We will apply these techniques with the goal of finding new p-type transparent conducting materials (TCMs). In solar cells, the TCOs are used as transparent electrodes. These must allow high optical transmittance across a wide spectrum, i.e. a large optical band gap (> 3.1 eV), and at the same time high conductivity. However, high conductivity and a large optical gap usually do not coexist. We plan to investigate trends in layered chalcogenides in order to identify new high performance TCMs, particularly p-type.

Publications

Investigators currently on this project published 115 journal papers with DOE support from 2009 to the present. The following is a selection:

[1] E.E. Rodriguez, F. Poineau, A. Llobet, B.J. Kennedy, M. Avdeev, G.J. Thorogood, M.L. Carter, R. Seshadri, D.J. Singh and A.K. Cheetham, “High temperature magnetic ordering in the 4d perovskite $SrTcO_3$”, Phys. Rev. Lett. **106**, 067201 (2011).

[2] M.B. Stone, M.D. Lumsden, S.E. Nagler, D.J. Singh, J. He, B.C. Sales and D. Mandrus, “Quasi-one-dimensional magnons in an intermetallic marcasite”, Phys. Rev. Lett. **108**, 167202 (2012).

[3] X. Ke, J. Peng, D.J. Singh, T. Hong, W. Dela Cruz and Z.Q. Mao, “Emergent electronic and magnetic state in $Ca_3Ru_2O_7$ induced by Ti doping”, Phys. Rev. B **84**, 201102 (2011).

[4] G. Cao, M.M. Korshunov, Y. Gao, M. Le Tacon, D.J. Singh and C. Lin, “Anomalous in-plane electronic scattering in charge ordered $Na_{0.41}CoO_2$ $0.6H_2O$”, Phys. Rev. Lett. **108**, 236401 (2012).

[5] K.P. Ong and D.J. Singh, “Three-dimensional magnetism and coupling to the conduction electrons in $PdCrO_2$”, Phys. Rev. B **85**, 134403 (2012).

[6] S. Takagi, A. Subedi, D.J. Singh and V.R. Cooper, “Polar behavior of the double perovskites $BiMZnNbO_6$ (M=Pb and Sr) from density functional calculations”, Phys. Rev. B **81**, 134106 (2010).

[7] W.S. Choi, M.F. Chisholm, D.J. Singh, T. Choi, G.E. Jellison, Jr., and H.N. Lee, “Wide bandgap tenability in complex transition metal oxides by site-specific substitution”, Nature Comm. **3**, 689 (2012).

[8] B. Xu, D.J. Singh, V.R. Cooper and Y.P. Feng, “Design of a low band gap oxide ferroelectric: $Bi_6Ti_4O_{17}$”, EPL **94**, 37006 (2011).

[9] V.R. Cooper, “Enhanced carrier mobilities in two-dimensional electron gasses at III-III/I-V oxide heterostructure interfaces”, Phys. Rev. B **85**, 235109 (2012).

[10] K. Biswas, M.H. Du, J.T. Thienprasert, S. Limpijumnong and D.J. Singh, “Comment on uncovering the complex behavior of hydrogen in Cu_2O”, Phys. Rev. Lett. **108**, 219703 (2012).

[11] Z.G. Yu, J. Zhang, D.J. Singh and P. Wu, “First principles investigation of nitrosyl formation in zirconia”, Phys. Rev. B **85**, 144106 (2012).

[12] B. Xu, V.R. Cooper, D.J. Singh and Y.P. Feng, “Relationship between bond stiffness and electrical energy storage capacity in oxides: density functional calculations for h-La_2O_3, MgO and BeO”, Phys. Rev. B **83**, 064115 (2011).

Metamaterials FWP

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Project Scope:

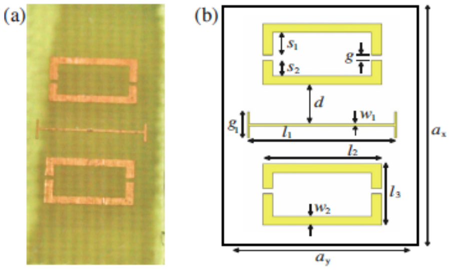
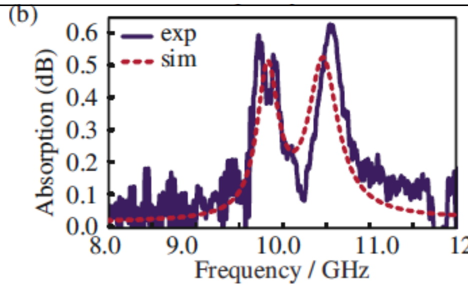
This FWP's purpose is the *theoretical understanding, analysis, development, fabrication, and testing of metamaterials*, particularly left-handed materials. This FWP collectively has been, and continues to be, a prime mover and initiator in the development of metamaterials. This revolutionary concept originally prompted objections, based on perceived violations of causality, momentum conservation, and Fermat's principle. This controversy is now settled, largely through the work of this FWP, clearing the way for new challenges to be addressed.

- Create new ideas and produce quantitative results via modeling before experimentalists attempt to fabricate, measure, and test the artificial novel materials. *This FWP improves the existing tools for modeling and simulating more complicated structures than can be completed today*. This group's ability to do so is demonstrated by the fact this FWP was instrumental in providing the theoretical background to determine the effective parameters of negative index materials. Currently, the entire metamaterials experimental community uses this technique extensively.
- *Design isotropic and 3D metamaterials with low absorption and high transmission that operate at THz and optical frequencies.* They are needed to explore the full potential of negative index metamaterials. New blueprints acknowledging the corresponding conceptual fabrication limitations will be pursued and designs will be fabricated.
- Chiral metamaterials can provide an alternative way to negative refraction. *This FWP will design, fabricate, and characterize chiral materials at GHz and THz frequencies.*
- In current optical metamaterials losses are too large for real-world applications. Presently it is unclear how much improvement is possible using alternative designs and constitutive materials. *This FWP strives to understand and reduce losses in metamaterials.*
- Incorporate active gain materials into optical metamaterials has been suggested theoretically, but no concrete designs and no experimental validations have been published. *This FWP works to develop optical metamaterials with gain and nonlinearity.*
- Embedding nonlinearities into metamaterials offers fascinating opportunities for ultrafast switching and dynamic control. While design, fabrication, and characterization of such "dynamic" metamaterials have been actively pursued, *the ultrafast excitation schemes demonstrated are still very limited and some fundamental questions, such as nonlinear gain and tunability, remain open. THz experiments will be performed within this FWP.*

Recent Progress:

Reduce Losses and the Speed of Light in Metamaterials Using EIT

A novel way confronting losses is based on a combination of electromagnetically-induced transparency (EIT) with non-linearity and gain components. EIT in metamaterials is based on asymmetrically coupled pairs of interacting resonators; one of the elements, according to our proposed design, incorporates the gain component and transfers the energy non-linearly to the other element. Under certain conditions, the spectral response of such a coupled structure can be significantly different from the mere superposition of the two independent resonances. Recently, we fabricated two EIT structures that showed low absorption and slow light velocity. The left figure shows the photograph and the schematic representation of our sample; the right figure shows the narrow absorption minimum (i.e. transmission window) in the broader Lorentzian-like absorption peak associated with the transition to the excited state.

	
(a) Photograph of the sample. (b) Schematic representation of our structure.	All spectra exhibit the typical features of EIT with low absorption inside a broader resonance.

Slow Light: EIT can be used to slow the velocity of light by a large factor. At the resonance frequency, the anomalous dispersion profile that is normally observed for a two-level resonance is transformed into an extremely steep normal dispersion, which results in simultaneously low group velocity and low loss. Most experimental work on EIT in metamaterials has not seen a strong absorption dip, and the reduction of the speed of light is very small—a factor of five to ten. So there is a strong need to experimentally demonstrate that metamaterials can reduce the speed of light dramatically. We have collaborated with Prof. Steven Anlage's group, from the Univ. of Maryland, which has expertise in fabricating superconducting films. We have fabricated EIT structures with metals and superconductors: the experimental results show a reduction of the speed of light by a factor of 500 and agree well with our theory and numerical simulations. Therefore, we can have a strong reduction in the speed of light and these new samples will be useful to construct light-slowing devices. In addition, by manipulation of the superconducting properties of the dark resonators through temperature or magnetic fields, the EIT effects are tunable to an unprecedented extent.

Relevant publications: Lei Zhang, P. Tassin, Th. Koschny, C. Kurter, S. M. Anlage, and C.M. Soukoulis, *Appl. Rhys. Lett.* **97**, 241904 (2010); C. Kurter, P. Tassin, Lei Zhang, Th. Koschny, A. P. Zhuravel, A. V. Ustinov, S. M. Anlage and C.M. Soukoulis, *Phys. Rev. Lett.* **107**, 043901 (2011); C. Kurter, P. Tassin, A. P. Zhuravel, Lei Zhang, Th. Koschny, A. V. Ustinov, S. M. Anlage and C.M. Soukoulis, *Appl. Phys. Lett.* **100**, 121906 (2012).

Bringing Gain in Metamaterials

After years of doubt, the scientific community now embraces the almost paradoxical properties of metamaterials, also known as negative index materials (NIMs), which include perfect lensing (beating the diffraction limit for electromagnetic waves), zero reflectance, and negative Snell's law angles. Acceptance of these phenomena has come with recent design, fabrication, demonstration, and detailed first principles simulations for operation at microwave and THz frequencies from the Ames Laboratory group. Most metamaterials are metal-based nanostructures and suffer from high dissipative losses at optical frequencies, which are still orders of magnitude too large for realistic applications. In addition, losses become an increasingly important issue, when moving from metamaterials made of only a few functional layers to the bulk case. Thus, reducing or even compensating of the losses is a key challenge for metamaterial technologies. One promising approach for overcoming the losses is the incorporating a gain material. This idea of combining a metamaterial with a optical gain medium has been investigated by several theoretical and experimental studies. From the experimentalist's point of view, realistic gain can be experimentally realized using fluorescent dyes, quantum dots, or semiconductor quantum wells. In any of these, loss-compensation is mainly attributed to the direct coupling between the metamaterial resonance and the gain medium. Without sufficient coupling, no loss-compensation can happen nor can the transmitted signal be amplified. Therefore, it is of vital importance to understand the mechanism of the coupling between metamaterials and the gain medium. In addition, these ideas can be used in plasmonics to incorporate gain to obtain new nano-plasmonic lasers.

Relevant publications: A. Fang, Th. Koschny, and C. M. Soukoulis, *Phys. Rev. B* **82**, 121101 (2010); A. Fang, Th. Koschny, and C. M. Soukoulis, *J. Opt.* **12**, 024013 (2010); A. Fang, Z. Huang, Th. Koschny, and C. M. Soukoulis, *Opt. Express* **19**, 12688 (2011); A. Fang, Z. Huang, Th. Koschny, and C. M. Soukoulis, *Photonics and Nanostructures - Fundamentals and* Applications **10**, 276 (2012); Z. Huang, Th. Koschny, and C. M. Soukoulis, *Phy. Rev. Lett.* **108**, 187402 (2012).

What are good conductors for metamaterials and plasmonics

We identify the material parameters related to the two most important limitations for optical metamaterials: (i) high dissipative loss in the metals they contain and (ii) the saturation of the resonance frequency at microscopic length scales. We develop a general model based on the quasi-static resonant metamaterial constituents in order to develop a figure-of-merit for conductors. This model takes into account the radiation damping of the resonators, which is becomes essential for low-loss metamaterials. We discuss various conductors (metals, transparent conducting oxides, graphene) and approaches to achieve high-quality optical metamaterials. In most cases, we find that the critical material parameter that gives direct information on the absorptive loss (real part) and on the frequency saturation caused by kinetic inductance (imaginary part) is the resistivity of the conducting material, rather than the conductivity or the permittivity. The resistivity of the conductor should therefore be taken as the figure-of-merit for use in resonant metamaterials. Fig. 1 below shows a corresponding classification of noble metals, alkali metals, noble-alkali intermetallics, and transparent conducting oxides.

Relevant publications: P. Tassin, Th. Koschny, M. Kafesaki and C. M. Soukoulis, *Nature Phot.* **6**, 259 (2012).

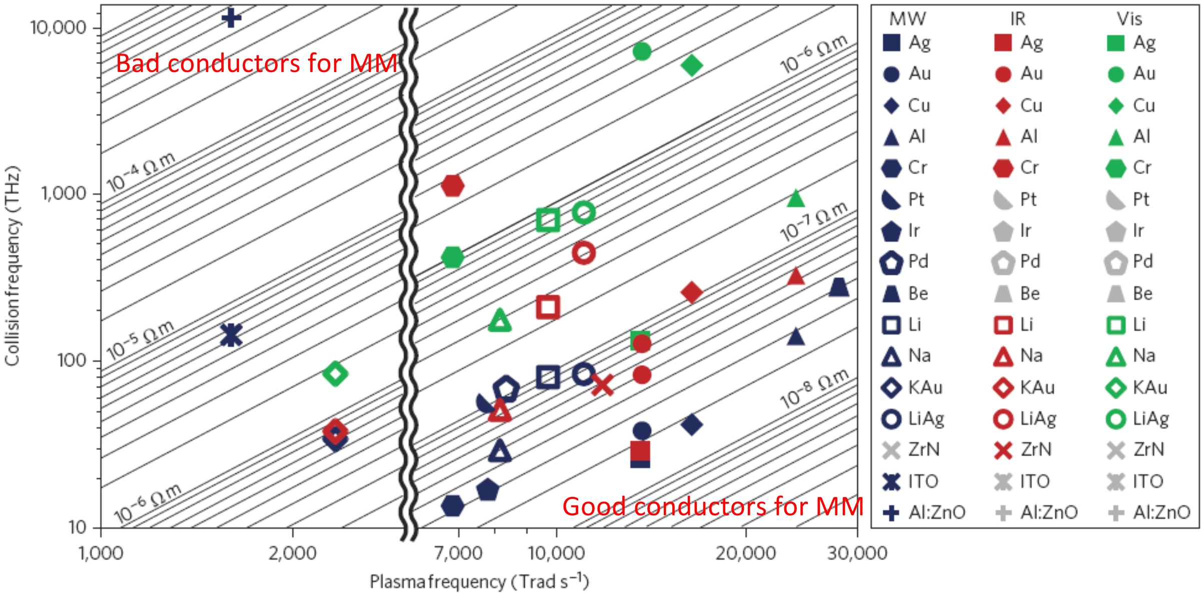


Figure 1 Overview of some noble metals, alkali metals, noble-alkali intermetallics, and transparent conducting oxides. The oblique lines represent constant real part of the resistivity. The best conductors for use in resonant metamaterials are in the bottom-right corner.

Dynamic Metamaterials

Metamaterials that can provide a switchable or tunable response controlled by an external parameter are highly desirable for the development of advanced devices, especially in the THz frequency range. We previously developed optically switchable THz modulators capable of dual-band operation using resonant metallic metamaterials structures fabricated on substrates with photo-excitable free charge carrier that modulate the metamaterials response. Recently, we extended this approach using optical charge carrier excitation to dynamically create the metamaterials resonant structures on photoconductive surfaces with arbitrarily configurable geometry by projection of a photo mask onto a GaAs surface. Tunable and power dependent switchable optical grating based ultrafast reversible THz modulation have been experimentally demonstrated.

Relevant publications: I. Chatzakis, L. Luo, J. Wang, N. Shen, Th. Koschny, and C. M. Soukoulis, *Phys. Rev. B.* (submitted).

Many-Body Theory of Energy Transport and Conversion at the Nanoscale

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1 Project Scope

This project addresses the fundamental challenge of understanding nanosystems far from equilibrium, while simultaneously exploring the potential of nanostructured materials for applications in energy-conversion technologies. The main focus of the project is the study of quantum-enhanced thermoelectrics. The PI and collaborators recently predicted a dramatic enhancement of thermoelectricity on the nanoscale due to quantum wave interference. This project builds upon these ideas by investigating quantum thermoelectric effects in multiterminal geometries—a largely unexplored problem—and by studying the effect of electron-electron interactions on higher-order quantum interference. Fundamental research on the nonequilibrium many-body theory of nanostructures is conducted in parallel, to enable the applied research on nanoscale energy conversion. The PI and collaborators recently developed a theory of charge and energy transport formulated in terms of the exact eigenstates of an interacting nanostructure. This approach reproduces the key features of both the Coulomb blockade and coherent transport regimes in a single unified transport theory. This theory will be extended to treat inelastic transport, dynamical screening, and spin-orbit interactions. Mapping the transport problem onto integrable models, and description of correlation effects within exact density-functional theory are also explored.

2 Recent Progress

2.1 Effective field theory of interacting π-electrons

We developed an effective field theory of interacting π-electrons [4]. The Hamiltonian is similar to that of the Pariser-Parr-Pople model, but the Coulomb interactions within a molecular junction are detemined based on fundamental principles (multipole expansion) rather than using an ad-hoc (but highly-accurate) parametrization. The advantage is that screening effects from nearby metal electrodes can be included with no additional adjustable parameters using an image multipole method [4]. The reduction of the HOMO-LUMO gap in a molecular junction [1] is comparable to that found in state-of-the-art GW calculations. An ab initio model of lead-molecule tunnel coupling was also developed [1] to enable more realistic modelling of transport in strongly-coupled molecular junctions, and qualitative insight was gained by comparing transport calculations using the full Green's functions to an isolated resonance approximation [1].

2.2 Mapping molecular junctions onto integrable models

Together with Kieron Burke, we developed an exact description of the Anderson model within the Kohn-Sham (KS) scheme of density-functional theory [2,3]. The PI also gave an invited talk on this work at the 2012 APS March meeting. We showed that single-particle KS theory reproduces the linear transport exactly at zero temperature, despite the lack of a Kondo peak in its spectral function. Using Bethe ansatz techniques, we calculated the KS potential for all coupling strengths, including the crossover from mean-field behavior to charge quantization caused by the derivative discontinuity (see Fig. 1). An exact result for the scaling form of the exchange-correlation potential

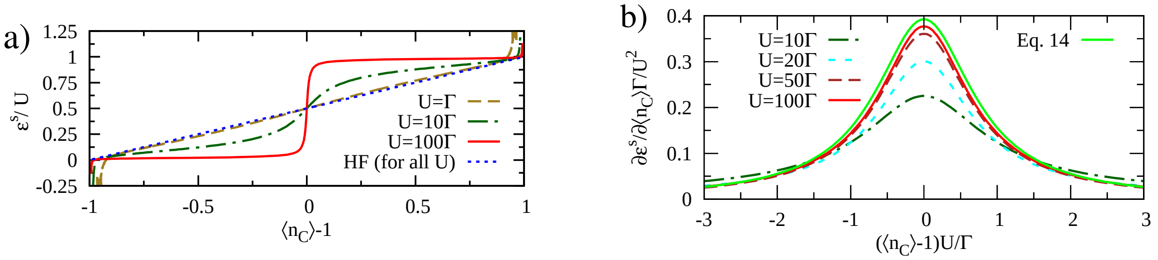

FIGURE 1: The exact KS potential ε^{s} of the Anderson model. (a) For $U \approx \Gamma$, HF is accurate; as U grows, an increasingly sharp step develops, due to the *derivative discontinuity* of the exchange-correlation energy as a function of particle number. (b) $\partial\varepsilon^{\mathrm{s}}/\partial\langle n_C\rangle$ for several large values of U/Γ. As $U/\Gamma \to \infty$, the exact (Lorentzian) asymptotic scaling form is recovered. Figure reproduced from Ref. [2].

due to the emergence of the derivative discontinuity was derived [2]

$$\varepsilon_{\mathrm{XC}} = \alpha\frac{U}{2}\left[1 - \langle n_{\mathrm{C}}\rangle - \frac{2}{\pi}\tan^{-1}\left(\frac{1-\langle n_{\mathrm{C}}\rangle}{\sigma}\right)\right], \tag{1}$$

where $\alpha \to 1$ and $\sigma \to 8\Gamma/\pi^2 U$ as $\Gamma/U \to 0$ are the weight and width of the emergent derivative discontinuity, respectively. Our results imply that the effects of the derivative discontinuity are quantitatively important for $U/\Gamma > 5$, and hence are relevant for many small molecular junctions. The accuracy of various approximate functionals was also investigated [3].

2.3 Effect of electron-electron interactions on higher-order quantum interference

In previous work, we showed that higher-order quantum interference could lead to very large enhancements of thermoelectric effects in nanoscale junctions. Higher-order interference arises when several interference-producing elements are combined in series in a quantum-coherent circuit. Based on previous calculations using Hückel theory and DFT, it was predicted that higher-order destructive interference would lead to degenerate transmission nodes and universal order-dependent enhancements of nanoscale thermoelectricity.

However, we found that such degenerate nodes are split by electronic correlations in linearly-conjugated polymers [5]. Most recently, we have extended our computational approach to treat electron correlations in much larger molecules by evaluating the Green's function directly using the Lanczos technique in systems whose Hamiltonian is too large to store in memory. Figure 2 shows the transmission spectrum and thermopower for biphenyldithiol-Au junctions with three different contact geometries. These results indicate that degenerate transmission nodes are also split in polycyclic molecular junctions. However, the calculated thermoelectric effects (thermopower, ZT) are *as large or larger* than expected based on our previous calculations, indicating increased potential for energy conversion applications. Further work is needed to elucidate the cause and nature of the splitting of degenerate transmission nodes.

2.4 Quantum thermoelectric effects in multiterminal geometries

Conventional thermocouples are three-terminal devices with two electrical and two thermal contacts. It is well-known that multiterminal transport can lead to a variety of interesting and counterintuitive effects in quantum devices. One of the major focuses of the current project is to investigate quantum thermoelectric effects in multiterminal geometries.

We have begun by investigating pure thermal transport in three-terminal devices with nonzero thermoelectric effects. We used a general solution of this problem in the linear-response regime

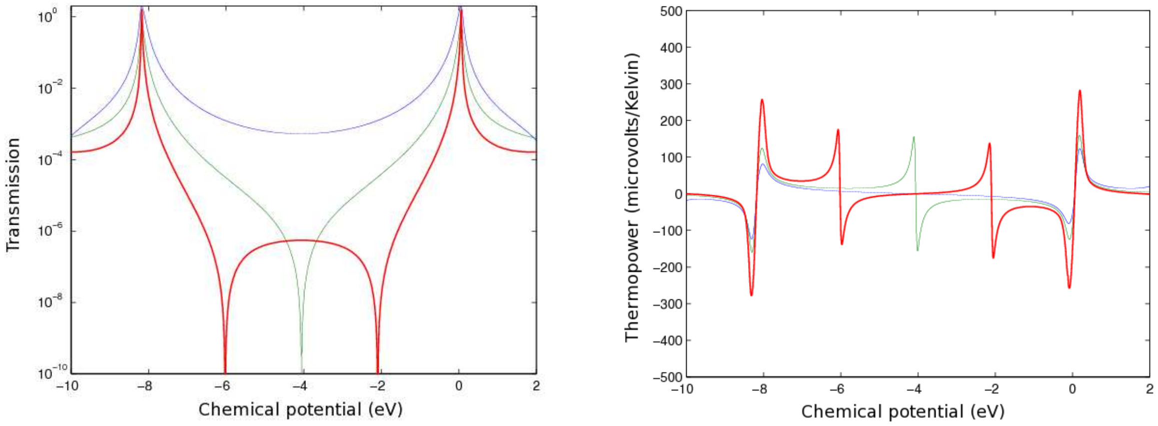

FIGURE 2: Left image: Transmission function for a biphenyldithiol-Au junction as a function of the electrode chemical potential. Three different contact geometries are shown: double-para (blue), para-meta (green), and double-meta (red). Note that the second-order transmission node in the double-meta junction is split into two first-order nodes by electron-electron interactions; the second-order node in double-meta junctions was previously predicted to be degenerate based on Hückel and DFT calculations. Right image: Thermopower of a biphenyldithiol-Au junction for three contact geometries (color code same as for transmission curves). Despite the phenomenon of node repulsion, the thermopower is very large near both transmission nodes and resonances, with corresponding values of the (electronic) figure of merit ZT of 1.9 and 10, respectively, larger than those predicted by calculations neglecting electron-electron interactions.

to formulate a precise definition of—and develop a realistic model of—a quantum electron thermometer with atomic resolution. The hypothetical nanoscale electron thermometer is a scanning probe microscope with an atomically-sharp tip operating in ultrahigh vacuum, so that the main coupling to the ambient environment is via black-body radiation. This unpublished work takes on added significance with the recent publication of work on a scanning thermal microscope with 10nm spatial resolution and 15mK temperature resolution by the group of Pramod Reddy.

3 Future Plans

In the next year, the new computational technique described in Sec. 2.3 will be applied to a variety of molecules of interest for potential thermoelectric applications. Larger molecules such as C_{60} will also be investigated using a constant interaction model derived from π-EFT. The phenomenon of "node repulsion" in interacting systems will be further investigated, to determine its cause and its generality (is there an analogy to level repulsion?). Quantum thermoelectric effects in multi-terminal geometries will be further investigated. The quantum electron thermometer described in Sec. 2.4 will be used to study the temperature distribution in a nanoscale junction driven out of equilibrium. Quantum interference effects on the temperature distribution, and the emergence of Fourier's law at larger length scales will be studied.

The possibility of extending our many-body computational framework to use realistic basis orbitals derived from DFT will be investigated. This would greatly simplify the treatment of various substituents and linker groups which can be used to tune quantum transport. It will also be of interest to compare our many-body method to the self-consistent GW approach.

Mapping molecular junctions onto integrable (or numerically solvable) models will be further investigated during a sabbatical visit to the group of Kieron Burke, who also has a collaboration with Steven White on a closely related theme. We speculate that the insights gleaned into the nature and importance of the derivative discontinuity in molecular junctions discussed in Sec. 2.2 may be quite general, but it will be essential to test them in model systems with more degrees of freedom, where the connection between occupancy and transport is not "protected" by the Friedel sum-rule.

Finally, inelastic effects due to electron-electron and electron-phonon scattering will be investigated, with a critical eye on their relevance for thermoelectricity. In this context, phonon heat transport is also important, and will be investigated, as described in the project narrative. Theoretically, inelastic processes are controlled by the frequency-dependent polarizability tensor of the junction, whose study will also allow calculation of optoelectronic response. At a more fundamental level, inclusion of inelastic effects will allow for a better description of the spectral function of interacting nanostructures. One strategy we will pursue is to consider generalized initial conditions in our nonequilibrium Green's function approach, chosen to minimize the correction to the Coulomb self-energy when lead-molecule tunneling is turned on.

4 Publications

1. J. P. Bergfield, J. D. Barr, and C. A. Stafford "Transmission Eigenvalue Distributions in Highly-conductive Molecular Junctions," Beilstein J. Nanotechnol. **3**, 40-51 (2012).

2. J. P. Bergfield, Z. F. Liu, K. Burke, and C. A. Stafford "Bethe Ansatz Approach to the Kondo Effect within Density-Functional Theory," Phys. Rev. Lett. **108**, 066801 (2012).

3. Z. F. Liu, J. P. Bergfield, K. Burke, and C. A. Stafford "Accuracy of density functionals for molecular electronics: The Anderson junction," Physical Review B **85**, 155117 (2012).

4. J. D. Barr, J. P. Bergfield, C. A. Stafford "Effective Field Theory of Interacting π-Electrons," arXiv:1108.0021; submitted to Physical Review B.

5. Gemma C. Solomon, Justin P. Bergfield, Charles A. Stafford, and Mark A. Ratner, "When 'small' terms matter: Coupled interference features in the transport properties of cross-conjugated molecules," Beilstein J. Nanotechnol. **2**, 862-871 (2011).

ELECTROLYTES AT SOLID-WATER INTERFACES

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SCOPE

The scope of our research program, supported by the DoE EPSCoR Program (until mid 2013), by the DoE Geosciences Program, and by NERSC, is to relate fundamental properties of aqueous systems near solid interfaces to practical applications. Our group conducts predominantly atomistic molecular dynamics (MD) simulations, both at equilibrium and non-equilibrium conditions. We conduct selected experiments to validate our predictions, and we rely on experienced collaborators for providing additional experimental insights. Successful collaborations have been established with Prof. David Cole, Ohio State University (formerly of the Oak Ridge National Laboratory), Dr. Paul Ashby, Lawrence Berkeley National Laboratory, and Dr. Juergen Biener, Lawrence Livermore National Laboratory. Understanding and controlling matter at the atomic and molecular level we strive to positively affect several materials and energy-related technologies. Applications of current interest are (1) separation of carbon nanotubes using surfactants, (2) water desalination, (3) energy storage in electric double layer capacitors, and (4) natural gas and oil recovery (e.g., hydraulic fracturing). In all these applications the fundamental aspects that are of interest to us are the preferential adsorption of various compounds (water as opposed to surfactants, electrolytes, organic molecules) at solid-fluid interfaces, the structure of the adsorbed aggregates, and the dynamics of individual molecules at interfaces, as well as their collective dynamic behavior, as they are affected by the presence of the interface. As we combine atomistic to macroscopic observations, our studies are meso-scopic in nature.

RECENT PROGRESS

We continue our systematic study of interfacial water at contact with mineral surfaces. In the latest contribution (*Ref. # 22 below*) we compared the properties of interfacial water on silicon dioxide, aluminum oxide, and magnesium oxide. The results were quantified in terms of density distribution in the directions perpendicular and parallel to the solid substrates, residence time for water at contact with the substrates, orientation of molecules near the substrates, self-diffusion coefficients, etc. In a separate contribution we discussed the relationship between preferential distribution of aqueous electrolytes within slit-shaped pores, and their mobility (*Ref. # 21 below*). The results are useful for environmental applications related, for example, to the diffusion of heavy metal ions in subsurface formations.

Three are the main results within the past year.

Water Can Slip on Hydrophilic Surfaces. Macroscopically, a surface is classified as hydrophilic or hydrophobic depending on the contact angle formed by a water droplet. Because hydrophobic surfaces tend to cause water slip while hydrophilic ones do not, the former surfaces can yield self-cleaning garments and ice-repellent materials while the latter cannot. The results obtained by our group suggest that this dichotomy might be purely coincidental. We demonstrated, using molecular dynamics simulations, that slip and no-slip boundary conditions can both be observed for liquid water flowing on solid surfaces on which the static water contact angle is less than 90°. The responsible molecular signature was found to be the distribution of water molecules within the contact layer at equilibrium, coupled with the strength of water-surface interactions. When preferential adsorption sites exist that are sufficiently close to each other that water migration from one to the next can occur without requiring hopping events, hydrodynamic liquid slip occurs. **Significance.** When verified experimentally our results could lead to the advancement of, e.g., the design of hydrophilic nano-porous membranes with high permeation and self-cleaning hydrophilic surfaces. More details can be found in *Ref. # 20* listed below.

The Electric Double Layers Capacitance Depends on Applied Potential. Pore size effects are believed to be the key to future performance improvements of electric double-layer capacitors. We performed MD simulations to study the pore-size dependent accumulation of aqueous electrolytes in slit-shaped graphitic carbon pores of different widths (0.65 - 1.6 nm). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used by our collaborators at LLNL to study the effect of potential and pore size on the capacitance of nanoporous carbon foams. Experimentally we observed a pronounced increase of the capacitance of sub-nm pores as the applied potential window gets wider, from a few F/g for narrow potential ranges (-0.3 V to 0.3 V vs. Ag/AgCl) to ~40 F/g for wider potential windows (-0.9 V to +0.9 V vs. Ag/AgCl). By contrast, the capacitance of wider pores does not depend significantly on the applied potential window. Our simulations confirmed that the penetration of ions into pores becomes more difficult with decreasing pore width and increasing strength of the hydration shell. Consistent with our experimental results, we observed a pore- and ion-size dependent threshold-like charging behavior when the pore width becomes comparable to the size of the hydrated ion, explained by changes in the hydration structure undergone by the ions entering the charged pores. **Significance**. The results contribute to our understanding of how ion-water, ion-ion and ion-pore interactions determine the performance of energy-storage devices and also of capacitive water-desalination technologies. More details can be found in *Ref. # 23* listed below.

Hydration Structure at the α-Al_2O_3 (0001) Surface: Excellent Agreement from Experimental AFM Force Spectroscopy and Atomistic Molecular Simulations. Atomic force spectroscopic data were obtained in water on the (0001) face of the α-Al_2O_3 substrate using a silicon tip. The data were interpreted by implementing the Brownian Force Profile Reconstruction method (BFPR) proposed by Ashby and Lieber [J. Am. Chem. Soc. 126 (2004) 16973]. The method allows for a detailed reconstruction of the force-distance curve that highlights the hydration structure. The experimental data were compared to massive atomistic MD simulations in which one silicon dioxide disc of ~ 2 nm in diameter represented the silicon AFM tip. A fully hydroxylated crystalline model represents the alumina substrate in the simulations. The umbrella sampling method was employed to obtain the water-mediated surface-disc effective force profile. Comparing simulations and experiments we clearly distinguished two hydration layers confined between tip and surface. The hydration layer found closest to the alumina substrate yields a pronounced repulsive force when the AFM tip penetrates it, suggesting highly structured interfacial water. The second hydration layer yields a much less intense repulsive force. The position of the peaks with respect to the solid substrate is consistent with recent experimental X-ray reflectivity data reported by Catalano [Geochim. Cosmochim Acta 75 (2011) 2062] and with previous atomistic simulations conducted for a thin film of water supported on sapphire (*Ref. #11 below*). **Significance**. Given the wide technological importance of alumina and the ubiquitous nature of water, the results just discussed have the potential of positively impacting a number of applications within fields as diverse as catalysis, geology, biology, and many others. More details can be found in *Ref. # 24* listed below.

FUTURE PLANS (2012-2013)

In the near future our goal is to secure a few more tangible contacts between the simulation results obtained in our group and experimental observations obtained by our collaborators, and in some cases already available in the literature. We provide below the three goals we are close to accomplish.

Ethanol-Water Mixtures On Alumina. We are conducting detailed studies for of ethanol – water mixtures supported on alumina. Alumina is a proxy for several minerals present in subsurface formations. Ethanol was chosen because a number of sum frequency generation spectroscopic data (J. Phys. Chem. Lett. 2 (2011) 1831) are available that we are using to validate our results. Our preliminary simulations suggest that ethanol form one solvation layer on this substrate with regular distribution of the fluid molecules along the plane parallel to the substrate. The details of the molecular distribution of ethanol molecules depend on the surface properties [e.g., we have compared ethanol adsorbed on the (001) and on the (102) planes of the alumina substrate]. The results are reliable, even though the force fields have been taken from the literature without adjustment to reproduce fluid-mineral interfaces. In particular, the data for the orientation of the ethanol molecule at the (102) plane reproduce very well experimental data reported for the same interface in 2011 [J. Phys. Chem. Lett. 2 (2011) 1831]. Further, we found that small modifications of the solid surface (i.e., a partial protonation of the non-bridging oxygen atoms) have a strong effect on the order of interfacial ethanol molecules. When a 50:50 mixture of water and ethanol was simulated at ambient conditions, it was found that water readily displaces ethanol from the solvation layer. This latter result awaits experimental verification, which we will attempt in collaboration with Dr. Paul Ashby. We are currently explaining this observation by calculating the potential of mean force between one ethanol molecule and the alumina substrate both in the presence of water and in the presence of ethanol. When ethanol is present our results provide evidence for a strong attractive well in correspondence of the first solvation layer. In the presence of water, this strongly attractive well essentially disappears. The results are currently being prepared for publication.

Orientation of Water near Charged Graphene. We are providing molecular-level insights to experimental observations that are being collected by Dr. Miquel Salmeron and his group at LBNL (Striolo has spent his sabbatical al LBNL). The experiments (ambient-pressure X-ray) are conducted to sample the orientation of liquid water molecules at contact with graphene, as a function of the applied voltage. The equilibrium MD simulations are being conducted for liquid water near a charged graphene surface. Because several models are available for water (rigid, flexible, polarizable) and because the simulated problem is rather simple, we decided to compare the results obtained when various models are implemented for water, and when image charges are described within the graphene support. So far only modest differences are observed when the results from the different models are compared. Direct comparison to experiments might help us identify the models that are most reliable in reproducing the experimental observations. Understanding the orientation of water near charged graphene will be important for further developing advanced energy-storage devices, including electric double layers.

Salt-Specific Effects in Carbon Nanotube Separations. Tremendous progress has been made to stabilize carbon nanotube dispersions using surfactants. Although theoretical investigations have uncovered, often using molecular simulations, some of the molecular phenomena thought to be responsible for the dispersions stability, many questions await answer to design surfactant formulations that selectively stabilize nanotubes mono-dispersed in diameter and chirality. Stimulated by recent experimental observations [*JACS*, 2010, 132, 16165–16175], we are attempting to quantify how changing the counter-ion (Cs^+ instead of Na^+) affects the morphology of dodecyl sulfate surfactants adsorbed on carbon nanotubes. Using atomistic MD we are simulating aqueous cesium dodecyl sulfate (CsDS) adsorbed on (6,6), (12,12), and (20,20) single-walled carbon nanotubes (SWNTs) at ambient conditions. When compared to results reported previously for sodium dodecyl sulfate (SDS) (*Ref. # 1 below*), our results suggest that Cs^+ ions, compared to Na^+, yield a more compact coverage of the nanotubes of narrow diameter, with the surfactant heads extended towards the bulk aqueous solution, and prevent water from accessing the nanotube surface. These morphological results suggest that CsDS should be more effective than SDS at stabilizing aqueous carbon nanotubes dispersions. For the wider nanotubes our simulations show limited, if any, differences in the morphology of the surfactant aggregates when the Na^+ ions are substituted with Cs^+ ones. The different salt-specific behavior observed for the surfactants in the presence of narrow vs. wide carbon nanotubes could be exploited for the selective stabilization of mono-dispersed carbon nanotube samples. Experimental validation is being attempted in collaboration with NIST.

DOE-SPONSORED PUBLICATIONS SINCE 2009

1. N.R. Tummala and A. Striolo, *SDS Surfactants on Carbon Nanotubes: Aggregate Morphology*, **ACS Nano** 3 (**2009**) 595-602.
2. L. Shi, M. Ghezzi, G. Caminati, P. Lo Nostro, B.P. Grady, A. Striolo, *Adsorption Isotherms of Aqueous $C_{12}E_6$ and CTAB Surfactants on Solid Surfaces in the Presence of Low-Molecular-Weight Co-Adsorbents,* **Langmuir** 25 (**2009**) 5536-5544.
3. D. Argyris, D.R. Cole, and A. Striolo, *Hydration Structure on Silica Crystalline Substrates*, **Langmuir** 25 (**2009**) 8025-8035.

4. B.H. Morrow and A. Striolo, *Assessing How Metal-Carbon Interactions Affect the Structure of Supported Platinum Nanoparticles*, **Molecular Simulation** 35 (**2009**) 795-803.
5. N.R. Tummala and A. Striolo, *Curvature Effects on the Adsorption of Aqueous SDS Surfactants on Carbonaceous Substrates: Structural Features and Counterion Dynamics*, **Physical Review E** 80 (**2009**) 021408. Also featured in **Virtual Journal of Nanoscale Science & Technology**, Vol. 20, Issue 11, September 14th, **2009**.
6. D. Argyris, D.R. Cole, and A. Striolo, *Dynamic Behavior of Interfacial Water at the Silica Surface*, **Journal of Physical Chemistry C**, 113 (**2009**) 19591-19600.
7. L. Shi, N.R. Tummala, and A. Striolo, *A Molecular Dynamics Study for $C_{12}E_6$ and SDS Surfactants at the Water-Vacuum Interface*, **Langmuir** 26 (**2010**) 5462-5474.
8. D. Argyris, D.R. Cole, and A. Striolo, *Ion-Specific Effects Under Confinement: The Role of Interfacial Water*, **ACS Nano** 4 (**2010**) 2035-2042.
9. B.H. Morrow and A. Striolo, *Supported Bimetallic Pt-Au Nanoparticles: Structural Features Predicted by Molecular Dynamics Simulations*, **Physical Review B** 81 (**2010**) 155437.
10. N.R. Tummala, B.H. Morrow, D.E. Resasco, A. Striolo, *Stabilization of Aqueous Carbon Nanotube Dispersions using Surfactants: Insights from Molecular Dynamics Simulations*, **ACS Nano** 4 (**2010**) 7193-7204.
11. D. Argyris, T.A. Ho, D.R. Cole, A. Striolo, *Molecular Dynamics Studies of Interfacial Water at the Alumina Surface*, **Journal of Physical Chemistry C** 115 (**2011**) 2038-2046.
12. T.A. Ho, D. Argyris, D.V. Papavassiliou, A. Striolo, L.L. Lee, D.R. Cole, *Interfacial Water on Crystalline Silica: A Comparative Molecular Dynamics Simulation Study*, **Molecular Simulation** 37 (**2011**) 172-195.
13. B.H. Morrow, D.E. Resasco, A. Striolo, M. Buongiorno Nardelli, *CO Adsorption on Noble Metal Clusters: Local-Environment Effects*, **Journal of Physical Chemistry C** 115 (**2011**) 5637-5647.
14. D. Argyris, P.D. Ashby, A. Striolo, *Assessing the Structure of Interfacial Water via AFM: Insights from Simulations*, **ACS Nano** 5 (**2011**) 2215-2223.
15. N.R. Tummala, L. Shi, A. Striolo, *Molecular Dynamics Simulations of Surfactants at the Silica-Water Interface: Anionic vs. Nonionic Headgroups*, **Journal of Colloid and Interface Science** 362 (**2011**) 135-143.
16. D. Argyris, T. Ho, D. Papavassiliou, A. Striolo, *Equilibrium and Transport Properties of Aqueous Electrolytes within Narrow Slit-Shaped Pores: From Molecular Dynamics Results to Nanofluidic Devices*, **Chemical Engineering Transactions** 24 (**2011**) 1363-1368.
17. R.K. Kalluri, D. Konatham, A. Striolo, *Aqueous NaCl Solutions within Charged Carbon-Slit Pores: Partition Coefficients and Density Distributions from Molecular Dynamics Simulations*, **Journal of Physical Chemistry C** 115 (**2011**) 13786-13795.
18. A. Striolo, *From Interfacial Water to Macroscopic Observables: A Review*, **Adsorption Science and Technology** 29 (**2011**) 211-258. Invited article. Also **featured on the cover page**.
19. M. Suttipong, N.R. Tummala, B. Kitiyanan, A. Striolo, *Role of Surfactant Molecular Structure on Self Assembly: Aqueous SDBS On Carbon Nanotubes*, **Journal of Physical Chemistry C** 115 (**2011**) 17286-17296. Also featured in the *cover art* of **J. Phys. Chem. C**, issue # 35, September 8th, **2011**.
20. T.A. Ho, D.V. Papavassiliou, L.L. Lee, A. Striolo, *Water Can Slip on a Hydrophilic Surface*, **Proceedings of the National Academy of Sciences of the United States of America** 108 (**2011**) 16170-16175.
21. T. Ho, D. Argyris, D.R. Cole, A. Striolo, *Aqueous NaCl and CsCl Solutions Confined in Crystalline Slit-Shaped Silica Nanopores of Varying Degree of Protonation*, **Langmuir** 28 (**2012**) 1256-1266.
22. A. Phan, T.A. Ho, D.R. Cole, A. Striolo, *Molecular Structure and Dynamics in Thin Water Films at Metal Oxide Surfaces: Magnesium, Aluminum, and Silicon Oxide Surfaces*, **Journal of Physical Chemistry C** (**2012**) in press. Selected for the **Cover Art of JPC C**. To appear in August, 2012.
23. R.K. Kalluri, M.M. Biener, M.E. Suss, M.D. Merrill, M. Stadermann, J.D. Santiago, T.F. Baumann, J. Biener, A. Striolo, *Unraveling the Potential and Pore-Size Dependent Capacitance of Slit-Shaped Graphitic Carbon Pores in Aqueous Electrolytes*, (**2012**) in preparation.
24. D. Argyris, A. Phan, P.D. Ashby, A. Striolo, *Hydration Structure at the α-Al_2O_3 (0001) Surface: Insights from Experimental AFM Force Spectroscopy Data and Atomistic Molecular Simulations*, (**2012**) in preparation.

Non-equilibrium relaxation and aging scaling of magnetic flux lines in disordered type-II superconductors

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Project scope

Technical applications of type-II superconductors, especially high-T_c compounds, in external magnetic fields require an effective flux pinning mechanism to reduce Ohmic losses due to flux creep and flow. The physics of interacting vortex lines subject to strong thermal fluctuations and point-like or extended disorder has therefore been a major research focus in condensed matter physics. In our work we aim for a thorough numerical investigation and theoretical characterization of the stochastic fluctuations and out-of-equilibrium relaxation processes of interacting magnetic flux lines subject to various pinning centers. Our studies have yielded considerable progress in our understanding of physical aging phenomena in type-II superconductors with uncorrelated point disorder, and revealed distinct intriguing temporal regimes that could be addressed separately in different sample and defect geometries. To this end, we employed a versatile three-dimensional Monte Carlo simulation code based on an elastic string representation of the magnetic flux lines, and extracted various steady-state observables as well as two-time correlation functions. Recently, we have developed an efficient Langevin molecular dynamics algorithm, and validated both numerical approaches through a comparison of the ensuing long-time, large-scale stationary state characteristics. We are now investigating in detail the dynamical relaxation features towards equilibrium as well as non-equilibrium steady states starting from experimentally realizable initial conditions, encompassing sudden thermal, magnetic field, and driving current quenches.

Recent progress

In type-II superconductors naturally abundant point defects such as oxygen vacancies or dislocations and twin boundaries provide pinning centers for magnetic vortices; artificially introduced extended defects, such as columnar damage tracks produced by heavy-ion irradiation, have proven to be strong binding sites for flux lines even at elevated temperatures. A thorough understanding of the equilibrium and transport properties of vortex matter is a clear prerogative to render these materials amenable to minimize dissipative losses, especially in high-field applications.

Following earlier work, we consider the type-II superconductor in the extreme London limit, and model the vortices as elastic lines with purely in-plane (perpendicular to the magnetic field) repulsive screened logarithmic interactions, and subject to attractive and localized pinning sites. An external current is included through a work term in the effective Hamiltonian, akin to the standard theoretical modeling of driven diffusive systems. This approach is valid in the linear response regime, but cannot be justified a-priori for large drives.

In our numerical studies we employed parameter values that describe high-T_c superconducting materials such as YBCO, and focus on the regime of low magnetic fields and temperatures in order for our disordered elastic line model to adequately represent a type-II superconductor with realistic material characteristics.

We characterized the non-equilibrium steady states of driven magnetic flux lines in layered type-II superconductors subject to various configurations of strong point or columnar pins through

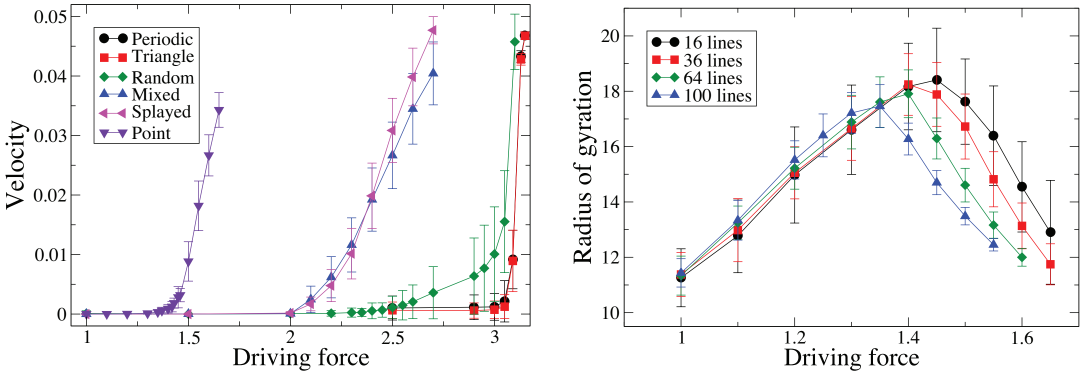

Figure 1: *(a) Force-velocity or I-V curves for systems with 16 flux lines and different defect configurations (1710 columnar defects or 1710 × 20 point defects in 20 layers). Each data point was obtained by averaging over 50 different defect realizations. (b) Mean radius of gyration along the drive direction for systems with point defects and different flux densities: 16 lines (circle), 36 lines (square), 64 lines (diamond), and 100 lines (triangle up).*

the force-velocity or current-voltage curve, static structure factor, mean vortex radius of gyration, number of double-kink and half-loop excitations, and velocity or voltage noise spectrum. Fig. 1(a) shows the I−V characteristics in systems with different defect configurations from which the critical currents can be determined. As expected, the systems with regularly arranged columnar defects display higher critical currents than samples with randomly placed columnar defects, splayed linear pins, a mixture of point and columnar defects, or pure point-like disorder, all with identical pinning strength per layer. We also studied the three-dimensional vortex line fluctuations in the ensuing driven steady states. For example, the radius of gyration starts to grow as the driving force increases, reaching its highest value near the critical current; at larger drives, it decreases again, see Fig. 1(b).

We also utilized our Monte Carlo simulation code to systematically analyze the relaxation dynamics of three-dimensional interacting vortex lines subject to attractive point pins at low temperatures, i.e., in the vortex glass phase. For simplicity, we selected as initial configurations parallel straight vortex lines randomly placed in the system, and studied the subsequent relaxation through the intrinsic dynamics towards the equilibrium state. We observed remarkably complex dynamical crossover phenomena, but were also able to disentangle the associated distinct relaxation mechanisms caused by the competitions of pinning and interaction-induced correlations. Fig. 2 illustrates the several distinct dynamical regimes that can be observed for repulsively interacting magnetic vortices subject to attractive point pinning centers of moderate strength: Whereas the flux lines broadly behave as if they were isolated at short times, at long times a glassy regime emerges with characteristics similar to that observed for structural glasses, approximately governed by a stretched exponential decay of correlations. These two regimes are separated by an intermediate stage where the interplay of repulsive vortex interactions and defect-induced pinning leads to a complicated dynamical crossover behavior.

Future plans

The goal of our future research is to attain a comprehensive understanding of the out-of-equilibrium

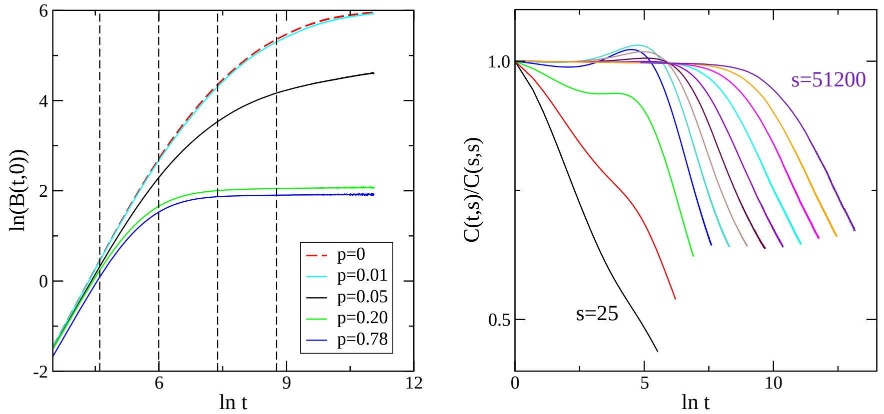

Figure 2: *(a) Mean-square displacement $B(t, 0)$ for interacting vortices subject to point defects with different pinning strengths p, showing the caging effect that constrains lateral displacements. (b) Transverse displacement (height) autocorrelation function $C(t, s)$ for interacting vortex lines in a system with point pins ($p = 0.05$). The waiting times range from $s = 25$ (left) to $s = 51200$ (right). Depending on the time elapsed since the preparation of the system, three distinct dynamical regimes are observed. For large waiting times, the kinetics displays similar characteristics as in structural glasses.*

relaxation dynamics of vortex matter in disordered type-II superconductors in different sample geometries with various types of pinning centers. Our extensive numerical investigations will be based on versatile Monte Carlo as well as Langevin dynamics simulation codes, representing different microscopic models for the kinetics of three-dimensional elastic lines subject to mutual long-range repulsive forces and localized attractive defects. Through detailed analysis of the stochastic fluctuations and relaxation features of different time-dependent observables, we aim to identify universal aging properties and separate them conceptually from intrinsic material characteristics. By studying thin film geometries, we shall furthermore isolate two-dimensional relaxation kinetics from the more complex dynamics in three dimensions, where transverse flux line fluctuations may contribute crucially.

Our studies will investigate in detail the dynamical relaxation features towards equilibrium as well as non-equilibrium steady states starting from experimentally realizable initial conditions, encompassing sudden thermal, magnetic field, and driving current quenches. We will explore universal and non-universal characteristics in the physical aging as well as glassy relaxation regimes, and thereby identify unique dynamical signatures that distinguish bulk from thin film samples, and differ in systems with point pins and extended correlated defects (columnar or planar defects). We thus aim to propose specific experimental configurations and procedures amenable to probing the different dynamical regimes. This should definitely enhance our conceptual understanding of the intriguing dynamical properties of vortex matter, and of non-equilibrium relaxation and aging scaling in disordered condensed matter in general. Furthermore, we hope that our investigations will stimulate the development of novel diagnostic tools for material characterization and optimization of flux pinning in high-temperature superconductors.

A more thorough analysis of the slow relaxation dynamics in the vortex glass therefore requires a more efficient computational tool, as is now available to us through our new Langevin molecular dynamics code. We can now extend our investigations to considerably larger time windows by means of the mescoscopic Langevin molecular dynamics approach. Thus we may explore each of the characteristic two-step relaxation processes in more detail: In the initial stationary β relaxation regime, where time translation invariance holds, the approach to the plateau should satisfy dynamic scaling with a characteristic temperature-dependent relaxation rate. This is followed by the very slow α process describing the ultimate decay of the correlations according to a stretched exponential or Kohlrausch law with a typical decorrelation rate that depends on the waiting time s. We would also like to better understand the intriguing non-monotonic shape of the transverse displacement (height) autocorrelations at intermediate waiting times, displaying a marked maximum that exceeds the value of $C(s,s)$, see Fig. 2(b). This feature appears to indicate a fundamental change in the nature of the emerging temporal correlations in the system, as the trapping of flux line segments at the pinning sites competes with the long-range vortex repulsion.

We can naturally address the non-equilibrium relaxation in disordered type-II superconducting thin films by reducing the number of layers perpendicular to the magnetic field in our simulations. Varying the number of coupled layers also enables us to investigate the crossover from two- to three-dimensional behavior, opening up intriguing possibilities to probe and distinguish either regime in experiment. Another interesting question is if the two-dimensional samples at low temperatures behave more like the Bose glass phase of a three-dimensional type-II superconductor with extended columnar pinning centers, or the vortex glass with uncorrelated point disorder. Additional fascinating crossover features can be expected through varying the length of linear defects from isolated points to columnar pins that extend through the entire system.

Publications

1) T. Klongcheongsan, T.J. Bullard, and U.C. Täuber, *Nonequilibrium steady states of driven magnetic flux lines in disordered type-II superconductors*, Supercond. Sci. Technol. **23**, 025023–1-13 (2010) [e-print `arXiv:0911.4066`].

2) M.T. Shimer, U.C. Täuber, and M. Pleimling, *Nonequilibrium relaxation and scaling properties of the two-dimensional Coulomb glass in the aging regime*, Europhys. Lett. (EPL) **91**, 67005–1-6 (2010) [e-print `arXiv:1007.1929`].

3) H. Park and M. Pleimling, *Aging in coarsening diluted ferromagnets*, Phys. Rev. B **82**, 144406–1-9 (2010) [e-print `arXiv:1009.1677`].

4) G.L. Daquila and U.C. Täuber, *Slow relaxation and aging kinetics for the driven lattice gas*, Phys. Rev. E **83**, 051107–1-11 (2011) [e-print `arXiv:1102.2824`].

5) M. Pleimling and U.C. Täuber, *Relaxation and glassy dynamics in disordered type-II superconductors*, Phys. Rev. B **84**, 174509–1-10 (2011) [e-print `arXiv:1106.1130`].

6) G.L. Daquila and U.C. Täuber, *Non-equilibrium relaxation and critical aging for driven Ising lattice gases*, Phys. Rev. Lett. **108**, 110602–1-5 (2012) [e-print `arXiv:1112.1605`].

7) H. Park and M. Pleimling, *Domain growth and aging scaling in coarsening disordered systems*, Eur. Phys. J. B, *in press* (2012) [e-print `arXiv:1207.3041`].

Orbital-free Quantum Simulation Methods for Applications to Warm Dense Matter

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(Dated: 16 July 2012)

I. PROJECT SCOPE

The *objective* of this project is to develop reliable finite-temperature, orbital-free density functional approximations for molecular dynamics (MD) simulations. Motivational issues include:

- A pressing need to eliminate the Kohn-Sham bottleneck in quantum-forces-driven molecular dynamics. Evident at T = 0 K, the bottleneck grows in severity such that it is a major limitation on simulation realism (system size, MD run length) in the Warm Dense Matter (WDM) regime.
- A major opportunity to enlarge the accessible physics of WDM systems by use of authentic free energy functionals rather than ground-state functionals.

The WDM regime is of rapidly growing interest (exo-planet interiors, path to inertial confinement fusion). It is characterized by electron temperatures $T \approx$ 1-15 eV, pressures up through at least 1 MBar, and densities from 10% of ambient solid to 150-fold or more compression. There is no small parameter, thus there is no perturbative approach. Neither solid-state electronic structure nor standard plasma methods work well.

In principle, orbital-free DFT (OF-DFT) provides a transformative response to the motivations. Core requirements include (a) non-interacting (Kohn-Sham system) kinetic energy and entropy functionals, and (b) exchange-correlation free-energy functionals. These must balance accuracy (realism), system size, and computational cost, and not rely on empirical fitting (loss of predictive power). Therefore, *thrusts* of the project so far have been

1. Investigation of formal properties of functionals to constrain the form and parameterizations of approximations [scaling, bounds, asymptotics . . .];
2. Generation of reference data from well-defined systems to expose behavior of functionals and to validate proposed approximate forms [finite-T Hartree-Fock, path-integral MD, near-exact 3-electron wavefunctions];
3. Comparison testing of existing explicit T-dependent functionals vs. ground state functionals ;
4. Construction, implementation, and testing of new approximate functionals, both finite-T and T = 0 K [as more realistic limits for finite-T functionals] ;
5. Making essential supporting developments, *e.g.* local pseudo-potentials, algorithms and codes;
6. Taking a leadership role in OF-DFT dissemination and education, especially as related to WDM [Sanibel Workshop (Feb. 2011), FCAM workshop Paris and CECAM proposal (May 2011), DPP mini-conference Salt Lake City (Nov. 2011), IPAM (UCLA) HEDP Long program, esp. Workshop IV (March-June 2012), CECAM Paris (Sept. 2012)]; see http:// www.qtp.ufl.edu/ofdft

II. PROGRESS

Summary

Before the research highlight (see next subsection), here is a summary of topics on which we have made substantial progress, with citations numbered according to the publication list at the end of this document.

- Approximate functionals -
  1. new finite-T generalized gradient approximation for the non-interacting system (kinetic energy and entropic functionals). Paper 2;
  2. systematic assessment of existing finite-T vs. ground state exchange-correlation functionals. (T-dependent disparities discussed separately below.). Paper 3 .
  3. new ground-state orbital-free exchange functionals (proper T = 0 K limit to preserve atomic and molecular physics realism). Papers 4, 9, 12, 13;
  4. discovery of an unexpected deficiency in a much-heralded, empirically calibrated ground-state exchange-correlation functional. Paper 14.
- Formal results (scaling relations, small-N modifications of Thomas-Fermi, proper definition of finite-T reduced density derivatives, limitations on information theoretic functionals, . . .). Papers 1, 2, 6, 8, 10, 11, 15, 16, 17.

- Computational innovation -
  1. first-ever implementation and use of the thermal Hartree-Fock (tHF) approximation in a confined system (new basis set, new code) and new results. (T-dependent disparities discussed separately below.) Paper 7;
  2. novel use of exact exchange features of Q-Espresso and VASP codes to perform tHF calculations in periodic systems (simple cubic H, bcc Li) over large ranges of T and densities.(T-dependent disparities discussed separately below.) Paper 3;
  3. systematic development of required local pseudo-potentials and PAW data sets. Papers 2, 3, 5;
  4. demonstration that SCF algorithms for standard KS equations work poorly or not at all as solvers of the OF-DFT Euler equation (effective KS equation). Paper 5.

Highlight - Important T-Dependence Differences in Functionals

We have discovered that there are qualitative differences in T-dependences of free energies and pressures delivered by various OF-KE and OF-$\mathcal{S}$ (entropy) functionals (both long-standing ones and our new ones). Similar differences are seen between the ground-state and finite-T exchange-correlation (XC) functionals.

The non-interacting system (*i.e.*, Kohn-Sham system) functionals typically contribute an order of magnitude more than the XC contribution magnitude. In a KS calculation, the T-dependence of the non-interacting part is explicit in the Fermi-Dirac occupation numbers f_i and implicit in the orbitals $\varphi_i(\mathbf{r})$ which appear in the KS KE (T_s) and entropy ($\mathcal{S}$):

$$\begin{aligned} \mathcal{T}_s[n] &= \tfrac{1}{2}\sum_i f_i \int d\mathbf{r}|\nabla\varphi_i|^2 \\ \mathcal{S}_s[n] &= -k_B\sum_i\{f_i\ln f_i + (1-f_i)\ln(1-f_i)\}\ . \end{aligned} \tag{1}$$

Here $n(\mathbf{r},\mathrm{T})$ is the electron density field. The OF-KE and OF-$\mathcal{S}$ functionals must reproduce this T-dependence without invoking f_i and $\varphi_i(\mathbf{r})$. The XC free energy is

$$\mathcal{F}_{xc}[n(\mathbf{r},\mathrm{T}),\mathrm{T}] := \int d\,\mathbf{r} n(\mathbf{r},\mathrm{T})\varepsilon_{xc}[n(\mathbf{r},\mathrm{T}),\mathrm{T}]\ , \tag{2}$$

with $\varepsilon_{xc}[n(\mathbf{r},\mathrm{T}),\mathrm{T}]$ the XC energy per electron which must be approximated. Current practice for predictive MD simulations is the ground-state functional approximation,

$$\varepsilon_{xc}[n(\mathbf{r},\mathrm{T}),\mathrm{T}] \approx \varepsilon_{xc,0}[n(\mathbf{r},\mathrm{T})]\,, \tag{3}$$

where the RHS is a ground-state XC approximation. The most popular are the Local Density Approximation (LDA) and Perdew-Burke-Ernzerhof generalized gradient approximation (PBE GGA).

Fig. 1 shows results from Paper 2. The target system is simple-cubic Hydrogen (sc-H). The comparison is of various non-interacting (KE, entropy) functionals. ft(VW+TF) is finite-T Thomas-Fermi plus full von Weizsäcker, ftGGA(KST2) is our new pair of finite-T GGA functionals, ftSGA is the second-order gradient approximation, ftGGA(TW) is based on the Tran-Wesolowski ground state functional, and ftTF is finite-T Thomas-Fermi. All are compared with a conventional KS calculation and on an equal footing: the same ground-state LDA XC functional (Perdew-Zunger) was used and the same local pseudo-potential (of our devising). The bulk density is 2.0 g/cm^3, roughly 4-fold compression. Similar results hold at 8-fold compression.

These free-energy differences cause pressure differences as shown for T = 50 kK in Fig. 2. Note that for both free energies and pressures, our new functional comes closer to the KS result than any of the others except for the formally unjustified combination ft(VW+TF).

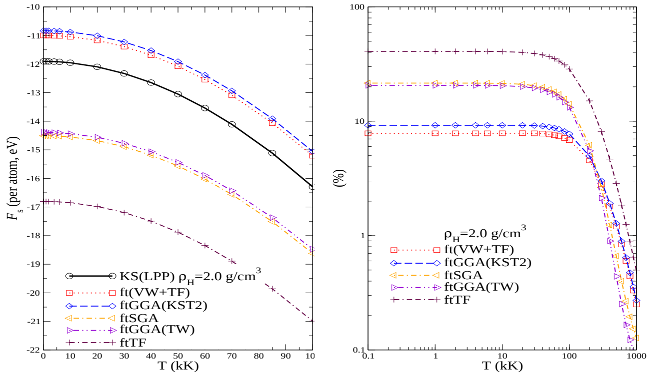

FIG. 1: Left: total free-energy per atom (eV/atom) as a function of T for local-pseudo-potential KS and OF-DFT calculations. Right: relative free energy differences with respect to KS values, $|(\mathcal{F}_s - \mathcal{F}_s^{\mathrm{KS}})/\mathcal{F}_s^{\mathrm{KS}}| \times 100\%$ for the ft(VW+TF), ftGGA(KST2), ftSGA, ftGGA(TW), and ftTF free energy functionals; see text. Material density $\rho_{\mathrm{H}} = 2.0$ g/cm^3.

In Papers 3 and 7, we studied T-dependence in XC. The system was bcc Li. A new all-electron (usually called 3-electron), small-core projector augmented wave data set was validated to compressions of more than 250 by comparison with all-electron KS calculations on Li_8 and Li_{16} clusters of bcc symmetry (Fig. 3).

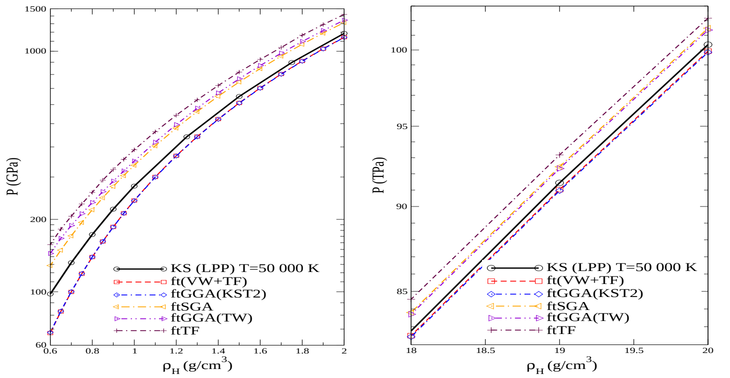

FIG. 2: P as a function of material density (low to intermediate at left, high at right) for sc-H at T=50,000K from conventional KS and OF-DFT calculations.

Figure 4 shows total free energy differences $\Delta\mathcal{F}_{\text{tot}}(\text{T}) = \mathcal{F}_{\text{tot}}(\text{T}) - \mathcal{F}_{\text{tot}}(100\text{K})$ as a function of T for X-only calculations. The explicitly T-dependent LDA X ("LDAx(T)") is qualitatively much like tHF, with differences not exceeding $1 - 2$ eV/atom. The results from ground-state LDA X ("LDAx") lie below the corresponding tHF values for all T and both densities. At T $\approx$ 20 kK, the interval is $\approx$ 2 eV/atom, growing to $\approx$ $4 - 5$ eV/atom by 40 kK. The pressure effects of explicitly T-dependent X may be estimated from the difference between the tHF or LDAx(T) and LDAx values. Fig. 5 provides this comparison. The LDAx and LDAx(T) curves both start above the tHF pressure, then cross and go below it at about 55-75 kK, depending upon the material density. The shift with respect to tHF is manifestly larger for LDAx than LDAx(T).

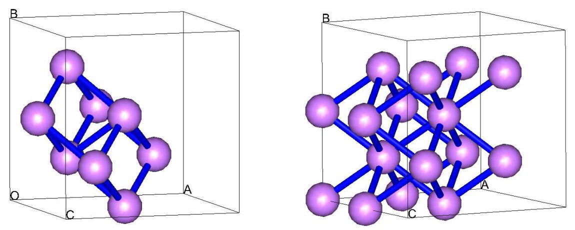

FIG. 3: Bcc-symmetry Li_8 (left) and Li_{16} (right) clusters treated with all-electron calculations to validate the new 3-electron, small-core PAW data set to at least 250-fold compression.

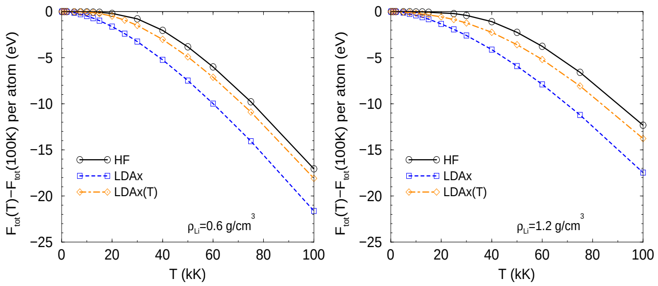

FIG. 4: Comparison tHF, ground-state LDA X-*only* (LDAx) and T-dependent LDA X-*only* (LDAx(T)) total free energy differences $\Delta\mathcal{F}_{\text{tot}}(\text{T}) = \mathcal{F}_{\text{tot}}(\text{T}) - \mathcal{F}_{\text{tot}}(100\text{K})$ per atom as a function of electronic temperature. Left: $\rho_{\text{Li}} = 0.6$ g/cm^3; right: $\rho_{\text{Li}} = 1.2$ g/cm^3.

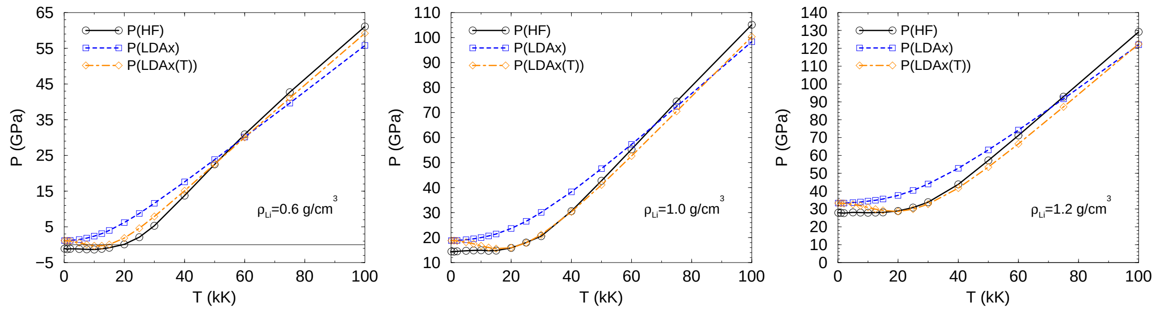

FIG. 5: Pressure as a function of electronic temperature as predicted by tHF, LDAx, and LDAx(T) calculations for bcc Li at bulk densities $\rho_{\text{Li}} = 0.6$, 1.0, and 1.2 g/cm^3.

III. PLANNED EFFORTS

- Do large-scale MD on confined H to test tHF vs. tDFT
- Develop better non-interacting free energy GGA forms by improving on our first approximate one via our newly developed finite-T GGA framework (Publication 2 below)
- Develop non-empirical, constraint-based parameterization criteria for non-interacting functionals (predictive capability) for:
  1. T = 0 K KE GGA functional (eliminate present fitted parameters)
  2. Free energy functionals with proper T-dependence relative to reference data and proper T = 0 K limits
  3. Beyond GGA functionals
- Develop and test better T-dependent XC functionals, with focus on T-dependence exposed in reference calculations (below)
- Exploit new version of classical map to get better functionals
- Complete PIMD calculations on T > 0 K electron gas, compare with Brown and Ceperley's new PIMC results, parameterize to gain functional form information
- Explore orbital-free calculation of transport coefficients
- Explore explicit orbital-free dynamics (including use of more modern functionals than TF)
- Codify and publish modifications to PROFESS code and interface of PROFESS with Q-Espresso

IV. PUBLICATIONS SINCE AUGUST 2009

1. "Local Density Approximation to the Kinetic Energy Functional for Finite N", T. Gál, J. Dufty, and S.B. Trickey, in preparation.
2. "Generalized Gradient Approximation Non-interacting Free Energy Functionals for Orbital-free Density Functional Calculations", V.V. Karasiev, T. Sjostrom, and S.B. Trickey, Phys. Rev. B [submitted].
3. "Comparison of Density Functional Approximations and the Finite-temperature Hartree-Fock Approximation in Warm Dense Lithium", V.V. Karasiev, T. Sjostrom, and S.B. Trickey, Phys. Rev. E [submitted].
4. "A New meta-GGA Exchange Functional Based on an Improved Constraint-based GGA", J.M. del Campo, J.L. Gázquez, S.B. Trickey, and A. Vela, Chem. Phys. Lett. [accepted]
5. "Issues and Challenges in Orbital-free Density Functional Calculations", V.V. Karasiev and S.B. Trickey, Comput. Phys. Commun. [accepted]
6. "Why the Traditional Concept of Local Hardness Does Not Work", T. Gál, Theor. Chem. Acc. **131**, 1223 (2012).
7. "Temperature-Dependent Behavior of Confined Many-electron Systems in the Hartree-Fock Approximation", T. Sjostrom, F.E. Harris, and S.B. Trickey, Phys. Rev. B **85**, 045125 (2012).
8. "Classical Representation of a Quantum System at Equilibrium", J.W. Dufty and S. Dutta, Contrib. Plasma Phys. **52**, 100 (2012).
9. "Scalable Properties of Metal Clusters: A Comparative Study of Modern Exchange-Correlation Functionals", R. Koitz, T.M. Soini, A. Genest, S.B. Trickey, and N. Rösch, J. Chem. Phys. **137**, 034102 (2012).
10. "Explicit Particle-number Dependence in Density Functional Theory", S.B. Trickey and A. Vela, J. Mex. Chem. Soc. [submitted].
11. "Analysis of the Generalized Gradient Approximation for the Exchange Energy", J.L. Gázquez, J.M. del Campo, S.B. Trickey, R.J. Alvarez-Mendez, and A. Vela, chapter in *Concepts and Methods in Modern Theoretical Chemistry*, Vol. 1, in honor of Prof. B.M. Deb; S.K. Ghosh and P.K. Chattaraj eds. [accepted]
12. "Non-empirical Improvement of PBE and Its Hybrid PBE0 for General Description of Molecular Properties", J.M. del Campo, J.L. Gázquez, S.B. Trickey, and A. Vela, J. Chem. Phys. **136**, 104108 [8 pp] (2012).
13. "Improved Constraint Satisfaction in a Simple GGA Exchange Functional", A. Vela, J.C. Pacheco-Kato, J.L. Gázquez, J.M. del Campo, and S.B. Trickey, J. Chem. Phys. **136**, 144115 [8 pp] (2012).
14. "Structure-dependence of the Magnetic Moment in Small Palladium Clusters: Surprising Results from the M06-L meta-GGA Functional", R. Koitz, T.M. Soini, A. Genest, S.B. Trickey, and N. Rösch, Internat. J. Quantum Chem. **112**, 113 (2012).
15. "Scaling, Bounds, and Inequalities for the Non-interacting Density Functionals at Finite Temperature", J. Dufty and S.B. Trickey, Phys. Rev. B **84**, 125118 (2011).
16. "Positivity Constraints and Information-theoretical Kinetic Energy Functionals", S.B. Trickey, V.V. Karasiev, and A. Vela, Phys. Rev. B **84**, 075146 (2011).
17. "Constraint-based Single-point Approximate Kinetic Energy Functionals", V.V. Karasiev, R.S. Jones, S.B. Trickey, and Frank E. Harris, Phys. Rev. B **80**, 245120 (2009).

Quantum simulations of orbitally controlled physics and nanoscale inhomogeneity in correlated oxides

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Project Scope:

Part I: We focus on superconductor-insulator transitions driven by disorder. Our aim is to understand how the interplay of disorder and interactions can lead to nano-scale inhomogeneity of the pairing amplitude and determine its consequences for local spectroscopic probes.

Part II: We investigate a new class of materials, the ruthenate perovskites $SrRu_{1-x}M_xO_3$ in which the orbital state of Ru can control the magnetism of the M=Cr,Mn,Fe ions. Our primary aim is to develop a comprehensive and fundamental theory of the mechanisms driving magnetism. This understanding is important to design heterostructures with desired magneto-transport properties.

Part III: We discuss algorithmic developments for the maximum entropy method constrained by sum rules for extracting frequency dependent spectral functions and dynamical susceptibilities from quantum Monte Carlo simulations. These developments are necessary for addressing the full complexity of disordered, correlated, multi-orbital oxides.

Recent Progress:

Part I: Emergent granularity on the meso-scale and the superconductor-insulator transition: We have used quantum Monte Carlo simulations that treat, on an equal footing, inhomogeneous amplitude variations and phase fluctuations, a major advance over previous theories. We gain new microscopic insights into the nature of the superconducting and insulating phases and the mechanism driving the transition. We make testable predictions for local spectroscopic probes. The energy gap in the density of states survives across the transition, but coherence peaks exist only in the superconductor. A characteristic pseudogap persists above the critical disorder and critical temperature, in contrast to conventional theories. Surprisingly, the insulator has a two-particle gap scale that vanishes at the superconductor–insulator transition, despite a robust single-particle gap. The results are encapsulated in the phase diagram given below and published in Nature Physics. Several follow-up works are in preparation.

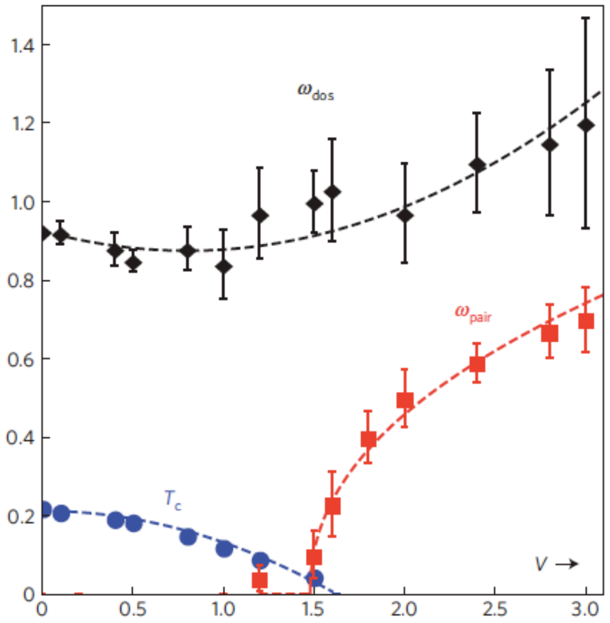

Figure 1: Energy and temperature scales across the superconductor-insulator transition: The superconducting Tc (blue dots) decreases to zero at the critical disorder strength Vc. The single-particle gap ω_{dos} (black diamonds), obtained from the density of states is large and finite in all states. The two-particle energy scale ω_{pair} (red squares), obtained from the dynamical pair susceptibility is non-zero in the insulator but vanishes at the SIT.

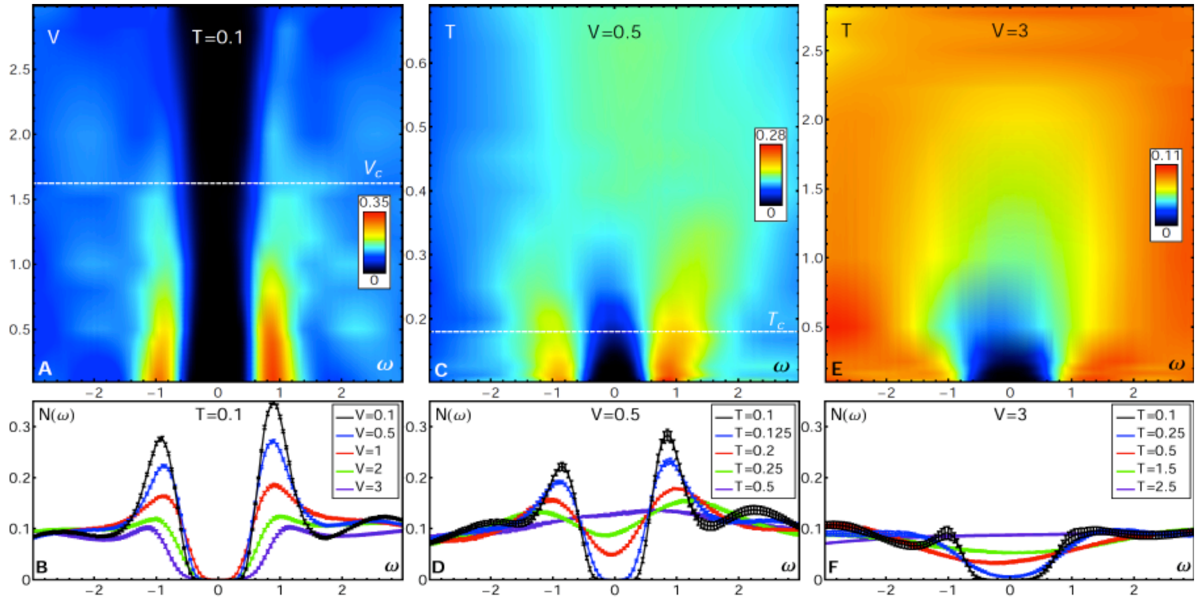

Figure 2: The single-particle DOS (upper panels) and representative spectra (lower panels) shown along three different cuts through the temperature-disorder plane. Left panels (A,B): Disorder dependence of DOS at a fixed low temperature. A hard gap (black region) persists for all V above and below the SIT (Vc =1.6), but the coherence peaks (red) exist only in the SC state and not in the insulator. Center panels (C,D): T-dependence of the DOS for the superconductor (V < Vc). The coherence peaks (red) visible in the SC state, vanish for T>Tc = 0.14t. A disorder-induced pseudogap, with loss of low-energy spectral weight, persists well above Tc. Right panels (E,F): T-dependence of DOS for the insulator (V > Vc). The hard insulating gap at low T evolves into a pseudogap at higher T. No coherence peaks are observed at any T. All panels show data averaged over 10-100 disorder realizations.

Future Plans (2012-2013):

Part II: Ruthenates-- Orbitally controlled magnetism:

Over the years the cuprates have been extensively studied for their high **T**c superconducting properties, and the manganites for their colossal magnetoresistive properties. In this proposal we will focus on a novel class of perovskites, the ruthenates in which the orbital state of Ru can potentially control the magnetic properties. We will investigate the coupling between chemical order, magnetism and transport properties in a class of quaternary ruthenate perovskites $ARu_{1-x}M_xO_3$, where M = Cr, Mn, Fe and A =Ba, Sr, Ca, La.

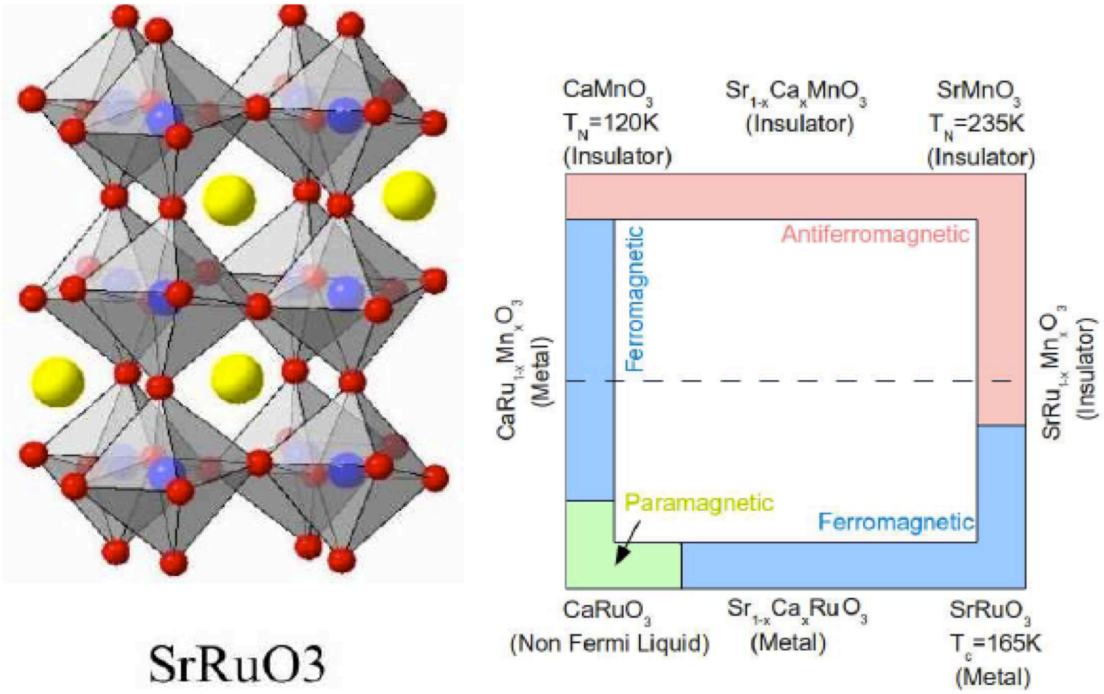

Figure 3: (a) Perovskite structure of Strontium Ruthenate showing the oxygen (red) octahedra around a ruthenium ion (blue); the alkali strontium ions are yellow. In these novel materials the orbital structure can control its magnetic properties.
(b) Magnetic and electrical behavior of $CaRuO_3$, $SrRuO_3$, $CaMnO_3$, and $SrMnO_3$ and their solid solutions. The dashed line represents the $Sr_{1-x}Ca_xMn_{0.5}Ru_{0.5}O_3$.

At present not only are the properties of the bulk samples poorly understood due to complications involving chemical disorder, but there is no clear understanding of what properties will emerge for even the various ordered arrangements. Our aim is to develop a theoretical understanding of these compounds using multi-pronged computational methods. We expect the theoretically calculated phase diagrams to guide the fabrication of films in specific phases for use as magnetic sensors, actuators and spintronic devices.

The box diagram above shows the end phases and is a useful way to highlight the main puzzles of the ruthenates related to:

(1) the mechanism of ferromagnetism in these materials;

(2) the reasons behind the asymmetry between the isoelectronic Sr and Ca compounds;

(3) lack of correlation between transport and magnetism, rather unexpected from the double exchange mechanism.

Modeling: The central computational challenge is to efficiently integrate the electronic structure codes with coupled classical-quantum Monte Carlo in order to realistically model the ruthenates. Insights gained from state-of the-art ab-initio calculations of the electronic structure coupled with disorder, either at the interface or in the bulk, will be invaluable to guide the design and growth of thin films and heterostructures. Our approach is to first understand the bulk materials modeled by tight-binding Hamiltonians involving the charge, spin, and orbital degrees of freedom. We will use the guidance from electronic structure calculations to tell us which orbitals are relevant, the approximate positions of the levels and the relevant range of tight-binding parameters. We will then develop effective Hamiltonians with the spin and orbital degrees by integrating out the electronic degrees. This should give a direct window into the coupling between the orbital and magnetic degrees. We will also look at finite temperature effects by including fluctuations of the magnetic and orbital degrees within a classical approach and calculating the electronic properties by exact diagonalization in a fixed classical field. These methods can be extended to include disorder. Coulomb correlations beyond Hartree-Fock can be included using quantum Monte Carlo methods, but this decision will be based on detailed comparisons with experiments.

Publications:

(1) Karim Bouadim, Yen Lee Loh, Mohit Randeria and Nandini Trivedi, “Single- and two-particle energy gaps across the disorder-driven superconductor–insulator transition”, **Nature Physics** 7, 884-889 (2011).

(2) Y. L. Loh, N. Trivedi, Y. M. Xiong, P.W. Adams, and G. Catelani, “Origin of Excess Low-Energy States in a Disordered Superconductor in a Zeeman Field”, **Phys. Rev. Lett.** 107, 067003 (2011).

Development of New Methods and Techniques in Theory of Strongly Correlated Systems

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Project Scope

During the recent years the activity of our FWP has been dedicated to development of new ideas in theory of strongly correlated systems and their applications to various experimental systems. Such systems included low-dimensional magnets and charge density wave materials, graphine, iron telluride, heavy fermion materials. A number of new theoretical results have been obtained in the form of non-perturbative solutions of various model systems with sometimes quite exotic applications such as the theory of density waves in quarkionic matter. Our theory group is working in a close contact with experimentalists: out of 29 papers published and submitted since 2009 seven ones are written in collaboration with experimentalists.

Recent Progress

Low-dimensional magnetism. The effect of spinon confinement in materials consisting of arrays of weakly coupled pairs of spin chains chains (spin ladders) predicted in 1996 by Shelton, Tsvelik and Nersesyan was experimentally observed by the group of B. Lake in Berlin (Ref. 2). The work was done in collaboration with A. Tsvelik who provided a theoretical support and the results published in “Nature Physics”. Thermal broadening of the spectral lines in 1D magnets is a non-perturbative effect which for years has resisted efforts of theorists. The description of this effect together with other thermal effects in 1D magnets with gapped spectrum was obtained by R. Konik in collaboration with F. H. L. Essler (Oxford) (ref. 26).

Majorana fermions . There is a great interest in Majorana fermions in relation to their possible use in quantum computation. Existing proposals of their material realization are centered on p-wave superconductors or complicated arrangements including nanowires with strong spin-orbit coupling in magnetic field in contact with s-wave superconductors. We have suggested a scheme based on nanowires of s- or d-wave superconductors without any spin-orbit interactions or magnetic fields (Refs. 14,15). An alternative method to obtain Majorana fermions and even more complicated (and better suited for quantum computing) generalizations – Z_N parafermions exists in cold atom systems consisting of parallel chains of quantum atomic dipoles (Ref. 18). The latter possibility is especially exciting since the dipole systems are optically active and can be effectively controlled by light.

New Numerical Method. The new numerical technique developed by R. Konik has been successfully applied to a number of problems in physics of strongly correlated systems.
In this technique one separates the Hamiltonian into an integrable part and a perturbation and uses the exact many-body wave eigenfunctions of the former as a basis for the computation. In this way the bulk of the interactions are taken into account on the very first step of the calculations. The subsequent numerical procedure uses a truncation of the Hilbert space and numerical diagonalization of the entire Hamiltonian as well as Wilson-type renormalization group procedure (Ref. 27). This technique has been successfully tested on models with known solutions (quantum Ising chain in magnetic field and 2D array of coupled quantum Ising chains).

In Ref. 24 it was used for the model where no non-perturbative results had been known, namely for a model of semiconducting carbon nanotube with strong long range Coulomb interaction (such problems are very ill suited for a more conventional DMRG method). The solution revealed existence of several optically active excitonic branches with a complicated dispersion. The theoretical predictions fit perfectly the experimental results obtained by J. Misewich group (unpublished). The method developed by R. Konik has been applied to such problems as energy level statistics in non-integrable systems (Ref. 25) and to strongly correlated systems out of equilibrium (Refs. 21,28).

Physics of Strongly Correlated Systems out of Equilibrium. This area of theory of strongly correlated systems is in its infancy. One of the questions persistently asked is whether equilibration of integrable systems proceeds differently from non-integrable ones and, if yes, whether this opens a possibility to have exotic pre-equilibrium states such as generalized Gibbs ensembles: $P = \frac{1}{Z}\exp\left(-\beta_i I_i\right)$, where I_i are integrals of motion. In such ensemble each integral of motion has its own temperature determined by the initial conditions.

Using our expertise in theory of integrable systems we managed to obtain several nontrivial results. In Ref. 17 we have studied the generalized Gibbs ensembles for integrable models with internal non-Abelian group symmetry. It was demonstrated that the spin dynamics in such systems has a *universal* form corresponding to the dynamics of a *ferromagnet* at thermal equilibrium (that is characterized by a *single* temperature).

Future Research. Excitations with non-Abelian statistics can be relatively easily realized in 1D systems. However, for the purposes of quantum computation one needs to find a way to exchange them which is possible only if one finds a way to overcome one-dimensionality of the problem. It has been suggested that such exchange can be realized in the so-called Y-junction (a junction of three chains). We intend to study a model of such junction of three quantum Ising models. The preliminary results indicate that such junction is described by the overscreened two-channel Kondo model which is interesting in its own right. We are going to study further non-equilibrium systems employing for this the powerful numerical technique developed by R. Konik.

In the area of Fe-based quasi-2D materials there is a controversy whether to use local or itinerant description. There are experimental evidence coming from ARPES, NMR and neutron scattering that some Fe-based materials such as FeTe are exactly in the middle, that is the local description is suitable for high and the itinerant one for low temperatures. In that respect FeTe resembles heavy fermion materials. A recognition of this analogy would constitute an entirely new paradigm in the physics of these compounds and open new avenues for research. Using these ideas we are going to develop a theoretical model for Fe(Te_{1-x} ,Se_x).

Iridium oxides constitute a new area of experimental research at BNL. We are going to continue to work with our local experimental teams on these materials.

New high quality ARPES on the quasi-1D Charge Density Wave material blue bronze (Ref. 20) show incoherent propagating excitations with very broad spectral function. The width of the spectral function peaks exceeds everything the theory predicts. In Ref. 20 we presented some ideas about a possible origin of this incoherence which exceeds everything one might expect even for one-dimensional models. We are going to develop these ideas further.

The studies of non-equilibrium systems will be continued.

Publications

1.``**Breakdown of the N=0 Quantum Hall State in graphene: two insulating regimes"**, by L. Zhang, J. Camacho, H. Cao, Y.P. Chen, M. Khodas, A. M. Tsvelik, T. Valla, I. Zaliznyak, Phys. Rev. B 80, 241412 (2009), Rapid Communications; also January 11, 2010 issue of Virtual Journal of Nanoscale Science & Technology.

2. ``**Confinement of Fractional Quantum Number Particles in a Condensed Matter System: Example of CaCu2O3"**.
B. Lake, A. M. Tsvelik, S. Notbohm, D.A. Tennant, T. G. Perring, M. Reehuis, C. Sekar, G. Krabbes, B. B�chner, Nature Physics, 6, 50 (2010).

3.``**On the spin-liquid phase of one dimensional spin-1 bosons"**, F. H. L. Essler, A. M. Tsvelik and G. V. Shlyapnikov, J. Stat. Mech., P02027 (2009).

4. ``**Excitations from a chiral magnetized state of a frustrated quantum spin liquid"**, by A. Zheludev, V. O. Garlea, A. Tsvelik, L.-P. Regnault, K. Habicht and B. Roessli, Phys. Rev. B 80, 214413 (2009).

5. ``**Influence of thermal phase fluctuations on the spectral function for a two-dimensional d-wave superconductor"**,
by M. Khodas and A. M. Tsvelik, Phys. Rev. B 81, 094514 (2010).

6. ``**Influence of thermal fluctuations of spin-density wave order parameter on the quasiparticle spectral function"**, by M. Khodas and A. M. Tsvelik, Phys. Rev. B 81, 155102 (2010).

7. ``**Superconductivity generated by coupling to a Cooperon in a 2-dimensional array of 4-leg Hubbard ladders"**,
Authors: R. M. Konik, T. M. Rice, A. M. Tsvelik, PRB, 82, 054501 (2010).

8. ``**Effects of thermal phase fluctuations in a 2D superconductor: an exact result for the spectral function",** with F. H. L. Essler, PRL 105, 027002 (2010).

9. ``**Covering the Fermi Surface with Patches of Quarkyonic Chiral Spirals",** Toru Kojo, Robert D. Pisarski, A. M. Tsvelik, Phys. Rev. D 82, 074015 (2010).

10. ``**A Field Theory for a Fermionic Ladder with Generic Intrachain Interactions"**, Phys. Rev. B 83, 104405 (2011).

11.**"Unconventional temperature enchanced magnetism in iron telluride"**, I. A. Zaliznyak, Z. Xu, J. M. Tranquada, G. Gu, A. M. Tsvelik, M. B. Stone, Phys. Rev. Lett. 107, 216403 (2011).

12. **``Polar Phase of 1D Bosons with Large Spin"**, A. M. Tsvelik, G. Shlyapnikov, New J. Phys. 13, 065012 (2011).

13. **``Long range magnetic ordering in Na$_2$IrO$_3$"**, X. Liu, T. Berlijn, W.-G. Yin, W. Ku, A. Tsvelik, Young-June Kim, H. Gretarsson, Yogesh Singh, P. Gegenwart, J. P. Hill, Phys. Rev. B 83, 220403 (2011).

14**. ``Zero energy Majorana modes in spin ladders and a possible realization of the Kitaev model",** A. A. Nersesyan, A. M. Tsvelik, EPL 96, 17002 (2011).

15. **"Riding a wild horse: Majorana fermions interacting with solitons of fast bosonic fields"**, A. M. Tsvelik, EPL 97, 17011 (2012).

16. **"Finite wave vector pairing in doped two-leg ladders"**, N. J. Robinson, F. H. L. Essler, E. Jeckelmann, A. M. Tsvelik, Phys. Rev. B 85, 195103 (2012).

17. **"Universal Features of the Excitation Spectrum in Generalized Gibbs Distribution Ensemble**", E. Demler, A. M. Tsvelik, accepted to Phys. Rev. B

18. **"Parafermion excitations in superfluid of quasi-molecular chains"**, A. B. Kuklov, A. M. Tsvelik, submitted to New J. Phys.

19. **"β-YbAlB4: a critical nodal metal",** Aline Ramires, Piers Coleman, Andriy H. Nevidomskyy, A. M. Tsvelik, arXiv:1207.6441.

20. " **Incoherent Soliton Excitations and Spin-Charge Separation in Blue Bronze"**, Daixiang Mou, R. M. Konik, A. M. Tsvelik, I. Zaliznyak, Xingjiang Zhou, arXiv: 1207.7066

21. **Quench dynamics in randomly generated extended quantum models**
Author(s): Brandino G. P.; De Luca A.; Konik R. M.; et al., PHYSICAL REVIEW B Volume: **85**, **214435**, **2012.**

22. **Uniaxial linear resistivity of superconducting La1.905Ba0.095CuO4 induced by an external magnetic field**
Author(s): Wen Jinsheng; Jie Qing; Li Qiang; et al., PHYSICAL REVIEW B Volume: **85**, **134513** , 2012.

23. **RKKY interaction and the nature of the ground state of double dots in parallel**
Author(s): Kulkarni M.; Konik R. M., PHYSICAL REVIEW B Volume: **83**, **245121, 2011.**

24. Exciton Hierarchies in Gapped Carbon Nanotubes
Author(s): Konik Robert M., PHYSICAL REVIEW LETTERS Volume: **106**, **136805, 2011.**

25. Energy level distribution of perturbed conformal field theories
Author(s): Brandino G. P.; Konik R. M.; Mussardo G.
JOURNAL OF STATISTICAL MECHANICS-THEORY AND EXPERIMENT, **P07013**, 2010.

26. **Finite-temperature dynamical correlations in massive integrable quantum field theories**
Author(s): Essler Fabian H. L.; Konik Robert M. JOURNAL OF STATISTICAL MECHANICS-THEORY AND EXPERIMENT, **P09018, 2009.**

27. **Renormalization Group for Treating 2D Coupled Arrays of Continuum 1D Systems**
Author(s): Konik Robert M.; Adamov Yury, PHYSICAL REVIEW LETTERS Volume: **102**, **097203, 2009.**

28. Numerical renormalization based on integrable theories: quantum quenches and their corresponding generalized Gibbs ensembles,
Jean-Sébastien Caux, R. M. Konik , arXiv: 1204.0901

29. **Magnetic Response in the Underdoped Cuprates**
A. J. A. James, R. M. Konik, T. M. Rice, arXiv: 1112.2676.

Charge and Spin Dynamics in Bulk and Heterostructured Dilute Magnetic Semiconductors

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1 Project Scope

The goal of this project is the theoretical and computational study of the collective charge and spin dynamics in semiconductors and semiconductor heterostructures, in particular dilute magnetic semiconductors (DMS). Materials such as (Ga,Mn)As have been widely studied, but a key question—whether the carriers are itinerant holes in the valence band or reside in an impurity band—is still not fully settled. The interplay between band structure, disorder, and many-body effects in collective excitations is ideal for testing microscopic models for the carrier dynamics in these materials. Plasmon modes, Stoner excitations and spin waves in p-type bulk DMS materials are investigated. We calculate line shapes of intersubband charge and spin plasmons in DMS quantum wells, which are very sensitive to spin-orbit coupling, phase transitions of the magnetic subsystem, and many-body effects such as the spin Coulomb drag. Many-body effects will be treated using time-dependent density-functional theory (TDDFT).

2 Recent Progress

2.1 Spin plasmons in quantum wells: many-body effects and spin-orbit coupling

The electron dynamics in metallic systems is dominated by collective plasmon-type excitations. The charge plasmon is the best known of these excitations: it can be viewed as a collective charge-density oscillation. But there are also collective spin-density plasmon oscillations. In bulk metals, these are suppressed by Landau damping, but they do exist in nanostructures such as doped quantum wells.

Spin plasmons in quantum wells are particularly interesting. While the charge plasmon is essentially a classical phenomenon (mainly due to classical Coulomb forces caused by displaced charges), the spin plasmon is entirely due to quantum mechanical exchange effects; in TDDFT language, it comes from the spin-polarized exchange-correlation (xc) kernel $f_{\mathrm{xc},\sigma\sigma'}$. Thus, spin plasmons are highly sensitive probes of xc effects. In particular, the intrinsic damping of spin plasmons is dominated by the spin Coulomb drag effect.[1] Furthermore, spin plasmons in doped semiconductors are sensitive to the internal crystal magnetic fields that come from spin-orbit coupling in the material (Rashba and Dresselhaus effect).

Over the past few years I have been engaged in a collaborative effort with Dr. Irene D'Amico from the University of York (UK) to study spin plasmon excitations. Very recently

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[1] I. D'Amico and C. A. Ullrich, Phys. Rev. B **74**, 121303(R) (2006); I. D'Amico and C. A. Ullrich, Physica Status Solidi (b) **247**, 235 (2010)

there have been exciting developments: we have teamed up with the experimental group of Dr. Florent Perez from the Université de Paris, who has conducted light scattering studies of spin plasmons in GaAs/AlGaAs quantum wells. We have discovered a new effect, namely a fine structure of the spin plasmons due to the Rashba and Dresselhaus spin-orbit fields, whose strength is enhanced through electronic many-body effects.[2] I predicted this effect ten years ago in work together with Michael Flatté (University of Iowa).[3]

Fig. 1 shows that the fine structure splitting cannot be directly resolved in the experiment, but it can be extracted from the compound linewidth. The linewidth is modulated with the in-plane scattering angle, where the symmetry and the magnitude of the modulation perfectly agrees with our TDDFT calculations.

We are currently finalizing efforts to calculate the spin plasmon linewidth from first principles, including spin Coulomb drag[5] and impurity scattering. We have discovered that the local approximation of TDDFT breaks down for plasmon linewidths, because of the quasi-2D nature of quantum wells. This opens up new directions in the development of TDDFT approaches specifically for nanostructures.

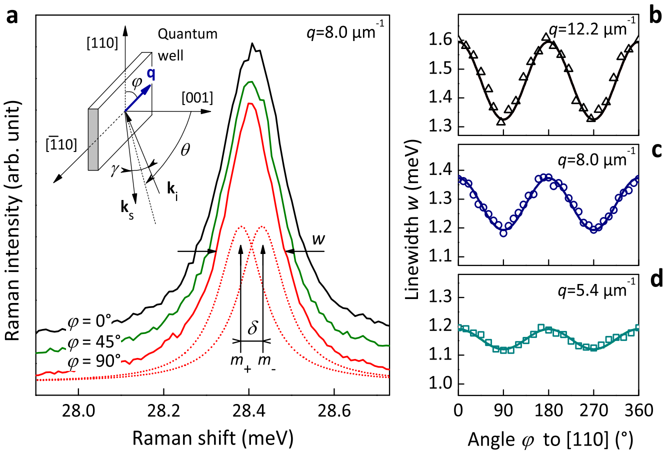

Figure 1: Left: Inelastic light scattering setup and spin plasmon peaks. Right: modulation of the spin plasmon linewidth for different in-plane plasmon wavevectors (dots: experiment, lines: theory).

2.2 Transport and optical response of dilute magnetic semiconductors

Dilute magnetic semiconductors (DMS) are semiconducting alloys whose lattices contain substitutional magnetic atoms. They are widely studied because of their interesting materials science and because of potential device applications in spintronics. A hotly debated question concerns the nature of the free carriers in (Ga,Mn)As, one of the most important representatives of DMS. Are they itinerant holes residing in the valence band, or do they live in a narrow impurity band? Experiments are conflicting, and theoretical evidence has so far not been fully convincing to tilt the scale to either side.

In a series of papers[4] [5] [6] [7] we have formulated a general theory of transport and optical

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[2] F. Baboux, F. Perez, C. A. Ullrich, I. D'Amico, J. Gómez, M. Bernard, submitted to Phys. Rev. Lett.

[3] C. A. Ullrich and M. E. Flatté, Phys. Rev. B **66**, 205305 (2002) and Phys. Rev. B **68**, 235310 (2003)

[4] F. V. Kyrychenko and C. A. Ullrich, Phys. Rev. B **75**, 045205 (2007)

[5] F. V. Kyrychenko and C. A. Ullrich, J. Phys.: Condens. Matter **21**, 084202 (2009)

[6] F. V. Kyrychenko and C. A. Ullrich, Phys. Rev. B **80**, 205202 (2009)

[7] F. V. Kyrychenko and C. A. Ullrich, Phys. Rev. B **83**, 205206 (2011)

response in DMS materials. The approach is based on the equation of motion of the current response function and considers both spin and charge disorder and electronic many-body effects on an equal footing. We calculate the current response of the disordered system, using the TDDFT response function of the clean system as input, coupled to given impurity scattering potentials. The resulting theory is self-consistent, but we evaluate it in the weak-disorder limit. We obtain excellent agreement with experiment, assuming that all carriers are itinerant holes in the valence band.

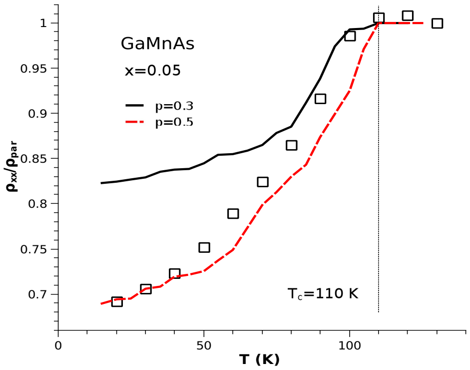

Figure 2: Temperature-dependent resistivity of (Ga, Mn)As *(experimental data from Potashnik* et al. *(2001)).*

Fig. 2 shows the temperature dependence of the static resistivity of (Ga,Mn)As, with a characteristic drop below the ferromagnetic transition temperature T_c. We discovered that scattering off the fluctuations of localized spin plays an unexpectedly large role.[6]

Fig. 3 shows the infrared optical conductivity of (Ga,Mn)As, in good agreement with experimental data, without the need to include an impurity band.[7] The valence band structure was described using an 8-band $\mathbf{k}\cdot\mathbf{p}$ model, random impurity scattering was included from first principles, and dynamical many-body effects were treated with TDDFT. We found that collective excitations within the valence band significantly increase the carrier relaxation rate by providing effective channels for momentum relaxation. This modification of the relaxation rate, however, has only a minor impact on the infrared optical conductivity in (Ga,Mn)As, which is mostly determined by the details of the valence-band structure.

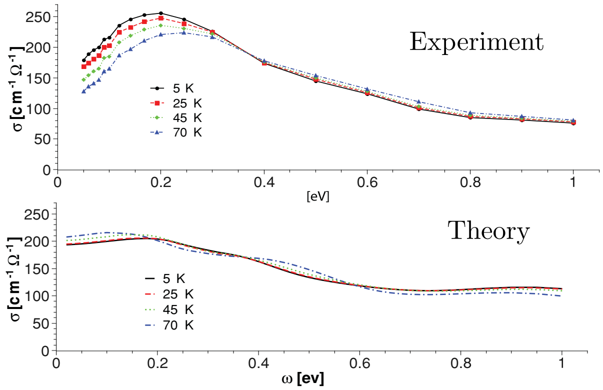

Figure 3. Temperature dependence of the infrared conductivity in (Ga,Mn)As ($T_c = 70K$).

3 Future Plans

We have developed theory of charge and spin dynamics in DMS based on linear current response theory, treating disorder from first principles and beyond the usual relaxation-time approximation. Dynamical many-body effects are included via time-dependent density functional theory, and the band structure is treated with an 8-band $\mathbf{k}\cdot\mathbf{p}$ approach. This formalism gave good results for resistivities and optical conductivities in (Ga,Mn)As, but these properties were not very sensitive to disorder and dynamical many-body effects. We therefore plan to focus on collective plasmon-type excitations, which are not only of interest in their own right, but will also be ideal for testing microscopic models for the carrier dynamics in DMS. The following problems will be studied:

Plasmon modes and spin waves in bulk DMS. Plasmons in p-type semiconductors are usually strongly Landau damped, but there are indications that it may be possible to find plasmon modes outside the particle-hole continua. Such modes will be sensitive to details of disorder broadening, such as correlated versus random disorder, or a self-consistent treatment of disorder scattering. We will also extend our formalism to study Stoner excitations and spin waves in ferromagnetic DMS.

Spin Coulomb drag beyond the local approximation. The spin Coulomb drag (SCD) is an intrinsic effect which represents an ultimate limitation for spintronics. The linewidth of intersubband spin plasmons in quantum wells represents a new and purely optical way to measure the SCD effect, using inelastic light scattering. We propose a new and more accurate way of calculating the SCD in quantum confined systems, beyond the usual local approximation. A detailed analysis of light scattering experiments, including Rashba and Dresselhaus spin-orbit coupling, will be performed.

Collective intersubband excitations in DMS heterostructures. We will extend our approach for charge and spin dynamics in DMS to lower-dimensional and quantum confined systems, with the goal of studying collective intersubband excitations in n- and p-type systems. In particular, changes of the line shape as the system undergoes a ferromagnetic transition will reveal how the carrier dynamics in DMS is influenced by disorder, band-structure, and electronic many-body effects.

The outcome of this work will be a better understanding of the itinerant carriers in DMS and how they are influenced by disorder. The collective excitations that are investigated here are not only of fundamental interest in condensed-matter physics, but will play a role whenever a spintronics device undergoes a sudden switching. This opens up new routes for improving material properties of DMS and, ultimately, for new spintronics technologies.

4 Publications since 2009

[1] *Transport and optical conductivity in dilute magnetic semiconductors.* F. V. Kyrychenko and C. A. Ullrich, J. Phys.: Condens. Matter **21**, 084202 (2009)

[2] *Intersubband spin-orbit coupling and spin splitting in symmetric quantum wells.* F.V. Kyrychenko, C. A. Ullrich, and I. D'Amico, Journal of Magnetism and Magnetic Materials **321**, 944 (2009)

[3] *Temperature-dependent resistivity of ferromagnetic GaMnAs: Interplay between impurity scattering and many-body effects.* F. V. Kyrychenko and C. A. Ullrich, Phys. Rev. B **80**, 205202 (2009)

[4] *Coulomb interactions and spin transport in semiconductors: the spin Coulomb drag effect.* I. D'Amico and C. A. Ullrich, Physica Status Solidi (b) **247**, 235 (2010)

[5] *Response properties of III-V dilute magnetic semiconductors including disorder, dynamical electron-electron interactions and band-structure effects.* F. V. Kyrychenko and C. A. Ullrich, Phys. Rev. B **83**, 205206 (2011)

[6] *Fine structure of intersubband spin plasmons in a quantum well.* F. Baboux, F. Perez, C. A. Ullrich, I. D'Amico, J. Gomez, and M. Bernard, submitted to Phys. Rev. Lett. (2012)

Quantum Chemistry via Walks in Determinant Space

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INTRODUCTION

The main purpose of this Collaborative Research Team (CRT) is to improve upon the recently developed initiator full-configuration interaction quantum Monte Carlo (i-FCIQMC) method [1–3], with the goal of developing a highly accurate method for treating difficult chemical systems of interest to the DOE. Another goal is to have cross-fertilization of ideas between i-FCIQMC and phaseless Auxilliary Field quantum Monte Carlo (AFQMC), developed by the Zhang-Krakauer group, since both methods employ walks in a space of determinants. The full configuration interaction (FCI) method is the most robust method for treating electronic correlations, but it is limited to a space of approximately 10^{10} determinants. In contrast the recently developed i-FCIQMC method can be used on a system with as many as 10^{108} determinants [3] at the cost of introducing a systematically improvable "initiator" approximation and of course a statistical error. The i-FCIQMC method has a cost that is exponential in the system size (though with an exponent that is much smaller than that for FCI). Consequently, it is very important to find ways to speed up the method to increase its range of applicability.

PROGRESS TO DATE

Semistochastic Projection and Improved Trial Wave Functions for Mixed Estimators

In collaboration with M. Peter Nightingale at the University of Rhode Island, we have already succeeded in making a very large improvement to the i-FCIQMC method. Quantum Monte Carlo is nothing but a stochastic implementation of the power method for projecting onto the dominant state of a matrix or integral kernel. Recognizing this, the basic idea of our Semistochastic Quantum Monte Carlo (SQMC) method is identify a small subspace of say $10^3 - 10^6$ important determinants in which the projection is done deterministically. Only transitions for which both the initial and the final state are within the subspace are treated deterministically, the rest are treated stochastically. Since deterministic projection has no statistical error and no sign problem this results in a large gain in efficiency.

It is well known that improving the trial wave functions for calculating the mixed estimator for the energy results in a reduction in the statistical error. Accordingly we have developed a procedure for using multideterminantal trial wave functions (the i-FCIQMC method uses just the Hartree-Fock determinant). The local energies required for calculating the mixed estimators are precomputed and so there is no increase in the computational time during the Monte Carlo part of the run.

The above two improvements have been implemented both for chemical systems and for the Hubbard model. We find that they result in 2-3 orders of magnitude gain in the computational efficiency. Consequently we are able to redo, using SQMC, on a single core calculations that required a sizable parallel computer using the i-FCIQMC method.

We demonstrate the improvements of SQMC relative to a purely stochastic method defined by a deterministic space which includes only the Hartree-Fock determinant. The most dramatic benefit of SQMC is in the efficiency, which is defined to be proportional to the inverse of the time required to obtain the ground state energy to a specified level of uncertainty.

Fig. 1 shows the efficiency gain of SQMC *vs.* the size of the deterministic space for the two-dimensional 8×8 Hubbard model with $U/t = 4$ and 10 electrons. The orders of magnitude increases in efficiency demonstrate not only the benefits of SQMC, but also the benefits that can be achieved by improving the trial wavefunction.

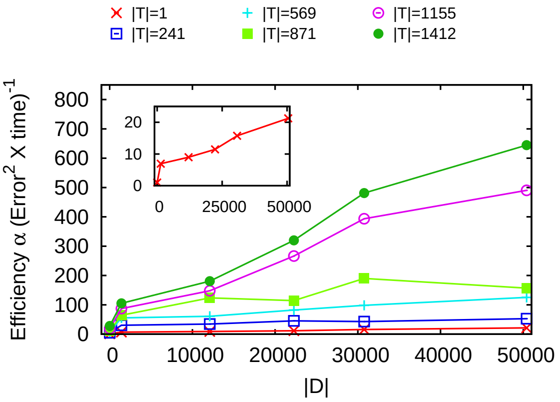

FIG. 1. Efficiency of SQMC *vs.* dimension $|\mathcal{D}|$ of the deterministic space for the two-dimensional 8×8 Hubbard model with $U/t = 4$ and 10 electrons. Results are shown for trial wavefunctions of increasing size. All values are normalized by the efficiency of the stochastic method ($|\mathcal{D}| = 1$) with $|\mathcal{T}| = 1$. The inset shows the $|\mathcal{T}| = 1$ curve on an expanded scale. For this system, $N \approx 10^{12}$.

Fig. 2 shows the efficiency gain of SQMC *vs.* filling fraction for the two-dimensional 8×8 Hubbard model with $U/t = 4$. The efficiency gains increase with increasing filling fraction, demonstrating the potential for SQMC to study strongly correlated systems.

SQMC produces large efficiency gains for chemical systems as well. Fig. 3 shows the efficiency gain of SQMC *vs.* the size of the deterministic space for the carbon dimer with a CC-pVDZ basis set. Like the Hubbard model calculation, there are orders of magnitude increases in efficiency. However, there is a qualitatively different behavior that the largest gains are not obtained in a smooth fashion but rather there is a jump in efficiency for the largest deterministic and trial spaces considered. This happens because the largest space includes some quadruple excitations which are important for correctly describing the ground state wavefunction.

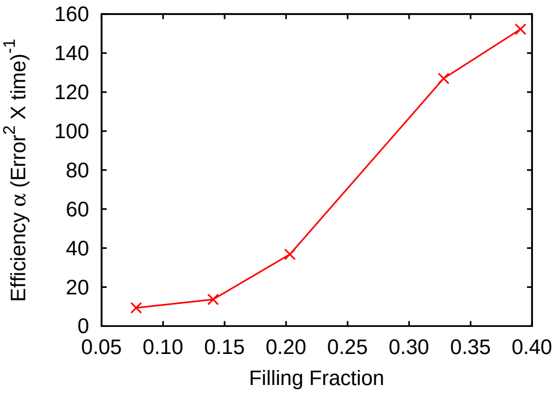

FIG. 2. Ratio of the efficiency of SQMC to the stochastic method at the same filling *vs.* filling fraction for the two-dimensional 8×8 Hubbard model with $U/t = 4$. The trial wavefunction for each of these calculations is the Hartree-Fock determinant. The deterministic space consists of states connected to the Hartree-Fock determinant by one application of the Hamiltonian, resulting in spaces of sizes 1412, 4088, 7424, 14160, 16540, respectively. N ranges from roughly 10^{12} to 10^{35}.

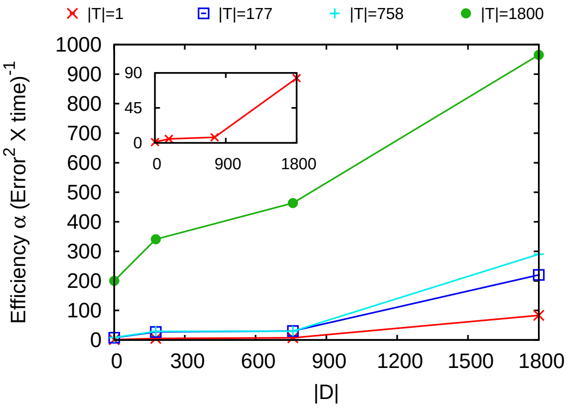

FIG. 3. Efficiency of SQMC *vs.* dimension $|\mathcal{D}|$ of the deterministic space for the carbon dimer with a CC-pVDZ basis. Results are shown for trial wavefunctions of increasing size. All values are normalized by the efficiency of the stochastic method ($|\mathcal{D}| = 1$) with $|\mathcal{T}| = 1$. The inset shows the $|\mathcal{T}| = 1$ curve on an expanded scale. For this system, $N \approx 2 \times 10^7$.

Not only is SQMC much more efficient than the stochastic method, but in some cases, the initiator bias is significantly reduced. Fig. 4 shows the biased estimates of the energy as obtained by both the SQMC and stochastic method *vs.* the average number of occupied determinants for the 8×8 Hubbard model with $U/t = 1$ and 50 electrons. SQMC has essentially no bias. A larger average number of occupied determinants corresponds to using a larger walker population in the calculation. The time required for a calculation is proportional to the walker population.

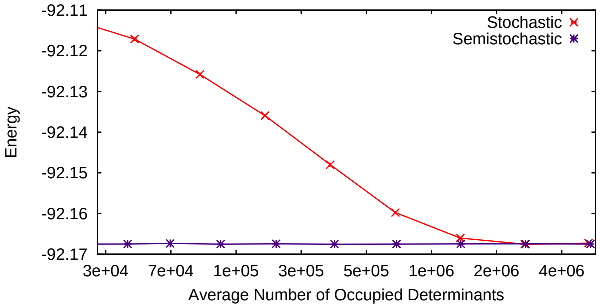

FIG. 4. Energy of SQMC and the stochastic method *vs.* the average number of occupied determinants for the two-dimensional 8×8 Hubbard model with $U/t = 1$ and 50 electrons. The trial wavefunction for each of these calculations is the Hartree-Fock determinant. The deterministic space consists of states connected to the Hartree-Fock determinant by one application of the Hamiltonian, yielding a deterministic space of 16540 determinants. For this system, $N \approx 10^{35}$.

The reduction in initiator bias is not always large. Fig. 5 shows both the SQMC and stochastic method energy *vs.* the average number of occupied determinants for the 8×8 Hubbard model with $U/t = 4$ and 10 electrons. SQMC has a reduced initiator bias for a small, but not for a large number of occupied determinants. However, for this system and all other systems studied SQMC has a smoother bias than the stochastic method.

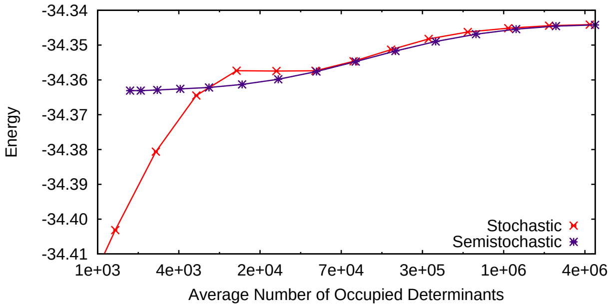

FIG. 5. Energy of SQMC and the stochastic method *vs.* the average number of occupied determinants for the two-dimensional 8×8 Hubbard model with $U/t = 4$ and 10 electrons. The trial wavefunction for each of these calculations is the Hartree-Fock determinant. The deterministic space reference state for each SQMC calculation is the Hartree-Fock determinant, yielding a deterministic space of 1412 determinants. For this system, $N \approx 10^{12}$.

Improving the Basis-Size Error using the F12-Method

The diffusion Monte Carlo (DMC) method has the advantage relative to i-FCIQMC or SQMC that it works directly in an infinite basis. In standard quantum chemistry methods it is becoming standard practice to employ so called F12 methods to enhance the convergence to the infinite basis limit. We have been working with Garnet Chan at Princeton University and Takeshi Yanai at the Institute for Molecular Science in Japan to use F12 methods to improve the basis set convergence of SQMC. We are testing the method on the small but challenging Be_2 dimer, and are in the process of writing a paper [4].

CONCLUSION

The semistochastic power method, a hybrid with deterministic and stochastic components, was introduced for finding the dominant eigenvalue and sampling the corresponding eigenvector of a matrix. We showed that introducing a deterministic component into the stochastic method significantly reduces the statistical noise while it does not compromise the ability of the method to deal with matrices well beyond the size that can be handled by deterministic methods. In particular, matrices ranging in order from 10^9 to 10^{35} were tackled. Besides being more efficient than a purely stochastic approach, the semistochastic method has in some cases the additional benefit of a much reduced initiator bias. The construction of a deterministic space is a vital ingredient of the method. The feasibility depends on the nature of the physics and will vary for different applications.

In addition to these major improvement, we mention two other improvements we have made that are of lesser importance. First, we use walker with real rather than integer weights. This reduces unnecessary fluctuations and enables us to use deterministic projection in the small but important subspace as described above. Second, in SQMC, we employ a graduated initiator rather than the fixed initiator used in i-FCIQMC and this allows us to have a better compromise between having a small systematic bias and a small statistical error.

All of the above mentioned improvements are described in a short paper that is currently under review [5]

[1] George H Booth, Alex J W Thom, and Ali Alavi. Fermion Monte Carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space. *J. Chem. Phys.*, 131:054106, 2009.

[2] Deidre Cleland, George H Booth, and Ali Alavi. Communications: Survival of the fittest: accelerating convergence in full configuration-interaction quantum Monte Carlo. *J. Chem. Phys.*, 132:041103, 2010.

[3] James J. Shepherd, George Booth, Andreas Grneis, and Ali Alavi. Full configuration interaction perspective on the homogeneous electron gas. *Phys. Rev. B*, 85:081103, 2012.

[4] Takeshi Yanai and Sandeep Sharma and A. A. Holmes and Hitesh J. Changlani and F. R. Petruzielo and Garnet Kin-Lic Chan and C. J. Umrigar. Explicitly correlated density matrix renormalization group and full configuration interaction quantum monte carlo through canonical transcorrelation, as applied to the beryllium dimer. in preparation.

[5] F. R. Petruzielo and A. A. Holmes and Hitesh J. Changlani and M. P. Nightingale and C. J. Umrigar. Semistochastic projection. submitted to Rapid Communications.

Dynamics and nonequilibrium effects in higher-order and pump-probe x-ray spectroscopy.
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Project Scope

The research in this project is primarily concerned with the theoretical study of materials research using X-ray techniques. The focus of the materials is on materials with strong electron correlations, in particular, transition-metal and rare-earth compounds. Special emphasis is placed on the development of an understanding of new spectroscopies and the information they can provide on the materials under investigation. For example, the research on resonant inelastic X-ray scattering has provided a more detailed understanding on how valence excitations are created in this second-order process. Recently, the focus of my research has also shifted towards X-ray spectroscopy on systems away from equilibrium, for example, through the excitation of the material with a laser pulse. Intriguing problems in this direction are the observation of the melting of charge, orbital, and magnetic excitation on a short timescale.

Recent Progress

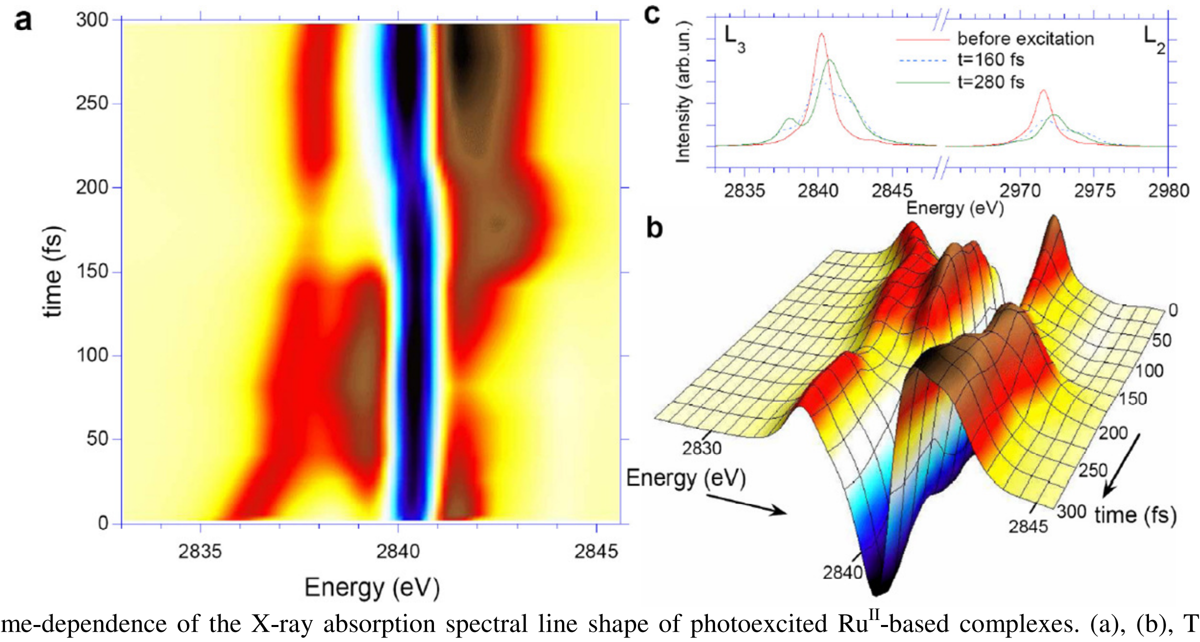
Fast intersystem crossing in transition-metal compounds

Fast intersystem crossing is an intriguing phenomenon that has puzzled many for several decades. In a wide variety of transition-metal complexes, laser excitation creates a photoinduced excited state that decays on the order of tens to hundreds of femtoseconds into a state with often a different spin and a significant change in transition metal-ligand distance. This is generally followed by a cascade of intersystem crossings. Examples are spin crossover phenomena in divalent iron. The iron atom is generally surrounded by an organic material. In the ground state, divalent Fe is in a low-spin state. Illumination by light causes a charge transfer to the ligands, followed by a cascade of intersystem crossings, turning the singlet configuration into a high-spin state. The high-spin state has a temperature-dependent decay time back into the low-spin state that can vary from nanoseconds up to days. Recent ultrafast x-ray spectroscopic measurements have provided more detailed information on the crucial first step that sets up the cascading process showing that the electronic transition occurs on the order of tens of femtoseconds whereas the lattice relaxes on a time scale related to the transition metal-ligand stretch mode. The mechanism behind fast intersystem crossing in transition-metal complexes was shown to be a result of the dephasing of the photoexcited state to the phonon continuum of a different state with a significantly different transition metal-ligand distance. The coupling is a result of the spin-orbit interaction causing a change in the local moment. A recurrence to the initial state is prevented by the damping of the phonon oscillation. The decay time is faster than the oscillation frequency of the transition metal-ligand stretch mode, in agreement with experiment

Additionally, we investigated the cascading decay mechanism for ultrafast intersystem crossing mediated by the spin-orbit coupling in transition-metal complexes. A quantum-mechanical description of the cascading process that occurs after photoexcitation was developed. The conditions for ultrafast cascading are given, which relate the energy difference between the levels in the cascading process to the electron-phonon self energy. These limitations aid in the determination of the cascade path. For divalent Fe spin-crossover complexes, this leads to the conclusion that the ultrafast decay primarily occurs in the manifold of antibonding metal-to-ligand charge-transfer states.

Similar effects provide an explanation for the ultrafast photo-excited electron dynamics in low-spin Ruthenium (II) organic complexes. The experimentally-observed singlet to triplet decay in the metal-to-ligand charge-transfer (MLCT) states contradicts the expectation that the system should oscillate between the singlet and triplet states in the presence of a large spin-orbit coupling and the absence of a significance change in metal-ligand bond length. This dilemma is solved with a novel quantum decay mechanism that causes a singlet to triplet decay in about 300 fs. The decay is mediated by the triplet metal-centered state (MC) state even though there is no direct coupling between the singlet MLCT and triplet MC states. The coupling between the triplet MLCT and triplet MC via excited phonon states leads to a vibrational cooling that allows the local system to dissipate the excess energy. In the relaxed state, the population of the triplet MC state is low and the metal-ligand bond length is almost unchanged with respect to the initial photoexcited state, in agreement with experiment.

These changes also have a large impact on the X-ray spectroscopy. Dynamic X-ray absorption spectra were calculated for the first several hundreds of femtoseconds. Dramatic changes in the spectral line shape are observed that can be directly related to nonequililibrium dynamics, see the Figure below.



Time-dependence of the X-ray absorption spectral line shape of photoexcited Ru^{II}-based complexes. (a), (b), The difference between the nonequilbrium X-ray absorption spectrum at time *t* after the photoexcitation and the spectrum starting from the ground state at the Ru L_3 edge. The same color scheme is used. (c), The XAS spectra at the L_3 edge before and at *t*=160 and 280 fs after the photoexcitation.

Future Plans

With the recent coming on-line of free-electron lasers, such as the LCLS at SLAC, Stanford, we have seen a wealth of new data using pulsed-X-ray sources. After the initial excitation with either a laser or teraherz pulse, ordered system can undergo rapid changes on the order of tens to hundreds of femtoseconds. In transition-metal compounds, this can lead to the quenching of charge, orbital, and spin order. Data obtained using resonant X-ray scattering at the *L*-edges shows the decrease of diffraction peaks corresponding to these various types of order. For the advance of the burgeoning field of fast X-ray science, it is important that a detailed understanding of these phenomena is obtained. In my research in the coming year, I will try to obtain an understanding how a locally created excitation can change the ordered structure. We do this by studying models that include the interactions between the electrons and the lattice.

In addition, we will continue to study spin crossover systems. These systems form nice model systems since they involve changes occurring on a single transition-metal site. After obtaining initial results for ruthenium complexes, it is important to develop a more general framework to study transition-metal complexes away from equilibrium. More understanding needs to be obtained on how the cascading between different levels affects the spectral line shape. For example, the intersystem crossings are often caused by the spin-orbit coupling. Changes in the ground-state expectation value of the coupling between the spin and orbital degrees of freedom have a strong influence on the branching ratios (in transition-metal systems, the intensity ratio between the L_3 and L_2 edges).

Publications

Pressure-tuning of spin-orbit coupled ground state in Sr_2IrO_4
D. Haskel, G. Fabbris, M. Zhernenkov, K. Panpan, C. Jin, G. Cao, and M. van Veenendaal, accepted for publication in Phys. Rev. Lett.

Spin-moment formation and reduced orbital polarization in $LaNiO_3$/ $LaAlO_3$ superlattices: LDA+*U* study
M. J. Han and M. van Veenendaal, Phys. Rev. B. **85**, 195102 (2012).

Magnetic excitation spectra of $Sr_2Ir_2O_4$ probed by resonant inelastic x-ray scattering: establishing links ot cuprate superconductors
J. H. Kim, D. Casa, M. H. Upton, T. Gog, Y.-J. Kim, J. F. Mitchell, M. van Veenendaal, M. Daghofer, J. van den Brink, G. Khaliullin, and B. J. Kim, Phys. Rev. Lett. **108**, 177003 (2012).

Electronic structure and orbital polarization of $LaNiO_3$ with a reduced coordination and under strain: A first-principles study
M. J. Han and M. van Veenendaal, Phys. Rev. B **84**, 125137 (2011).

Stability of ferromagnetic ground state against large compressive stress in magnetodielectric oxide La_2MnNiO_6
D. Haskel, G. Fabbris, N. M. Souza-Neto, M. van Veenendaal, G. Shen, A. E. Smith, and M. A. Subramanian, Phys. Rev. B Rapid Commun. **84**, 100403 (2011).

Determining the electron-phonon coupling strength in correlated electron systems from resonant inelastic x-ray scattering
L. J. P. Ament, M. van Veenendaal, and J. van den Brink, Europhys Lett. **95**, 27008 (2011).

Resonant inelastic X-ray scattering studies of valence excitations

L. Ament, M. van Veenendaal, T. P. Devereaux, J. Hill, and J. van den Brink, Rev. Mod. Phys. **83**, 705 (2011).

3*j* Symbols: To normalize or not to normalize?

M. van Veenendaal, Eur. J. Phys. **32**, 947 (2011).

Quantum confinement of Mott electrons in ultrathin $LaNiO_3$/$LaAlO_3$ superlattice

J. Liu, S. Okamoto, M. van Veenendaal, M. Kareev, B. Gray, P. Ryan, J. W. Freeland, and J. Chakhalian, Phys. Rev. Rapid Commun. **83**, 161102 (2011) (Editor's Selection).

Observation of *dd* excitations via 4*p*-3*d* Coulomb scattering in transition-metal *K*-edge resonant inelastic x-ray scattering

M. van Veenendaal, X. Liu, M. H. Carpenter, and S. P. Cramer, Phys. Rev. B. **83**, 045101 (2011).

Orbital magnetism and spin-orbit effects in the electronic structure of $BaIrO_3$

M. A. Laguna-Marco, D. Haskel, N. Souza-Neto, V. V. Krishnamurthy, S. Chikara, G. Cao, and M. van Veenendaal, Phys. Rev. Lett. **105**, 216407 (2010).

Unexpected Resonant Effect in Phonon Spectra: Electron-Phonon Coupling in Cupric Oxide

H. Yavas, M. van Veenendaal, J. van den Brink, L. J. P. Ament, A. Alatas, B. M. Leu, M.-O. Apostu, Nadia Wizent, Gunter Behr, W. Sturhahn, E. E. Alp, Harald Sinn, J. Phys.: Cond. Mat. **22**, 485601 (2010).

Theoretical design of high-brightness photocathodes based on ultra-thin surface layers on metals and on nanostructures

K. Németh, K. C. Harkay, M. van Veenendaal, L. Spentzouris, M. White, K. Attenkofer, and G. Srajer, AIP Conf. Proc. **1299**, 522 (2010).

Ultrafast cascading theory in intersystem crossings in transition-metal complexes

J. Chang, A. J. Fedro, and M. van Veenendaal, Phys. Rev B. **82**, 075124 (2010).

The choice of internal coordinates in complex chemical systems

K. Németh, M. Challacombe, and M. van Veenendaal, J. Computational Chem. **31**, 2078 (2010).

Fast intersystem crossing in transition-metal compounds

M. van Veenendaal, J. Chang, and A. J. Fedro, Phys. Rev. Lett. **104**, 067401 (2010).

High brightness photocathodes through ultra-thin surface layers on metals

K. Németh, K. C. Harkay, M. van Veenendaal, L. Spentzouris, M. White, K. Attenkofer, and G. Srajer, Phys. Rev. Lett. **104**, 046801 (2010).

Pressure-induced magnetic transition in manganite ($La_{0.75}$ $Ca_{0.25}MnO_3$)

Y. Ding, D. Haskel, Y.-C. Tseng, E. Kaneshita, M. van Veenendaal, J. F. Mitchell, S. V. Sinogeigin, V. Prakapenka, and H. Mao, Phys. Rev. Lett. **102**, 237201 (2009).

Non-zero orbital moment in high coercivity ε- Fe_2O_3 and low temperature collapse of the magnetocrystalline anisotropy

Y. C. Tseng, N. M. Souza-Neto, D. Haskel, M. Gich, C. Frontera, A. Roig, M. van Veenendaal, J. Nogués, Phys. Rev. B. **79**, 094404 (2009).

Thermally or magnetically induced polarization reversal in the multiferroic $CoCr_2O_4$

Y. J. Choi, J. Okamoto, D. J. Huang, K. S. Chao, H. J. Lin, C. T. Chen, M. van Veenendaal, T. A. Kaplan, and S.-W. Cheong, Phys. Rev. Lett. **102**, 067601 (2009).

Dynamics and spectral weights of shake-up valence excitations in transition metal *K*-edge resonant inelastic x-ray scattering

K. H. Ahn, A.J. Fedro, and Michel van Veenendaal, Phys. Rev. B. **79**, 045103 (2009).

Computational studies of hydrogen interactions with storage materials

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Project Scope

We use state-of-the-art electronic structure calculations to study the kinetics of hydrogen uptake and release in high-capacity hydrogen storage materials. Our goals are to provide interpretations for experimental observations and to contribute to the design of better storage materials. Mass transport requires formation and migration of point defects in the host material, which we study by first-principles calculations based on density functional theory. For greater accuracy, we have used a hybrid functional approach, which provides improved descriptions of the electronic structure. Our approach takes into account that defects and impurities in non-metallic systems can occur in charge states other than the neutral state; this important aspect of the problem had previously been overlooked. However, our investigations have shown that this has important consequences for kinetics, and can explain phenomena such as the increase in release rates upon addition of dopants. We have applied the methodology to a variety of materials, including alanates, amides, and borohydrides. We have also applied a multiscale approach, combining results from density functional theory with Kinetic Monte Carlo simulations to provide results for dehydrogenation curves.

Recent Progress

Decomposition of $LiNH_2$: surface-specific effects and particle-size dependence

Lithium amide ($LiNH_2$) is promising for reversible hydrogen storage, yet the atomistic mechanisms behind the decomposition and dehydrogenation processes are still unknown. The activation energy for decomposition strongly varies with ball milling, suggesting a dependence of the thermodynamics and kinetics of the decomposition on the particle size. The question we addressed is how the change in surface-to-volume ratio affects the reaction mechanisms.

The first step was to perform first-principles calculations for all relevant native point defects and defect complexes. We found that both $LiNH_2$ and Li_2NH are prone to Frenkel disorder on the Li sublattice. Lithium interstitials and vacancies have low formation energies and are highly mobile, and therefore play an important role in mass transport and ionic conduction. Hydrogen interstitials and vacancies, on the other hand, are responsible for forming and breaking N-H bonds, which is essential in the Li amide/imide decomposition reaction

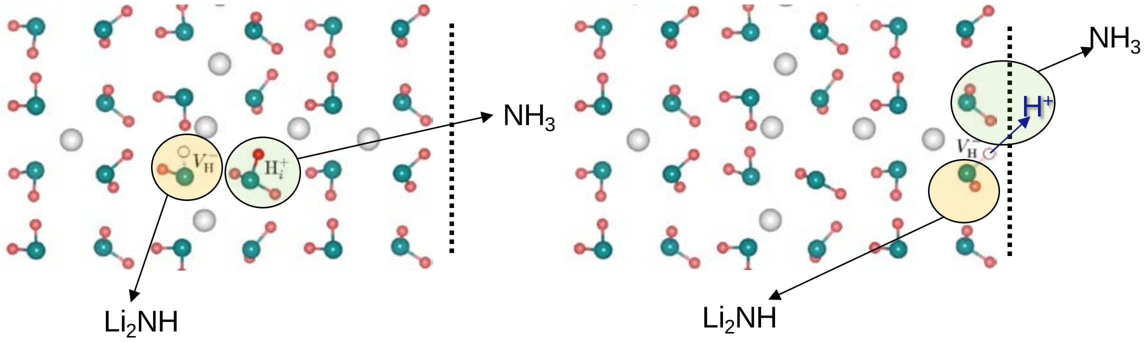

Figure 1: Mechanisms for decomposition of $LiNH_2$: on the left, involving the formation of native defects in the *interior* of the material, on the right, at the *surface*.

Based on the structure, energetics, and migration of hydrogen-, lithium-, and nitrogen-related defects, we have proposed [7,12] that $LiNH_2$ decomposes into Li_2NH and NH_3 according to two competing mechanisms with different activation energies (see Figure 1): one mechanism involves the formation of native defects in the interior of the material, the other at the surface. As a result, the prevailing mechanism and hence the effective activation energy for decomposition depend on the surface-to-volume ratio or the specific surface area, which changes with particle size during ball milling.

We feel that this result has broader repercussions for kinetics of reactions in bulk *versus* nanoscale systems in general, i.e., not just in hydrogen storage materials. Differences have often been observed but a rigorous explanation for the effects has been lacking. Our model that attributes the differences to the formation of native defects (which are always necessary for diffusion and reactions) in the bulk as opposed to on the surface provides a general framework for explaining such differences.

Decomposition of AlH_3 via a vacancy clustering mechanism

Aluminum hydride (AlH_3) has emerged as a prime candidate for hydrogen storage applications. Its further development as a hydrogen storage system will depend on a systematic understanding of hydrogen uptake and release. Though thermodynamically unstable at room temperature, AlH_3 does not decompose and remains stable on a timescale of years. Above 150°C it rapidly decomposes into Al and H_2. Our goal was to elucidate the microscopic origins of this metastability, which has been controversially debated amongst experimental groups, as well as clarify the reaction mechanisms.

We used of state-of-the-art first-principles calculations, based on a hybrid functional to calculate the formation energies and migration barriers of relevant point defects in AlH_3. This enabled us to calculate diffusion activation energies, and to propose an explanation for the kinetic inhibition effect, namely that that vacancy-mediated mass transport across the hydride bulk is the kinetic bottleneck, preventing the dehydrogenation of AlH_3 at room temperature. The decomposition of AlH_3 thus initiates at localized sites throughout the hydride bulk material, the growth of which eventually drives the dehydrogenation reaction, in contrast to the nucleation at the surface that had been previously proposed. While our first-principles results strongly points towards a diffusion-limited mechanism, the shape of the experimental reaction curves seemed to contradict such a mechanism: the observed S-shaped onset of the curves is indeed traditionally interpreted as an indication that diffusion can be ruled out as a rate-limiting factor.

We therefore employed a multiscale modeling approach to examine the microscopic mechanisms that drive the nucleation and growth of dehydrogenation sites within the AlH_3 bulk by combining first-principles hybrid functional results for formation and clustering of vacancies with Kinetic Monte Carlo simulations of the nucleation and growth of the resulting Al phase (Figure 2) [6,8,10]. The resulting dehydrogenation curves were found to be in very good agreement with experimental data, establishing the validity and reliability of the kinetic model.

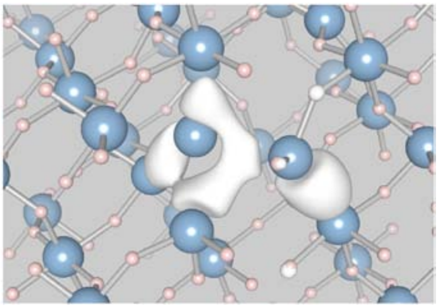

Figure 2: Structure of a cluster with 10 vacancies in AlH_3. The white isosurface denotes the partial charge density distribution corresponding to the defect states in the band gap.

Equally significantly, our study also allows us to make a more general point that transcends the specific case of AlH_3. Solid-state chemists frequently classify reaction kinetics based on the shape of reaction curves, using rules proposed in the 1930s. E.g., for diffusion-controlled processes a “square-root-like” onset of the curves is expected, in contrast to an “S-shape-like” onset for phase-boundary controlled processes. In the case of dehydrogenation of AlH_3, an S-shape-like onset is observed, and on this basis it was concluded that the kinetics must be phase-boundary controlled. Our study, however, clearly demonstrates that the self-diffusion of point defects is the rate-limiting step–and still the reaction curves have an S-shape (see Figure 3)! The present example illustrates that care should be exercised in the interpretation of reaction mechanisms based on the shape of reaction curves.

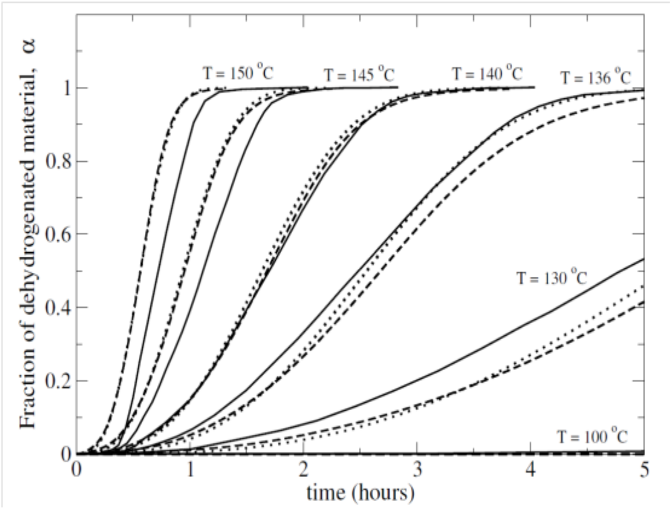

Figure 3. Dehydrogenation curves for AlH_3. The fraction of decomposed material, α, is plotted as a function of time for various temperatures. Solid lines show experimental results [P. J. Herley and O. Christofferson, J. Phys. Chem. **85**, 1887 (1981)]; dashed lines denote the results of our kinetic model; and the dotted lines denote our results based on Kinetic Monte Carlo simulations.

Future Plans

Decomposition mechanisms of other complex hydrides

In the course of our project we have carried out calculations on a number of complex hydrides, with the aim of determining rate-limiting steps in the dehydrogenation process and the mechanism by which additives enhance kinetics. Our proposal that transition metal impurities can act beneficially by shifting the Fermi level and thus modifying formation energies of rate-limiting point defects has explained a number of experimental observations [1,3,5]. In addition to calculations for the prototype complex hydride $NaAlH_4$ and the $LiNH_2/Li_2NH$ system mentioned above, we have also investigated $LiAlH_4$ [9] and $LiBH_4$ [11]. For the latter, and also for $Li_4BN_3H_{10}$, we are performing additional calculations to investigate the effects of dopant impurities.

In the context of $LiNH_2/Li_2NH$, the role of LiH has emerged as a topic of interest. Preliminary investigations have already revealed intriguing behavior of the hydrogen vacancy. We are also investigating Na_3AlH_6 and Li_3AlH_6, not only because of the role of these compounds in the decomposition of $NaAlH_4$ and $LiAlH_4$, but also because these materials have been found to have very high ionic conductivities.

Role of transition metal doping and alloying in MgH_2

These studies build on our previous investigations of hydrogen interactions with Mg metal [2] and point-defect formation in MgH_2 [4]. Magnesium is a good candidate for hydrogen storage, because of its gravimetric hydrogen density (7.6 wt. % in MgH_2), non-toxicity, and low cost. However, pure Mg is not directly applicable because of the poor kinetics of dehydrogenation and due to its unfavorable thermodynamics–the decomposition temperature of MgH_2 is higher than 300° C. The addition of transition metals (TMs) has been observed to significantly improve the kinetics and to lower the decomposition temperature. Various mechanisms have been invoked to explain these improvements, including catalytic surface effects, substitution of the TMs in the Mg matrix, and micro-structural modifications. .

We are investigating the two most prominent and effective TM additives, Ni and Fe, by calculating formation energies and migration barriers of point defects in the MgH_2-TM hydride and in a Mg matrix doped with Fe or Ni impurities in the dilute limit. Our goal is to quantify the impact of the transition metals: to what extent can the effect of the TM (as observed in experiments) be explained by electronic doping?

Role of hydrogen-related Frenkel pairs for the dehydrogenation kinetics

Our studies to date have highlighted the important role played by Frenkel pairs (interstitial-vacancy pairs) in many hydrides, either directly in mass transport or as a means of mediating charge neutrality. We are pursuing a systematic study of Frenkel pairs in a wide range of materials, including $LiBH_4$, $Li_4BN_3H_{10}$, $LiNH_2$, Li_2NH, MgH_2, Na_3AlH_6, $LiAlH_4$, and Li_3AlH_6, in addition to $NaAlH_4$.

List of publications

1. "First-principles study of the formation and migration of native defects in $NaAlH_4$", G. B. Wilson-Short, A. Janotti, K. Hoang, A. Peles, and C. G. Van de Walle, Phys. Rev. B **80**, 224102 (2009).
2. "Interactions between hydrogen impurities and vacancies in Mg and Al: A comparative analysis based on density functional theory", L. Ismer, M. S. Park, A, Janotti, and C. G. Van de Walle, Phys. Rev. B **80**, 184110 (2009).
3. "First-principles investigations of F and Cl impurities in $NaAlH_4$", G. B. Wilson-Short, A. Janotti, A. Peles, and C. G. Van de Walle, J. Alloys Compd. **484**, 347 (2009).
4. "Formation and migration of charged native point defects in MgH_2: First-principles calculations", M. S. Park, A. Janotti, and C. G. Van de Walle, Phys. Rev. B **80**, 064102 (2009).
5. "Atomic and electronic structure of hydrogen-related centers in hydrogen storage materials", C. G. Van de Walle, A. Peles, A. Janotti, and G. B. Wilson-Short, Physica B **404**, 793 (2009).
6. "Point-defect-mediated dehydrogenation of AlH_3", L. Ismer, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **97**, 201902 (2010).
7. "The particle-size dependence of the activation energy for decomposition of lithium amide", K. Hoang, A. Janotti, and C. G. Van de Walle, Angew. Chem. Int. Ed. **123**, 10352 (2011).
8. "Stability and mobility of native point defects in AlH_3", L. Ismer, A. Janotti, and C. G. Van de Walle, J. Alloys Compd. **509S**, S658 (2011).
9. "Decomposition mechanism and the effects of metal additives on the kinetics of lithium alanate", K. Hoang, A. Janotti, and C. G. Van de Walle, Phys. Chem. Chem. Phys. **14**, 2840 (2012).
10. "Dehydrogenation of AlH_3 via the vacancy clustering mechanism", L. Ismer, A. Janotti, and C. G. Van de Walle, J. Phys. Chem. C. **116**, 12995 (2012).
11. "Mechanism for the decomposition of lithium borohydride", K. Hoang and C. G. Van de Walle, Int. J. Hydrogen Energy **37,** 5825 (2012).
12. "Mechanisms for the decomposition and dehydrogenation of Li amide/imide", K. Hoang, A. Janotti, and C. G. Van de Walle, Phys. Rev. B **85**, 064115 (2012).

Thermomechanical Properties of Thin Films and Membranes of Functionalized Nanocrystals and Nanowire Arrays: Multimillion-to-Billion Atom Simulations

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Project Scope

This project focuses on thermomechanical properties of a new class of thin films and membranes consisting of functionalized nanocrystals and nanowires. We perform multimillion-to-billion atom reactive molecular dynamics (RMD) simulations based on quantum mechanically informed force fields to investigate interfacial structure and thermomechanical properties including adhesion and delamination, viscoelastic/viscoplastic behavior, and fracture in hybrid systems consisting of thin films and membranes embedded with nanocrystals and core/shell nanowires that are functionalized with organic molecules. Our recent quantum molecular dynamics (QMD) simulations have revealed atomistic mechanisms of rapid hydrogen production by aluminum nanoclusters in liquid water. We are currently performing RMD simulations to identify atomistic mechanisms underlying the remarkable ability of silicon carbide nanoparticles to heal surface cracks, which could help sustainable deployment of high-temperature materials for energy applications such as power generation systems.

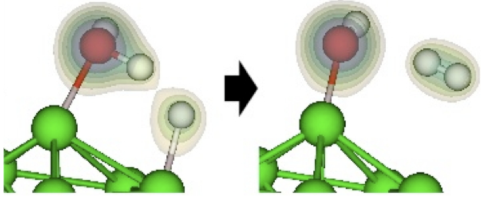

Fig. 1: Initial (left) and final (right) configurations of H_2 production. White, red and green spheres are H, O and Al atoms, respectively.

Recent Progress

Experimental background: Metal particles react with water to produce hydrogen gas. This exothermic reaction, followed by solar powered reduction of the metal-oxide product to regenerate metal fuel, could provide a renewable energy cycle. The problem is that conventional metal-water reaction kinetics is too slow to make it commercially viable [J. Petrovic and G. Thomas, *Reaction of Aluminum with Water to Produce Hydrogen* (U.S. Department of Energy, '08)]. A possible solution to this problem may be provided by nanotechnology, since chemical reactivity at the nanoscale differs drastically from its macroscopic counterpart. A remarkable example is size-selective reactivity of aluminum (Al) clusters with water, where an anion of Al cluster, Al^-_n (*e.g.*, $n = 12$ or 17), reacts strongly with water molecules in gas phase [P. J. Roach, W. H. Woodward, A. W. Castleman, A. C. Reber, and S. N. Khanna, *Science* **323**, 492 ('09)]. The enhanced reactivity has been attributed to the dissociative chemisorption of water at two specific surface sites that respectively act as Lewis acid and Lewis base where OH and H preferentially bind. In the proposed gas-phase reaction mechanism with the adsorption of multiple water molecules onto an Al_{17} cluster, the energy barrier for the production of H_2 from two H atoms generated on the cluster surface has been estimated to be about 1 eV.

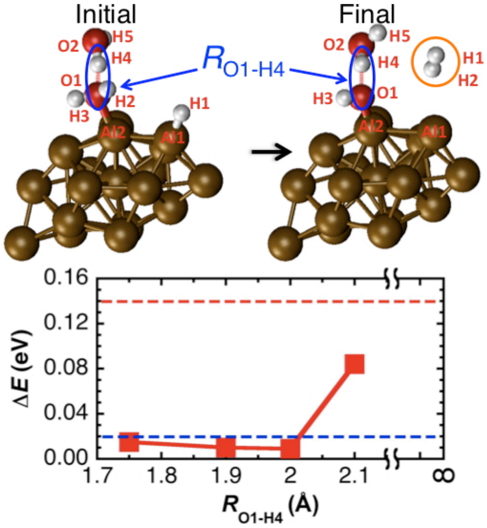

Fig. 2: (Top) Initial and final states for H_2 production involving Al_{18} in the presence of a surrounding water molecule H4-O2-H5. (Bottom) The reaction barrier for H_2 production for different length R_{H4-O1}. The red dashed line is the asymptotic barrier of 0.14 eV for $r_{H4-O1} \rightarrow \infty$. The blue dashed line is at 0.02 eV.

However, the reactivity of these Al "superatoms" with bulk water remains unknown.

Quantum dynamics simulations: We have carried out QMD simulations to investigate atomistic mechanisms of molecular hydrogen production by Al_n (n = 12 or 17) in liquid water [1, 4]. We have found a new mechanism with low activation barrier, in which a hydrogen molecule (H_2) is produced from a water molecule adsorbed at a Lewis acid site and hydrogen adsorbed at a Lewis base site on the cluster surface (Fig. 1). This reaction is assisted by rapid proton transport in water via a chain of hydrogen-bond (H-bond) switching events similar to the Grotthuss mechanism, which supplies hydrogen atoms at Lewis-base sites, and converts hydroxide ions back to water molecules at Lewis-acid sites. The activation free energy of the H_2-production reaction at a temperature of 300 K has been estimated to be 0.08 eV using thermodynamic integration. The corresponding reaction is 10^{11} s^{-1} according to the transition state theory.

More recently, we have performed QMD simulations of Al_n (n = 16-18) in liquid water [5] in order to investigate: (1) the role of a solvation shell formed by non-reacting H-bonds surrounding the H-bond chain; and (2) the high size-selectivity observed in gas-phase Al_n-water reaction persists in liquid phase.

Lowering of activation barrier by solvation shells: The simulation results show that the solvation shell plays a crucial role in facilitating proton transfer and hence H_2 production. Namely, it greatly modifies the energy barrier, generally to much lower values. Figure 2 shows the activation barrier for one of the H_2-production reactions in Al_{18} in the presence of a surrounding H_2O molecule (denoted H4-O2-H5) that is not directly involved in the reaction, $\text{Al-OH}_2 + \text{Al-H} \rightarrow \text{Al-OH} + \text{Al} + H_2$. The energy barrier is reduced to below 0.02 eV (the blue dashed line) when $R_{\text{O1-H4}}$ is 1.75~2.0 Å (O1 is the oxygen atom involved in the reaction), which is much lower than that in the absence of the solvation shell (*i.e.* $R_{\text{O1-H4}} \rightarrow \infty$).

No size selectivity: We have also found that the H_2 production by Al_n in liquid water does not depend strongly on the cluster size, in contrast to the existence of magic numbers (*e.g.* n = 17) in gas-phase reaction [P. J. Roach, *et al.* ('09)]. In our QMD simulations, three H_2 molecules are produced each in the Al_{16} and Al_{17} systems, while six H_2 molecules are produced in the Al_{18} system, within 20 ps (Fig. 3).

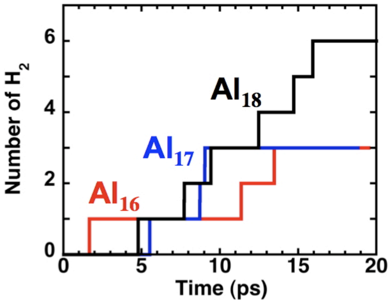

Fig. 3: The number of H_2 molecules as a function of time *t*.

Work in Progress and Future Plans: Self-healing Ceramic Composites

We are performing and will continue to perform multibillion-atom molecular dynamics (MD) simulations and multimillion-to-billion atom RMD simulations of nanostructured materials under extreme environments to identify atomistic mechanisms of self-healing.

Experimental background: Nanoparticles and nanowires exhibit thermo-mechanical properties that are distinct from their bulk properties. A notable example is the recent discovery of ductility in nanowires made of nominally brittle materials below a critical diameter for which our recent MD simulations suggest an essential role of surface relaxation and the resulting 'intrinsic' core/shell structure [9]. Such nanoductility [3, 9] (see also our previous billion-atom MD simulation in Y. Chen, *et al.*, *Phys. Rev. Lett.* **99**, 155506 ('07)) is expected to play an essential role in the recently demonstrated self-healing of cracks in alumina (Al_2O_3)/silicon carbide (SiC) matrix-nanoparticle composites at the service temperatures expected in their applications [W. Nakao and S. Abe, *Smart Mater. Struct.* **21**, 025002 ('12)] (Fig. 4). Near the cracked region, SiC nanoparticles get oxidized in high-temperature oxygen environment, resulting in the formation of silica (SiO_2) glass. Silica flows into the damage zone, healing the crack. Thermo-mechanical behavior of the matrix-nanoparticle composite is thus recovered. Experiments show that smaller SiC nanoparticles oxidize at lower temperatures, and consequently the temperature to recover the strength of a cracked specimen is lowered from 1300 to 950 °C as the SiC particle size is reduced from 270 to 30 nm. Here, the use of nanoparticles to lower the strength-recovery temperature is crucial for the self-healing to occur during service.

Atomistic mechanisms of self-healing—reactive molecular dynamics simulations: We will perform multibillion atom MD simulations combined with multimillion-to-billion atom RMD simulations to study self-healing of cracks in Al_2O_3/SiC matrix-nanoparticle composites. We will study: (1) the interaction of cracks with nanoparticles and grain boundaries (GBs) to determine crack paths; and (2) nanoparticle size- and temperature-dependent oxidation, oxide flow, and self-healing behaviors. The goal is to provide atomistic understanding to guide the optimal design of nanoparticle size and distribution for self-healing of structural ceramics in energy applications at their high service temperatures.

Currently, we are performing 10^8-atom MD simulations to study fracture of Al_2O_3 embedded with 18 volume % of SiC nanoparticles under uniaxial tension (Fig. 5). We use an environment-dependent interpolation scheme to combine the interatomic potentials developed by our group for SiC, SiO_2 and Al_2O_3. Calculated fracture energies of SiC and Al_2O_3 agree reasonably with density functional theory (DFT) results, and we are validating the interpolation scheme against DFT calculations of SiC/Al_2O_3 interfaces.

To perform larger MD simulations of realistic nanostructures, we have recently benchmarked 10^{12}-atom MD simulation on the 163,840-core IBM BlueGene/P computer at the Argonne Leadership Computing Facility (ALCF), and are discussing with the ALCF Science Director, Paul Messina, to perform multibillion-atom production runs for long trajectories on the new 786,432-core BlueGene/Q at Argonne.

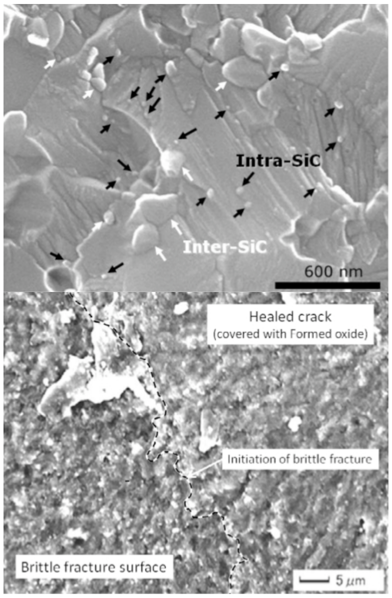

Fig. 4: (Top) Nanostructures of Al_2O_3-SiC composite. (Bottom) Scanning electron microscope image of a healed crack in a specimen heat-treated at 1000 °C. [Taken from W. Nakao and S. Abe, *Smart Mater. Struct.* **21**, 025002 ('12)].

We will also investigate the validity of an emerging concept in the engineering of material interfaces called complexions [Baram, *et al.*, *Science* **332**, 206 ('11)]. Recent high-resolution transmission electron microscopy experiments have identified the existence of nanofilm complexions in high-temperature ceramic interfaces. Theoretical calculations and experiments suggest the existence of five additional interfacial complexions: Pure (no layer between interfaces), monolayer, bilayer, trilayer, and wetting films. Some of these GB complexions have been observed and well characterized in a comprehensive experimental study of Al_2O_3. We will investigate the possible existence of GB complexions in Al_2O_3 and Al_2O_3/SiC interfaces and their role in determining crack paths.

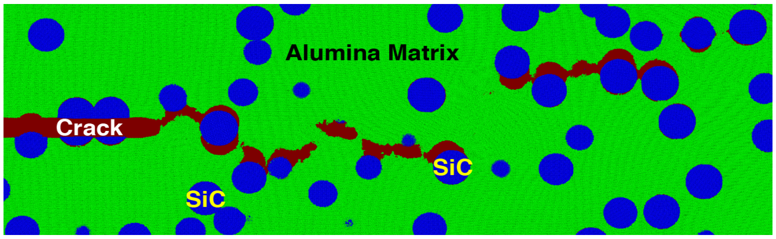

Fig. 5: MD simulation of fracture in ceramic nanocomposite **-** Al_2O_3 embedded with SiC nanoparticles.

In addition, we will perform multimillion-to-billion atom RMD simulations to study high-temperature oxidation of SiC nanoparticles and the flow of the resulting SiO_2 product to fill cracks in Al_2O_3. We will use recently developed reactive force fields (ReaxFF) for the oxidation of SiC by O_2 and H_2O [Newsome, *et al.*, *J. Phys. Chem. C.*, accepted ('12)] along with ReaxFF for Al/O systems. The goal is to identify

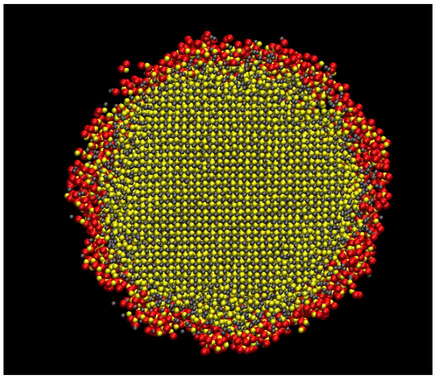

Fig. 6: RMD simulation of the oxidation of a SiC nanoparticle in oxygen environment. Yellow, gray, and red spheres represent Si, C and O atoms, respectively.

atomistic mechanisms underlying the observed reduction of strength-recovery temperatures for smaller SiC nanoparticles, which may include the reduced oxidation temperature of SiC nanoparticles and the enhanced flow of silica. We will also investigate the potential role of water moisture, which could essentially modify the self-healing behavior. We are currently performing RMD simulation of oxidation of a SiC nanoparticle in oxygen environment (Fig. 6).

Hybrid simulations—reactive molecular dynamics and dissipative particle dynamics: We will use the dissipative particle dynamics (DPD) technique for mesoscopic simulations to study thermomechanical properties self-healing nanocomposites, in which particles correspond to coarse-grained entities representing a collection of atoms. We will develop an automated model-transitioning scheme to embed RMD near crack surfaces inside DPD simulation. We have considerable experience in a hybrid RMD and finite-element approach that seamlessly couples atomistic and continuum descriptions [E. Lidorikis, M. E. Bachlechner, R. K. Kalia, A. Nakano, P. Vashishta, G. Z. Voyiadjis, *Phys. Rev. Lett*. **87**, 086104 ('01)].

Dealing with big data—computation of correlation functions using compressed sensing: We will use compressed sensing (CS) to handle large data from petascale simulations of self-healing nanomaterial systems. CS is revolutionizing a wide variety of engineering and medical applications. In their seminal papers, Candés and collaborators have shown that the limitation imposed by Shannon's theorem for sampling of a signal could be overcome if the signal is sparse and measured incoherently. We will use CS in petascale materials simulations to compute on-the-fly structural and dynamic correlations from atomic trajectories to reduce the data size. Each 2 billion-atom MD simulation for 10^5 steps will produce 0.5 KB/atom × 2 billion atoms × 10^5 steps = 100 petabytes of data if all the quantities are sampled. We will use CS to calculate stresses and correlation functions on-the-fly and thus save far fewer atomic positions and velocities for post simulation data analytics.

Experimental validation at DOE facilities: MD and RMD simulation results on structural relaxation in ps-ns time scales will be validated against time-resolved X-ray scattering and pump-probe experiments at the Advanced Photon Source at Argonne National Laboratory and the X-ray free electron laser at the Linac Coherent Light Source at Stanford.

Publications Since 2010

1. "Molecular dynamics simulations of rapid hydrogen production from water using aluminum clusters as catalyzers," F. Shimojo, S. Ohmura, R. Kalia, A. Nakano, and P. Vashishta, *Phys. Rev. Lett.* **104**, 126102 ('10).
2. "Structure and dynamics of shock-induced nanobubble collapse in water," M. Vedadi, A. Choubey, K. Nomura, R. K. Kalia, A. Nakano, and P. Vashishta, *Physical Review Letters* **105**, 014503 ('10).
3. "Nanoductility induced brittle fracture in shocked high performance ceramics," P. S. Branicio, R. K. Kalia, A. Nakano, and P. Vashishta, *Applied Physics Letters* **97**, 111903: 1-3 ('10).
4. "Reaction of aluminum clusters with water," S. Ohmura, F. Shimojo, R. K. Kalia, M. Kunaseth, A. Nakano, and P. Vashishta, *Journal of Chemical Physics* **134**, 244702 ('11).
5. "Effects of solvation shells and cluster size on the reaction of aluminum clusters with water," W. Mou, S. Ohmura, A. Hemeryck, F. Shimojo, R. K. Kalia, A. Nakano, and P. Vashishta, *AIP Advances* **1**, 042149 ('11)
6. "Interaction potential for aluminum nitride: a molecular dynamics study of mechanical and thermal properties of crystalline and amorphous aluminum nitride," P. Vashishta, R. K. Kalia, A. Nakano, and J. P. Rino, *Journal of Applied Physics* **109**, 033514 ('11)
7. "Sulfur-impurity induced amorphization of nickel," Z. Yuan, H.-P. Chen, W. Wang, K. Nomura, R. K. Kalia, A. Nakano, and P. Vashishta, *Journal of Applied Physics* **110**, 063501 ('11)
8. "Molecular control of photoexcited charge transfer and recombination at a quaterthiophene/zinc oxide interface," W. Mou, S. Ohmura, F. Shimojo, and A. Nakano, *Applied Physics Letters* **100**, 203306 ('12).
9. "Core/shell structural transformation and brittle-to-ductile transition in nanowires," *Applied Physics Letters* **100**, 153116 ('12).
10. "Ion dynamics at porous alumina surfaces," S. Hattori, R. K. Kalia, A. Nakano, K. Nomura, and P. Vashishta, *Applied Physics Le*tters, in press.
11. "Large nonadiabatic quantum molecular dynamics simulations on parallel computers," F. Shimojo, S. Ohmura, W. Mou, R. K. Kalia, A. Nakano, and P. Vashishta, *Computer Physics Communications*, in press.

Time-dependent current-density-functional theory of charge, energy and spin transport and dynamics in nanoscale systems

GRANT # DE-FG02-05ER46203

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Project scope

The focus of this research program is on developing time-dependent density functional methods for the calculation of non-equilibrium phenomena of the transport type (finite wavelength, low frequency) and of the dynamical type (long wavelength, high frequency). One such method is the time-dependent current density functional theory, in which the evolution of the physical system is mimicked in a fictitious non-interacting system subjected to an effective one-particle potential, which we approximate as a function of the equilibrium density and non-equilibrium current density. A second approach is the quantum continuum mechanics -- an orbital-free method in which the quantum stress tensor is expressed as a functional of the nonequilibrium current density, leading to a closed equation of motion for the latter. In addition, we plan to extend these approaches to systems in magnetic field, thermal currents, and spins. Part of this work, e.g. the work on dynamical corrections to the conductance of nanojunctions, is done in collaboration with Max Di Ventra at UCSD. In the following I briefly describe the work we have recently done on quantum continuum mechanics for systems in magnetic field, and then I concentrate on the success we have had in predicting the optical spectra of semiconductors by combining the approximation known as meta-GGA with the time-dependent density functional theory. I will argue that this success points towards the exciting possibility of including the energy density and the corresponding energy current as basic variables in time-dependent DFT and in quantum continuum mechanics.

Recent progress

1. Quantum continuum mechanics in magnetic fields

The fourth-order differential equation for the current density that we derived in Ref. 5 by making a high-frequency (elastic, or "antiadiabatic") approximation for the quantum stress tensor leads to a simplified excitation spectrum in which groups of excitations are merged together, while the integrated spectral strength is preserved. The same approximation has recently proved useful in speeding up the evaluation of the density-response function for a homogeneous non-interacting system (the bottleneck for calculations of correlation energy and van der Waals forces within the random phase approximation (RPA) [Gould and Dobson, Phys. Rev. B **84**, 241108 (2011)]. These early successes encourage us to pursue this direction of research. Recent Raman scattering experiments on artificial nanostructures (arrays of quantum dots in a magnetic field) further motivate us to extend the theory to include magnetic field. In these experiments, new and unexpected collective modes are discovered, which we think could be effectively handled by quantum continuum mechanics (QMC) (See Fig. 1 and its caption).

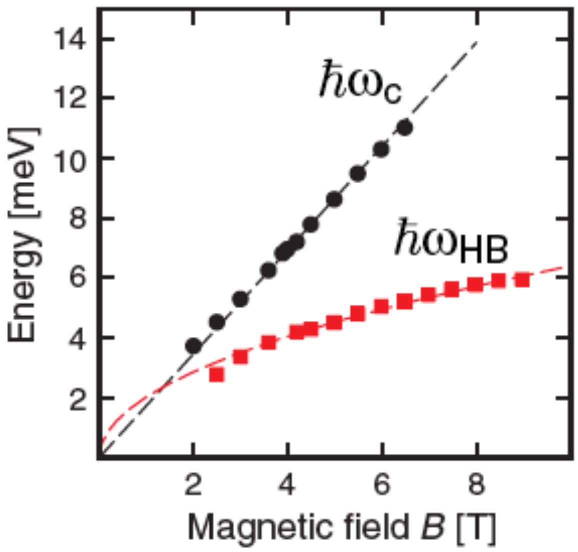


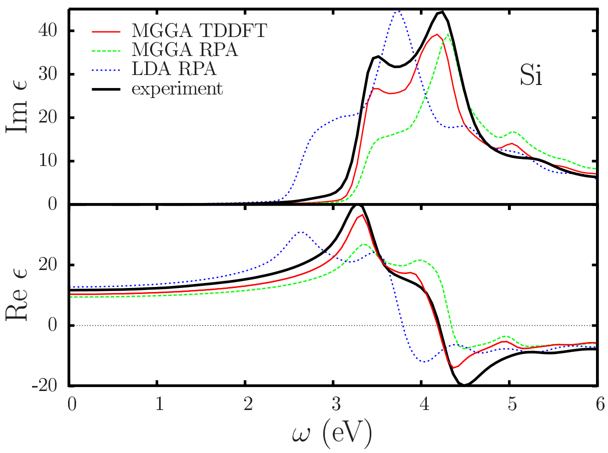
Fig. 1 - Collective modes of a honeycomb lattice of antidots measured by Raman scattering experiments as reported by Singha *et al.*, Science **332**, 1176 (2011). The black dashed line is identified with the cyclotron mode, while the red dashed line is interpreted as a manifestation of split Hubbard bands within a Landau level.

The extension of QMC to systems in magnetic field turns out to be highly nontrivial, and it has been accomplished only very recently, through research done under this project. The difficulty stems from the fact that the ground state of a quantum system in magnetic field carries an equilibrium current $\mathbf{j}_0$. A time-independent deformation of the ground state changes the equilibrium current. Hence the relationship between current density, $\mathbf{j}$, and displacement field, $\mathbf{u}$, which, in the absence of magnetic field, is simply given by $\mathbf{j}=n_0\, d\mathbf{u}/dt$ (n_0 being the ground-state density), must be modified to include a term proportional to the curl of the displacement field: $\mathbf{j}= \mathbf{j}_0 + n_0\, d\mathbf{u}/dt+\nabla\times(\mathbf{u}\times\mathbf{j}_0)$, where $\mathbf{j}_0$ is the ground-state current. The situation is similar to the one encountered in macroscopic electrodynamics, where the current is the sum of two terms: the time derivative of the polarization field and the curl of the magnetization. Making use of this relation we have been able (see Ref. 2) to obtain a closed equation of motion which generalizes the one previously obtained at $B=0$ (Ref. 5). The other main difference is the replacement in the equation of motion for $\mathbf{u}$ of the time derivative by the convective derivative $d/dt+\mathbf{v}_0\cdot\nabla$, with convection velocity $\mathbf{v}_0=\mathbf{j}_0/n_0$. While this theory has not yet been tested in concrete calculations, we feel that we now have a solid basis for calculating collective modes such as the ones observed by Singha *et al.* (see caption of Fig. 1), using as an input only ground-state properties of the antidot lattice in a magnetic field.

2. Meta-GGA for optical spectra

Meta-GGA (Generalized-Gradient Approximation) denotes a class of approximations for the exchange-correlation energy functional in static density functional theory (DFT). While in the ordinary GGA this *functional* is approximated as a simple *function* of the density and its gradient, the meta-GGA renders it also a function of the non-interacting kinetic energy density $\tau(\mathbf{r})$. However, $\tau(\mathbf{r})$ does not have a local or semi-local expression in terms of the density; it can be expressed locally, but only in terms of the Kohn-Sham orbitals, which have a non-local dependence on the density. For this reason, the meta-GGA succeeds in capturing some of the non-locality of the exact exchange-correlation (xc) energy functional, while correctly reducing, in the appropriate limit, to the basic paradigms of condensed matter physics (uniform electron gas) and quantum chemistry (two electrons in a bond).

It had been known for a while that the Meta-GGA improvement in the treatment of non-locality could result in considerable improvements in the calculation of the band gaps of semiconductors (these are systematically underestimated in LDA, for reasons that are now well understood, and ultimately related to strongly nonlocal behavior of the functional).



Dielectric function of silicon vs frequency. Thin solid (red) line is the result obtained with MGGA band structure and including the many-body interactions through fxc. Dashed (green) line is the result obtained by doing the RPA on top of the MGGA band structure. Dotted (blue) line is obtained with LDA band structure within RPA. Thick solid line is the experiment. [V. U. Nazarov ang G. Vgnale, Phys. Rev. Lett.. **107**, 216402 (2011)]

What came as a surprise is that even the optical spectra of semiconductors - in particular their characteristic two-peak structure above the gap - are much improved in a treatment that combines meta-GGA with the adiabatic local density approximation (LDA) of time-dependent density functional theory. This is the content of our latest paper on the subject (Ref. 1). Some illustrative results for Si are presented in the figures. Similar results have been obtained for other semiconductors, such as Ge and GaAs. The fundamental reason for the success of the calculation is that the inclusion of $\tau(\mathbf{r})$ as an argument of the local energy functional produces the qualitatively correct long-range behavior of the exchange-correlation kernel f_{xc} -- a crucial feature of the exact kernel that we have long been trying to approximate from first principles with a variety of methods (including the time-dependent current DFT), without much success. Remarkably, the coefficient α that controls the strength of the long-ranged part of f_{xc} emerges from the meta-GGA calculation with a value (α=-0.26) that is pretty much in line with values that had been proposed earlier, on purely empirical grounds, to explain the observed spectra. Our approximate formula for α is also consistent with the empirical observations that have been embodied in the so-called "bootstrap approximation" for the xc kernel, recently introduced by Sharma *et al*. [Phys. Rev. Lett. **107**, 186401 (2011)] . These results are very encouraging and exciting. On the one hand, they encourage us to pursue this line of research towards better approximations for f_{xc}, which might explain not only the part of the spectrum above the gap, but also the below-gap or excitonic part of the spectrum -- a very important component of the spectrum in strong insulators like LiF. On the other hand, the success of $\tau(\mathbf{r})$ as a tracker of nonlocality opens new vistas on both DFT and QCM. These will be briefly outlined in the next section.

Planned activities

An obvious extension of the meta-GGA work is to try and get rid of some of the approximations we have made in calculating the f_{xc} kernel, e.g., the approximation of replacing the derivative of the local xc energy density with respect to τ, $d\varepsilon_{xc}/d\tau$, by its average over the unit cell. This may lead to improved results for the excitonic part of the spectrum (i.e., the part of the spectrum below the gap). We should also understand why certain forms of the meta-GGA functional, when used as an input for the time-dependent theory, work so much better than others. Thus far, the kinetic energy density has been introduced as an auxiliary variable, helping us to get a better representation of a density functional. We are presently exploring (in collaboration with Max Di Ventra, UCSD) the possibility of promoting the full energy density (not just its non-interacting part) to the status of basic variable of the time-dependent theory. This new variable would complement the current density just as, in hydrodynamics, the equation of motion for the current (Euler equation) is coupled with an equation of motion for the energy density, which describes the exchange of heat between different parts of the system. The implementation of the energy density as a basic variable can be done both in time-dependent DFT and in the quantum-continuum mechanics. In the latter case, a time-dependent variational derivation of the QCM, which we have recently discovered, could be naturally extended to include energy fluctuations. The variational formulation of QCM can also be used to approach long-standing challenges of our theory, e.g., the problem of finding a smooth connection between the adiabatic and the elastic approximation limit. Lastly, we will try to develop applications of QCM to genuine many-particle systems: for example, to the "artificial graphene" system on which the Raman scattering experiments illustrated in Fig. 1 have been performed.

Publications

1. Optics of semiconductors from meta-GGA-based time-dependent density-functional theory - Phys. Rev. Lett. 107, 216402 (2011).
V. U. Nazarov, G. Vignale

2. Quantum continuum mechanics in a strong magnetic field - Phys. Rev. B 84, 245118 (2011). S.Pittalis, G. Vignale, I. V. Tokatly

3. Viscous corrections to the resistance of nano-junctions: a dispersion relation approach - Phys. Rev. B 83, 075428 (2011). Dibyendu Roy, G. Vignale, M. Di Ventra

4. Anti-adiabatic limit of the exchange-correlation kernels of an inhomogeneous electron gas - Phys. Rev. B 81, 245101 (2010). V. U. Nazarov, I. V. Tokatly, S. Pittalis, G. Vignale.

5. Continuum Mechanics for Quantum Many-Body Systems: The Linear Response Regime, Phys. Rev. B 81, 195106 (2010). Xianlong Gao, Jianmin Tao, G. Vignale, I. V. Tokatly.

Quantum Mesoscopic Materials

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Project scope

The project aims at developing of qualitative understanding and quantitative description of electronic properties of mesoscopic quantum materials, the materials where quantum interference of wave functions is important at lengths well exceeding the electronic wavelength. Properties of these materials are governed by the interplay between electron correlations, quantum and temperature fluctuations and disorder. Building on recent breakthroughs in understanding the role played by the topological aspects of matter, we define the main direction of our research as *topological quantum materials*. Examples of quantum phenomena characterized by topology include quantization of vortices in superconductors and superfluids, Aharonov-Bohm and Aharonov-Casher effects of interference of electron wave functions. We will address topological quantum physics with the emphasis on the confluence of internal symmetries of an electronic structure (global phase coherence, spin-orbit interactions, and broken inversion symmetry) and topological effects on macroscopic wave functions due to geometrical restrictions (multi-connectivity). The exemplary directions are magnetic field-induced superconductivity and related effects in multiconnected superconducting films and topological phenomena and Majorana states in nanowire – superconductor contacts. We will pursue physics of fluctuations and far from equilibrium processes focusing on the related aspects of topological quantum physics and non-equilibrium dynamics and large fluctuations in nanomagnetic and nanomechanical devices. The latter hold a fundamental appeal: while statistics of small deviations from deterministic behavior is well understood, the large deviations (also known as rare events) present a scientific challenge. Importantly, that despite being rare, the large deviations qualitatively change the system's evolution by, e.g., switching it into metastable states.

Recent progress

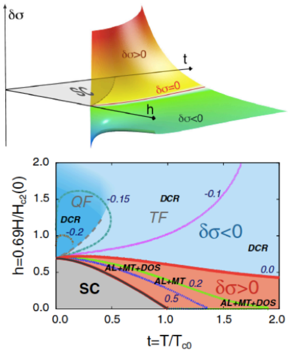


Fig. 1. Top: fluctuation correction to conductivity as function of reduced temperature t =T/T$_{c0}$ and magnetic field h=0.69H/H_{c2}(0). Bottom: map of the fluctuation contributions.

Fluctuation spectroscopy

We derived the expression for fluctuation conductivity in 2D superconductors as a function of temperature and magnetic field in the fluctuation region above the upper critical field $H_{c2}(T)$. This enables to infer the macroscopic and microscopic material parameters of a superconductor using, as an input, the temperature and magnetic field dependences of fluctuation conductivity. Focusing on the vicinity of the quantum phase transition near T=0, we predicted that above but near $H_{c2}(0)$ forms a novel dynamic state consisting of clusters of coherently rotating fluctuation Cooper pairs. We found the zero-temperature magnetic-field dependence of the transverse magnetoconductivity above $H_{c2}(0)$ in layered superconductors.

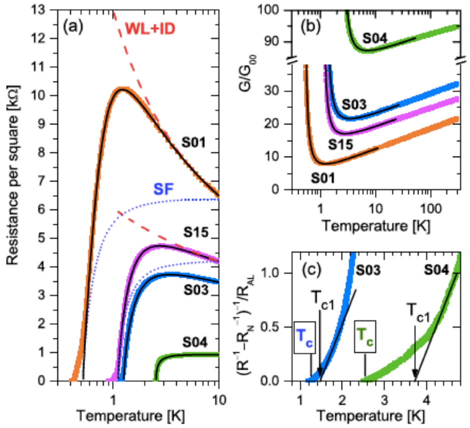


Fig. 2. (a) Resistance per square vs. temperature of TiN films; solid lines show the quantum contributions fits. (b) The same data as conductances. (c) Traditional and correct (in squares) determination of T_c.

Building on the complete account of quantum contributions to conductivity, we have demonstrated that the resistance of thin superconducting films exhibits a non-monotonic temperature behavior due to the competition of weak localization, electron-electron interaction, and superconducting fluctuation effects. We developed a method for precise determination of the superconducting transition temperature. We showed that superconducting fluctuations give rise to an appreciable decrease in the resistance even at temperatures well exceeding T_c.

Nanopattern-stimulated superconductor-insulator transition in a multi-connected film

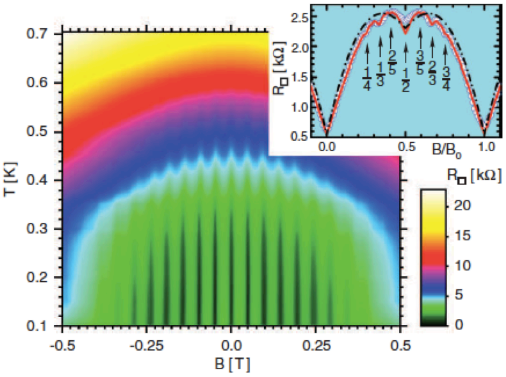
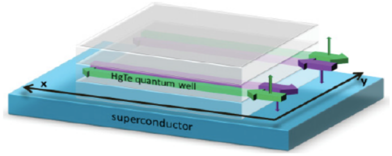


Fig. 3. Color map of the resistance of the multi-connected film in the temperature - magnetic field plane. The inset: the experimental data of the magnetoresistance (open circles) vs. magnetic field B/B_0 ($B_0 = \Phi_0/a^2$), at temperature 0.11K.

Nanopatterning transforms a thin TiN film into an array of superconducting weak links and *eo ipso* stimulates the disorder– and magnetic-field–driven superconductor-to-insulator transitions, shifting both transitions to a lower degree of microscopic disorder. We observed magnetoresistance oscillations reflecting collective phase-frustration in the multi-connected weak link network in a wide range of temperatures. We found that nanopatterning enhanced the role of Coulomb interaction and changed the characteristic energies of the film on the scales much exceeding both the mean free path and coherence length.

Instability of topological order in HgTe/superconductor structure



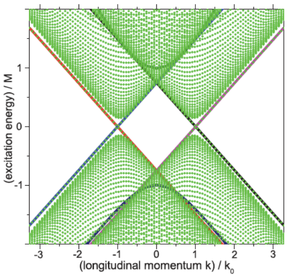


Fig. 4. Left: Sketch of the 2D topological insulator coupled to a superconductor. Right: Spectrum in 2D TI for the proximity-induced potential.

We investigated a two-layer hybrid structure comprising HgTe quantum-well-based topological insulator (TI) coupled to an *s*-wave superconductor and showed that it contains terms describing the mixing of TI subband branches by superconducting correlations induced by the proximity effect. We found that the proximity effect breaks down the rotational symmetry of the TI spectrum. We showed that the edge states acquire a gap, as follows from the standard theory and can become localized by the Andreev-backscattering mechanism in weak-coupling regime. In a strong-coupling regime the edge states merge with the bulk states, and the TI transforms into a narrow-gap semiconductor.

Planned research

Arrested vortex motion in superconducting nanostructures

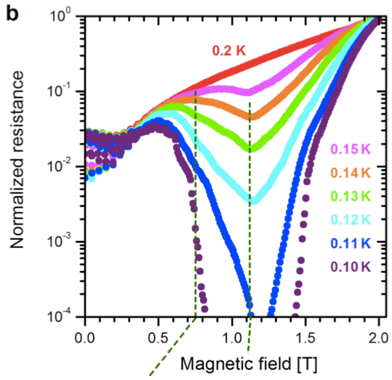


Fig. 5. Magnetoresistance of the perforated TiN SC film. Reentrant zero-resistance state, 0.7 T-wide, is observed at T=0.1 K.

It is commonly accepted that magnetic field destroys superconductivity since it promotes vortices, which move under the applied current and dissipate the energy. Utilizing a specific design of multi-connected film we reverse the detrimental effect of the magnetic field and find a remarkable reentrant dissipation-free state induced by the magnetic field in the perforated TiN film, see Fig. 5. The key observation is that the characteristic lateral size of superconducting constrictions confining vortices is comparable to the vortex core. As a result vortex motion is arrested by the combined (i) surface superconductivity pushing vortices together and (ii) self-induced potential well due to the collective suppression of order parameter by densely packed vortices. We will construct a theory of reentrant superconductivity in nanostructures within the framework of Ginzburg-Landau (GL) approach. Our tentative estimates show that indeed the abovementioned effects can result in 5-6 orders of magnitude suppression of the resistance. Our project promises to resolve the pinning problem remaining a major obstacle for technological use of superconductors at elevated temperatures and magnetic fields.

Topological quantum phenomena

The objective of the planned research is to investigate dynamic effects related to tuning Majorana bound states accompanied by odd frequency pairing. In particular, we investigate dynamics of transformation of usual Andreev bound states into chiral Majorana edge modes in Rashba Superconductors, i.e. quantum phase transition into the so called topological phase of Rashba Superconductors. Manipulation by Majorana states in hybrids is one of the most promising avenues for quantum computations and a remarkable problem of its own fundamental merit. We will study the anomalous proximity effect and odd-frequency pairing in hybrid systems consisting of a nanowire in the contact with a superconductor. Previous studies, limited to possible existence of the Majorana states under certain conditions, showed that Maojorana fermions can appear at the edge of a 1D spin-orbit-coupled wire in parallel magnetic field brought into a contact with a superconductor (see Fig. 6). However, the dynamical issues were not addressed so far and will constitute the core of our research.

We will study nucleation/decay of Majorana states under the magnetic field switching on/off, and dynamical braiding effects due to interchanging the Majorana states. The temporal manipulation by these states is critical to quantum computing. The theoretical approach will be based on the new approach including the time-dependent Bogoljubov-de Gennes formalism. The important aspect of the nanowire/superconductor junctions is the anomalous proximity effect, where the odd-frequency pairing state is generated. We will employ the original theory of the odd-frequency pairing in hybrid systems and study theoretically the local density of states (LDoS) as a function of the impurity scattering, in order to understand conditions of realization of zero-energy peak in LDoS. The robustness of LDoS peak will serve a fingerprint of the existence of Majorana bound states and their coupling to odd-frequency superconductivity. We will study

Josephson coupling across the surface of a 3D topological insulator, where we expect proximity-induced odd-frequency pairing states. We will investigate fully unexplored role of two-dimensional fluctuations and multi-connectivity in topological hybrids utilizing our original theory of superconducting fluctuations and multi-connectivity effects. We will pursue interface superconductivity (IS) where the admixture of order parameter components with different symmetry (s-wave, d-wave, p-wave) can arise due to Rashba spin-orbit coupling. We will study a new class of tunable quantum phase transitions between the different topological phases in SC/2DEG/FM hybrids driven by the gate-controlled chemical potential and Zeeman splitting.

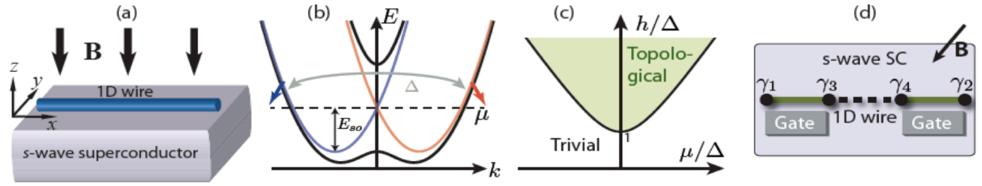


Fig. 6. Stabilizing topological superconducting state in a 1D spin-orbit-coupled wire. (b) Wire band structure in the presence of time-reversal symmetry (red and blue curves) and when it is broken by magnetic field (black curves). If the chemical potential lies within the field-induced gap at k = 0, the wire appears 'spinless'. Incorporating the pairing induced by the proximate superconductor leads to the phase diagram in (c). Endpoints of topological (green) segments of the wire host localized, zero-energy Majorana modes (d).

Publications 2009 – 2012

1. N. B. Kopnin, Yu. M. Galperin, and V. M. Vinokur, Phys. Rev. B **79**, 035319 (2009).
2. L. Yu. Barash, T. P. Bigioni, V. M. Vinokur, and L. N. Shchur, Phys. Rev. E **79**, 046301 (2009).
3. S. V. Syzranov, K. B. Efetov, and B. L. Altshuler, Phys. Rev. Lett. **103**, 127001 (2009).
4. M. V. Fistul, V. M. Vinokur, and T. I. Baturina, Phys. Rev. Lett., **102**, 49702 (2009).
5. N. B. Kopnin, Y. M. Galperin, J. Bergli, and V. M. Vinokur, Phys. Rev. B **80**, 134502 (2009).
6. B. L. Altshuler, V. E. Kravtsov, I. V. Lerner, I. L. Aleiner, Phys. Rev. Lett. **102**, 176803 (2009).
7. N. M. Chtchelkatchev, V. M. Vinokur, and T. I. Baturina, Phys. Rev. Lett. **103**, 247003 (2009).
8. A. Petković, V. M. Vinokur, and T. Nattermann, Rev. B **80**, 212504 (2009).
9. T.I.Schelkacheva, E.E.Tareyeva, and N.M.Chtchelkachev, Phys. Rev. E **79**, 021105 (2009).
10. Andreas Glatz and I.S. Beloborodov, Phys. Rev. B **80**, 245440 (2009).
11. A. Glatz, I. S. Beloborodov, EuroPhys. Lett **87**, 57009 (2009).
12. Andreas Glatz and I.S. Beloborodov, Phys. Rev. B **79**, 235403 (2009).
13. Andreas Glatz and I.S. Beloborodov, Phys. Rev. B **79**, 041404(R) (2009).
14. M. G. Vasin, N. M. Chtchelkatchev, V. M. Vinokur, Theor. Math. Phys, **163**, 537 – 548 (2010).
15. N. B. Kopnin, Y. M. Galperin, and V. M. Vinokur, Phys. Rev. B **82**, 012503 (2010).
16. N. M. Chtchelkatchev, T. I. Baturina, A. Glatz, V. M. Vinokur, Phys. Rev. B **82**, 024526 (2010).
17. A. Petkovic, N. Chtchelkatchev, T. I. Baturina, V. Vinokur, Phys. Rev. Lett. **105**, 187003 (2010).
18. B. Sacépé, C. Chapelier, T. I. Baturina, V. M. Vinokur, et al, NATURE COMMUNICATIONS, DOI: 10.1038/ncomms1140.
19. A. Glatz, I. Beloborodov, N. M. Chtchelkatchev, V. M. Vinokur, Phys. Rev. B **82**, 075314 (2010).
20. A. Glatz and A.E. Koshelev, Phys. Rev. B **82**, 012507 (2010).
21. S. V. Syzranov, I. L. Aleiner, B. L. Altshuler, and K. B. Efetov, Phys. Rev. Lett. **105**, 137001 (2010).
22. M. Belkin, A. Glatz, A. Snezhko, I.S. Aranson, Phys. Rev. E (Rapid) **82**, 015301 (2010).
23. B. Surer, A. Glatz, H. G. Katzgraber, G. T. Zimanyi, et al, Phys. Rev. Lett. **105**, 039702 (2010).
24. A. Glatz and I.S. Beloborodov, Phys. Rev. B **81**, 033408 (2010).
25. T.I. Schelkacheva, E.E. Tareyeva, and N.M. Chtchelkachev, Phys. Rev. B **82**, 134208 (2010).
26. Ya.I. Rodionov, I.S. Burmistrov, and N.M. Chtchelkatchev, Phys. Rev. B **82**, 155317 (2010).
27. T.I. Baturina, A.Yu. Mironov, V.M. Vinokur, et al., Physica C **470**, S810 (2010).
28. I. L. Aleiner, B. L. Altshuler, G. Shlyapnikov, Nature Physics, doi:10.1038/nphys1758 (2010).
29. A. Mironov, T. Baturina, V. Vinokur, et al, Physica C **470** SI Supplement I, S808-S809 (2010).
30. N. Chtchelkatchev, V. Vinokur, T. Baturina, Physica C **470** SI Supplement I, S935-S936 (2010).
31. T. I. Baturina, V. M. Vinokur, A. Yu. Mironov, et al, EPL **93**, 47002 (2011).
32. A. Glatz, A. A. Varlamov, and V. M. Vinokur, EPL **94**, 47005 (2011).
33. A. Glatz, I. Aranson, V. M. Vinokur, et al, Phys. Rev. B **84**, 024508 (2011).
34. V. Vakaryuk and V. M. Vinokur, Phys. Rev. Lett. **107**, 037003 (2011).
35. I. M. Khaimovich, N. M. Chtchelkatchev, and V. M. Vinokur, Phys. Rev. B **84**, 075142 (2011).
36. A. Petkovic, N. M. Chtchelkatchev, and V. M. Vinokur, Phys. Rev. B **84**, 064510 (2011).
37. A. Glatz, A. A. Varlamov, and V. M. Vinokur, Phys. Rev. B **84**, 104510 (2011).
38. A. Glatz, N. M. Chtchelkatchev, I. Beloborodov, V. M. Vinokur, Phys. Rev. B **84**, 235101 (2011).
39. A. Glatz, H. Roberts, I. S. Aranson, K. Levin, Phys. Rev. B **84**, 180501(R) (2011).
40. T. Baturina, S. Postolova, A. Mironov, A. Glatz, M. Baklanov, V. Vinokur, EPL **97**, 17012 (2012).

Accelerated Molecular Dynamics Methods

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BES Program Summary, July 2012

Project Scope

The primary goal of this project is to develop high-quality computational methods for reaching long time scales in atomistic simulation of materials. While direct molecular dynamics (MD) is limited to roughly one microsecond, it is often crucial to understand the dynamics on longer time scales.   We focus on infrequent-events, typically activated processes, as this characterizes the long-time dynamics of many, if not most, important materials processes (e.g.,surface growth, bulk diffusion, precipitate clustering, radiation-damage annealing, grain growth, dislocation climb, etc.), and thus nearly every material process of importance to LANL and DOE missions. For this type of system, we can exploit the infrequent-event nature to shorten the time between successive events that take the system from state to state, and hence probe the behavior at much longer times. Largely under this BES program, we have developed the *accelerated molecular dynamics* (AMD) approach, in which we let the system trajectory itself find an appropriate way out of each state, eliminating the need to pre-specify, or search for, all possible escape paths from a state.   The key is to find the next escape path more quickly than MD would, with the guiding principle of maintaining high accuracy in the resulting state-to-state dynamics. The methods in this AMD class are hyperdynamics, in which the potential surface is carefully modified to accelerate the escape dynamics, parallel-replica dynamics, in which many replicas of the system are evolved simultaneously to effectively parallelize time, and temperature accelerated dynamics, in which a high-temperature trajectory is employed to quickly scan for the first escape that should occur at the lower temperature. With these core methods in place, our main focus now is on making them more powerful and efficient for a wide variety of realistic systems, fully exploiting upcoming computer architectures, and making the methods available and effective for materials experts at LANL and elsewhere. One of the key obstacles is the persistent presence of low barriers, which limits the computational speedup.

Recent Progress

In the last year, our method development efforts concentrated primarily on two important generalizations of existing AMD methods -- namely, a local version of hyperdynamics and an improved understanding of the behavior of parallel-replica dynamics when applied to coarse-grained representations of state-space. In the case of hyperdynamics, application of the standard formulation are limited to rather small systems because as the number of available transitions increases, the probability that somewhere in the system the vicinity of a dividing surface is visited increases rapidly, leading to a rapid decrease of the effectiveness of the bias potential, and hence of the acceleration. In principle this limitation can be circumvented because most transitions are local in nature, i.e., they involve atoms located in a very small region of space. Hence, transitions that are sufficiently separated occur independently from one another. This fact is key to our new local hyperdynamics formulation: the bias force has to be turned off locally in the vicinity of a potential transition but can remain active elsewhere. This way, the acceleration is limited by the size of the local region, and not by the overall size of the system. While simple to state, this generalization turns out to be quite subtle to achieve in practice. We have now demonstrated its efficiency and accuracy on realistic systems and are proceeding to implementing it within SPaSM, a large-scale, massively-parallel MD code developed at LANL. In the case of parallel-replica dynamics, we derived a solid formal understanding of the method in its full generality, where the states of the system are defined by *arbitrary* volumes in configuration space. We demonstrated that, despite this fully general choice, parallel-replica dynamics will remain arbitrarily accurate, but that its efficiency will be dictated by the particular nature of the states. This flexibility can be exploited to tailor the states to the system at hand, thereby greatly improving its flexibility and parallel efficiency for complex systems.

We also applied AMD techniques to a wide variety of problems of technological importance. For example, we studied nanoscale friction in the context of friction force microscopy (FFM) experiments. We used parallel-replica dynamics over a wide range of temperatures and scanning velocities to validate a complete rate-theory model based on harmonic transition state theory. We also directly compared parallel-replica dynamics simulations with actual FFM experiments. We were able to achieve the same thermally activated regime and obtained very good agreement in terms of energetics and scaling with velocity and temperature. We however showed that discrepancies exist because of the very large mismatch in terms of inertia between the virtual and real cantilevers. Other recent applications of the AMD techniques include the grain-boundary-assisted healing of radiation damage in metals, the transformation of nanotube fragements into graphene, and the dynamics of interstitial clusters in Zr.

Finally, we contributed to the fundamental understanding of MD by investigating the synchronization behavior of Langevin thermostats (the tendency of trajectories originating at different points in phase space to synchronize when exposed to the same stochastic forcing). Specifically, we addressed the spatio-temporal behavior of synchronization upon local disruption of the dynamics. We demonstrated that, in three dimensions, a local disturbance only locally disrupts synchronization. This new understanding will allow us to exploit the synchronization effect to increase the effectiveness of the AMD methods.

Future Plans

Our future work will be articulated around three important, and often inter-related, challenges: addressing the low-barrier problem, improving scalability (with respect to system size and number of CPUs), and further generalizing the methods to enable the investigation of more complex systems. To address the low-barrier problem, one of the most promising strategies is to coarse-grain state-space in such a way that most low-barriers connect internal sub-states, while higher barriers lead out of the states. For example, we recently showed that parallel-replica dynamics can be made arbitrarily accurate for *any* definition of states, and that the efficiency of the method can be drastically improved if good states can be identified. This observation is the key to applying parallel-replica dynamics to systems with very heterogeneous distributions of barriers, or even in cases so complex (such as soft matter) that super-states cannot be created by grouping discrete states. The main challenge we will have to tackle is to develop heuristics to identify (quasi-)optimal definitions of states and to estimate the correlation time of the dynamics in these states. These strategies might, for example, involve "scouting" trajectories, perhaps at higher temperatures, exploring the neighborhood in front of the official trajectory to identify good states as fast as possible. This will also give us an opportunity to revisit the core structure of the different methods in order to identify and exploit all available parallelism. This will be crucial on the path to the exascale, where the number of available cores will literally explode. Efficiently harvesting that computing power will be a challenge but also an opportunity as it opens the door to yet unexploited strategies, such as speculation (for example, temporarily assuming that each transition observed in TAD might be accepted, so that work on the next putative transition can begin). This will be done in collaboration with the computational co-design efforts at LANL. Another extension of an AMD method that will help address both scaling with system size and, to some extent, low-barriers, is the local formulation of hyperdynamics. We will demonstrate the method on very large systems --- e.g., up to 10^9 atoms --- that are only amenable with massively parallel MD. This will allow us to explore a completely new regime where problems requiring both long time and large length-scales would become directly amenable to MD simulations. In certain instances of such problems however, large length-scales are mostly inert in terms of slow structural changes but are critical in providing the right elastic and vibrational boundary conditions to "active" regions, where the structure of the material evolves on long timescales. In such cases, a full atomistic treatment would be inefficient. We will investigate the coupling of multiscale techniques (such as the finite-temperature quasicontinuum method) and advanced boundary conditions (e.g., based on the projection operator formalism) with small atomistic domains where the AMD would be targeted. This would be ideal to tackle problems such as friction at the tip of a friction force microscope, where we recently demonstrated that capturing the effect of the huge inertia of the (large) cantilever is crucial for a proper description of the dynamics of the (small) contact region, and hence of friction.

Publications, 2009-present

"Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism, O.U. Uche, D. Perez, A.F. Voter, and J.C. Hamilton, Phys. Rev. Lett. **103**, 046101 (2009).

"Bad seeds sprout perilous dynamics: Stochastic thermostat induced trajectory synchronization in biomolecules," D.J. Sindhikara, S. Kim, A.F. Voter, and A.E. Roitberg, J. Chem. Theory Comput. **5**, 1624 (2009).

"Low-Speed Atomistic Simulation of Stick–Slip Friction using Parallel Replica Dynamics," A. Martini, Y. Dong, D. Perez, and A.F. Voter, Tribol. Lett., **36**, 63 (2009).

“Accelerated Molecular Dynamics Methods: Introduction and Recent Developments,” D. Perez, B.P. Uberuaga, Y. Shim, J.G. Amar, and A.F. Voter, Annual Reports in Comp. Chem. **5**, 79, (2009).

“Accurate acceleration of kinetic Monte Carlo simulations through the modification of rate constants,” A. Chatterjee and A.F. Voter, J. Chem. Phys. **132**, 194101 (2010).

“Rate theory description of atomic stick-slip friction,” D. Perez, Y. Dong, A. Martini, and A.F. Voter, Phys. Rev. B **81**, 245415 (2010).

“Isomerization rates and mechanisms for the 38-atom Lennard- Jones cluster determined using molecular dynamics and temperature accelerated dynamics,” J.C. Hamilton, D.J. Siegel, B.P. Uberuaga, and A.F. Voter, submitted to J. Chem. Phys., 2010.

“Efficient Annealing of Radiation Damage Near Grain Boundaries via Interstitial Emission," X.-M. Bai, A.F. Voter, R.G. Hoagland, M. Nastasi, and B.P. Uberuaga, Science **327**, 1631 (2010).

“The roles of statics and dynamics in determining transitions between atomic friction regimes,” Yalin Dong, Danny Perez, Arthur F. Voter, and Ashlie Martini, Tribology Letters **42**, 99 (2011).

“Speed Dependence of Atomic Stick-Slip Friction in Optimally Matched Experiments and Molecular Dynamics Simulations,” Qunyang Li, Yalin Dong, Danny Perez, Ashlie Martini, and Robert W. Carpick, Physical Review Letters **106**, 126101 (2011).

“Understanding the Surface Diffusion Processes during Magnetron Sputter-Deposition of Complex Oxide Mg-Al-O Thin Films,” V. Georgieva, A.F. Voter, and A. Bogaerts, Crystal Growth and Design **11**, 2553 (2011).

“Fullerene and graphene formation from carbon nanotube fragments,” B.P. Uberuaga, S.J. Stuart, W. Windl, M. Masquelier, and A.F. Voter, Computational and Theoretical Chemistry, **987**, 115 (2012).

“Thermal Activation in Atomic Friction: Revisiting the Theoretical Analysis,” Yalin Dong, Danny Perez, Hongyu Gao, and Ashlie Martini, Journal of Physics: Condensed Matter, in press (2012).

“The role of atomic structure on grain boundary-defect interactions in Cu,” Xian-Ming Bai, Louis J. Vernon, Richard G. Hoagland, Arthur F. Voter, Michael Nastasi, and Blas Pedro Uberuaga, Physical Review B, **85**, 214103 (2012).

“Accelerated Molecular Dynamics Methods,” Danny Perez, Blas P. Uberuaga, and Arthur F. Voter, in Hierarchical Methods for Dynamics in Complex Molecular Systems, Forshungszentrum Julich, (2012).

“Locally disrupted synchronization in Langevin molecular dynamics,” A.I. Georgescu, S. Denny, E. Joly, G. Chen, D. Perez, and A.F. Voter, Phys. Rev. E, in press.

“Atomistic simulation methods for long-time dynamics in materials for nuclear energy systems,” B. P. Uberuaga, D. Perez, and A.F. Voter. Review article on AMD methods prepared for the Nuclear Energy Agency; in press, 2012.

Exploratory Development of Theoretical Methods

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I. Project Scope

The purpose of this FWP is to generate new theories, models, and algorithms that will be beneficial to the research programs at the Ames Laboratory and to the mission of DOE. This FWP will lead the development of theoretical tools to study a broad range of problems in physics, materials science, and chemical as well as biological systems. The generality of these tools allows the cross-fertilization of ideas from one problem to problems in an entirely different area through the common link of the mathematical formulation of the problem. Such leaps across topic areas and in some cases across disciplines are characteristic of the power of a fundamental physics-based approach to the development of new theoretical methods, facilitated by the availability of general theoretical tools applicable to very different sets of problems. Current research is along the following three directions:

1. Development of methods for crystal structure prediction and materials discovery
2. Development of methods for calculation of strongly-correlated electron systems
3. Development of methods for accurate calculation and quantum control of spin dynamics

II. Recent Progress

Methods for Crystal Structure Prediction and Material Discovery

We have developed a fast and efficient adaptive genetic algorithm (GA) method for crystal structure prediction [1-4]. Our method performs GA searches using auxiliary classical potentials to screen the energies of candidate structures, and select only a few of them for more extensive first-principles evaluation. Parameters of the auxiliary potentials are adaptively adjusted to reproduce the first-principles results during the course of the GA search. This method combines the speed of empirical potential searches with the accuracy of first-principles calculations. The efficiency of the adaptive GA method allows a great increase in the size and complexity of systems that can be studied. The performance of adaptive GA is demonstrated by the predictions of several new high pressure phases for SiO_2, ice, and $MgSiO_3$. We also developed strong interactions with the magnetism group at Ames Laboratory to describe and predict the structures and properties of new magnetic materials. Results have been obtained for systems where experimental structures are either unknown or questionable (e.g., Zr-Co, Hf-Co systems). The combination of our computational techniques with experimental efforts at Ames Laboratory represents a unique approach for new materials design and discovery.

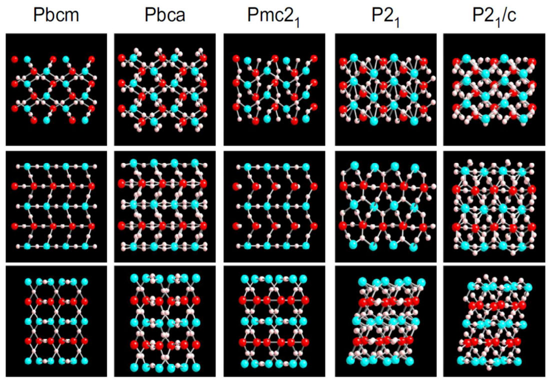

Fig. 1 New ultrahigh pressure phases of H_2O-ice are predicted using adaptive GA method.

First-Principles Methods for Strongly Correlated Electron Systems

The objective of this task is to develop theories and computational approaches that can incorporate strong correlation effects in a truly first-principles, self-consistent manner without the usual empirical U and J parameters. Towards this goal, we have studied the problem using two related approaches:

Gutzwiller density functional theory (G-DFT) [8-10] and correlated matrix renormalization (CMR) approximation [7].

G-DFT: In contrast to the Kohn-Sham approach where the kinetic energy functional is introduced in reference to a non-interacting electron system, we introduce a new kinetic energy functional in reference to an interacting electron system with exact treatment of onsite kinetic energy and Coulomb repulsion while using the Gutzwiller approximation for interactions between localized and delocalized electrons. This new energy functional yields a set of self-consistent one-particle Schrödinger equations analogous to LDA. At the same time, it also introduces additional variational degrees of freedom in the problem corresponding to the occupations of various local (many-body) electronic configurations in the system. By a proper choice of the residual exchange-correlation functional, we have applied the G-DFT to investigate the dissociation problem in H_2 molecules.

CMR Approximation: Following Levy's constrained search formulation of DFT, we recently extended our Gutzwiller DFT approach to obtain new forms for the exchange-correlation functional for calculation of the ground state energy of the system when the variation is made within the subspace of interacting trial wave functions with the Gutzwiller form. In this approach, we replace the Gutzwiller approximation by the more general correlation matrix renormalization (CMR) approximation in which both the one-particle density matrix and the two-particle correlation matrix of the system are renormalized from the Hartree-Fock (HF) results due to local electron correlation effects. Using this approximation, we can derive an exact closed form for the total energy of the system, which can be used to obtain a set of equations to solve for the ground state of the system using interacting variational wave functions in an analysis analogous to the Hartree-Fock analysis for non-interacting variational wave functions. The method is free of screened Coulomb interaction parameters by directly taking the Coulomb integrals over the basis of local orbitals. It is also free of double counting issues commonly encountered in many previous many-body approaches.

Ab initio Method for Spin Fluctuation Calculations

We developed a new technique to incorporate spin fluctuations into modern band structure calculations [11-13]. This technique is based on a many body perturbation theory treatment of electron-electron interaction and represents an addition of particle-hole diagrams to the mean field solution obtained by such static methods as LDA, GW, etc. This is a generalization of our previous ab-initio calculations of dynamic spin susceptibility in magnetically ordered or paramagnetic systems and consecutive estimation of particle-hole ladder diagrams, representing electron-magnon interactions. Our results indicate that this method is important for magnetic materials under pressure in general as well as itinerant magnet systems. We show significant improvement of the description of magnetic properties in pure ferromagnetic 3d transition metals under pressure and in iron superconductor compounds. In other materials (e.g., graphene) our results have predictive character.

Quantum dynamics and control of individual spins in diamond

Understanding and controlling matter at the level of individual quantum particles is an exciting scientific endeavor, and is one of the Grand Challenges identified by the DOE Office of Science. Beside fundamental interest, this research is important for applications ranging from nanosciences to advanced sensing and quantum information processing. In order to meet this challenge, new theoretical approaches and experimental tools are being actively explored. We have developed novel theoretical techniques for investigating and controlling the

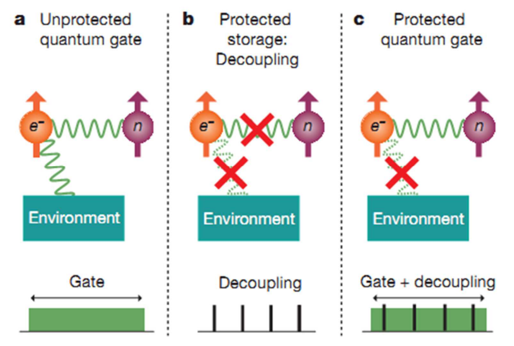

Fig. 2 An integration of dynamical decoupling and internal resonance in the coupled-spin system to resolve the conflict between gate operation and decoupling

quantum spin dynamics of individual electronic and nuclear spins in diamond, which are coupled to their solid-state environment [14-26]. With these tools, we are able to design efficient approaches for controlling quantum spins, including realistic imperfections, and reliably assess the protocols' performance. We demonstrate how our theoretical work helped understand the quantum dynamics of individual spin impurities in diamond, and guided our joint theory/experiment work on controlling a single quantum spin in solid-state environment [19] and implementing decoherence-protected controlled dynamics of two coupled spins. As a result, we were able to realize the first quantum computation (quantum search algorithm) on two individual solid-state spin qubits [14], and, using this advance, demonstrate extremely sensitive nanoscale tomography with single-spin resolution in solids.

III. Future Plans

Methods for Crystal Structure Prediction and Material Discovery

We will develop algorithms and methods for free energy and phase diagram calculations in order to predict the stabilities of the alloy phases at finite temperatures. We will explore the efficiency of using genetic algorithm to generate a good set of low-energy structures for configuration free energy calculations. Methods will also be developed to study the magnetic structure stability at both zero and finite temperatures. We will further improve the efficiency of the adaptive GA method for large and complex systems. We will also develop efficient parallel and GPU algorithms to further optimize the adaptive GA code to get better performance on DOE peta-scale computers.

First-Principles Methods for Strongly Correlated Electron Systems

We will continue to develop the CMR approach for strongly correlated electron systems. One of the key steps is how to accurately evaluate the renormalization factors for the one-particle and two-particle density matrices. We will benchmark the CMR method against the accurate quantum chemistry method (e.g. CI) for small molecules in order to develop a robust scheme for accurate evaluation of the renormalization factors in the CMR method. The method developed will then apply to solid-state systems.

Method for Spin Fluctuation Calculations and Quantum Control of Spins

We will develop methods and codes for studying spin dynamics and spin fluctuation based on *ab-initio* FLEX approach. Methods will also be developed for handling finite temperature *ab initio* quantum spin dynamics for metals and molecules.

We will investigate the influence of the spin decoherence of the NV centers in diamond on its optical properties, which is needed for better characterization and future functionalization of these very promising system. We will investigate joint dynamics of the electronic and nuclear spins of the NV centers, and study the possibility of using it for magnetic sensing at nanoscale, as well as for other applications in nanosciences. We will study the spin-phonon interaction and the possible role of the dynamic Jahn-Teller effect on the excited states of NV centers in diamond. In this way, we will establish the effect of the phonons on the electronic properties and spin coherence of NV centers, a current hot topic in the race to functionalize this promising 'defects'. We will also further develop advanced approaches to modeling of spin dynamics in complex nanostructures, including organic LEDs and organic spin valves. In this way, we will be able to better model these important novel energy-efficient devices.

IV. Publications

[1] "Adaptive Genetic Algorithm Method for Crystal Structure Prediction", S. Q. Wu, M. Ji, C. Z. Wang, M. C. Nguyen, K. Umemoto, R. M. Wentzcovitch, K. M. Ho, *Phys. Rev. Lett*. submitted.

[2] "Atomic structure and magnetic proper ties of $Fe_{1-x}Co_x$ alloys", M. C. Nguyen, Xin Zhao, Min Ji, Cai-Zhuang Wang, Bruce Harmon, and Kai-Ming Ho, J. *Appl. Phys*., **111**, 07E338 (2012).

[3] "New ultrahigh pressure phases of H_2O-ice using an adaptive genetic algorithm", Min Ji, K. Umemoto, C. Z. Wang, K. M. Ho and R. M. Wentzcovitch,, *Phys. Rev. B* **84**, 220105(R) (2011).

[4] "Identification of post-pyrite phase transitions in SiO_2 by a genetic algorithm", S. Q. Wu, K. Umemoto, M. Ji, C. Z. Wang, K. M. Ho, and R. M. Wentzcovitch, *Phys. Rev. B* **83**, 184102 (2011).

[5] "Comparing efficiencies of genetic and minima hopping algorithms for crystal structure prediction", M. Ji, C. Z. Wang, and K. M. Ho, *Phys. Chem. Chem. Phys*. **12**, 11617 (2010).

[6] "Appearance of bulk-like motifs in Si, Ge, and Al clusters", Wen-Cai Lu, C. Z. Wang , Li-Zhen Zhao , Wei Zhang , Wei Qin , K. M. Ho, *Phys. Chem. Chem. Phys*. **12**, 8551 (2010).

[7] "Correlation matrix renormalization approximation for total energy calculations of correlated electron systems", Y. X. Yao, J. Liu, C. Z. Wang, and K. M. Ho, *Phys. Rev. B*, submitted.

[8] "The benchmark of Gutzwiller density functional theory in hydrogen systems" ,Y. X. Yao, C. Z. Wang and K. M. Ho, *International J. Quant. Chem.* **112**, 240 (2012).

[9] "Comparative study of the electronic and magnetic properties of BaFe2As2 and BaMn2As2 using the Gutzwiller approximation", Y. X. Yao, J. Schmalian, C. Z. Wang, K. M. Ho, G. Kotliar, *Phys Rev. B* **84**, 245112 (2011).

[10] "Including many-body screening into self-consistent calculations: Tight-binding model studies with the Gutzwiller approximation", Y. X. Yao, C. Z. Wang, and K. M. Ho, *Phys. Rev. B* **83**, 245139 (2011).

[11] "Consistent Model of Magnetism in Ferropnictides", A . L. Wysocki, K. D. Belashchenko, and V. P. Antropov, *Nature Physics*, **7**, 485-89 (2011).

[12] "Low-Energy Coherent Stoner-Like Excitations in $CaFe_2As_2$", L. Q. Ke, M. van Schilfgaarde, J. J. Pulikkotil, T. K. Kotani, and V. Antropov, *Phys. Rev. B*, **83**, 060404 (2011).

[13] "The Influence of Quantum Spin Fluctuations on Magnetic Instability", V. P. Antropov, and A. Solontsov, *J. Appl. Phys*., **109**, 07E116 (2011).

[14] "Decoherence-protected quantum gates for a hybrid solid-state spin register", T. van der Sar, Z. H. Wang, M. S. Blok, H. Bernien, T. H. Taminiau, D. Toyli, D. Lidar, D. D. Awschalom, R. Hanson, and V. V. Dobrovitski, *Nature* **484**, 82 (2012).

[15] "Comparison of dynamical decoupling protocols for a nitrogen-vacancy center in diamond", Zhi-Hui Wang, G. de Lange, D. Riste, R. Hanson, V. V. Dobrovitski , *Phys. Rev. B* **85**, 155204 (2012).

[16] "Spin Coherence During Optical Excitation of a Single NV Center in Diamond", G. D. Fuchs, A. L. Falk, V. V. Dobrovitski, D. D. Awschalom, *Phys. Rev. Lett.* **108**, 157602 (2012).

[17] "Controlling the quantum dynamics of a mesoscopic spin bath in diamond", G. de Lange, T. van der Sar, M.S. Blok, Z.H. Wang, V.V. Dobrovitski, R. Hanson, *Scientific Reports*, submitted (2012).

[18] "Effect of pulse error accumulation on dynamical decoupling of the electron spins of phosphorus donors in silicon", Zhi-Hui Wang, Wenxian Zhang; A. M. Tyryshkin et al., *Phys. Rev. B* **85**, 085206 (2012).

[19] "Universal dynamical decoupling of a single solid-state spin from a spin bath" , G. de Lange, Z. H. Wang, D. Riste, V. V. Dobrovitski, and R. Hanson, *Science* **330**, 60 (2010).

[20] "Time-optimal rotation of a spin 1/2: Application to the NV center spin in diamond", Z. H. Wang and V. V. Dobrovitski, *Phys. Rev. B* **84**, 045303 (2011).

[21] "Vibrational modes and lattice distortion of a nitrogen-vacancy center in diamond from first-principles calculations", J. H. Zhang, C. Z. Wang, Z. Z. Zhu, and V. V. Dobrovitski, *Phys. Rev. B* **84**, 035211 (2011).

[22] "Aperiodic dynamical decoupling sequences in the presence of pulse errors", Z. H. Wang and V. V. Dobrovitski, J. *Phys. B* **44**, 154004 (2011).

[23] "Single-Spin Magnetometry with Multipulse Sensing Sequences", G. de Lange, D. Riste, V. V. Dobrovitski *et al*., *Phys. Rev. Lett*. **106**, 080802 (2011).

[24] "Bootstrap tomography of the pulses for quantum control", V. V. Dobrovitski, G. de Lange, D. Riste, and R. Hanson, *Phys. Rev. Lett.* **105**, 077601 (2010).

[25] "Spin echo decay at low magnetic fields in a nuclear spin bath", L. Cywinski, V. V. Dobrovitski, and S. Das Sarma, *Phys. Rev. B* **82**, 035315 (2010).

[26] "Excited-state spin coherence of a single nitrogen-vacancy centre in diamond" G. D. Fuchs, V. V. Dobrovitsk, D. M. Toyli et al. *Nature Phys* **6**, 668 (2010).

Charge patching method for electronic structures and charge transports of organic and organic/inorganic mixed nanostructures

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Project scope

The goal of this project is to develop large scale simulation methods to study inorganic and organic nanostructures, including their atomic configurations, electronic structures and carrier transports. In particular, we like to develop the charge patching method (CPM), which uses charge motifs generated from small prototype systems to construct the charge densities of large nanosystems without doing selfconsistent calculations. This CPM has been used to study inorganic nanocrystals as well as organic polymers. We also develop other linear scaling methods for large system calculations. These include the divide-and-conquer linear scaling three dimensional fragment method (LS3DF) for large system density functional theory (DFT) total energy calculations; the potential patching methods for shallow impurity calculations. We have also developed a series of new methods for carrier dynamics simulations. One is a variational method to calculate the electron-phonon coupling constants for all the phonon modes all at once from a single selfconsistent calculation. Another is an accelerated non-adiabatic molecular dynamics with proper approximations for carrier transport simulations. The method can simulate a few thousand atom system for a few ps within a few hours using large super computers. Finally, we also carried out code development. Our GPU implemented plane wave pseudopotential code PEtot_GPU can perform a molecular dynamics (MD) simulation of a 512 atom system at the speed of 12 second per MD step.

We have used the above developed methods to study the atomic structure, electronic structures, and transport properties of nanocrystals and organic systems. These include: dipole moments in nanorods; excitons in nanocrystals; electron density of states in disordered polymers; carrier hopping transport in disordered polymers; carrier transport mechanism in a monolayer of self-assembled oligomers; carrier transport in molecular linked quantum dot arrays; nonradiative carrier trapping by deep levels; shallow impurity levels; solid-liquid hybrid phases. We have also forged broad collaborations with experimental groups both inside and outside Lawrence Berkeley National Laboratory (LBNL).

Recent progress

Nonradiative carrier trapping in GaN: We have developed a method to calculate the nanoradiative trapping rate by a deep impurity level. In our example of GaN, this deep level is a Zn substituting Ga and N vacancy complex (Zn_{Ga}-V_N). The nonradiative decay process is induced by electron-phonon interaction. There could be thousands of related coupling constants. Direct calculation based on numerical displacement of atoms will thus require thousands of selfconsistent calculations. We have developed a novel method based on variational principle, which allows the calculations of all these coupling constants between a pair of electron eigen states to be calculated all at once in a single selfconsistent calculation. This makes it practical to study the nonradiative carrier recombination by a deep level using a few hundred atom supercell. Figure 1 shows the phonon density of states and their contributions to the nonradiativ decay rate.

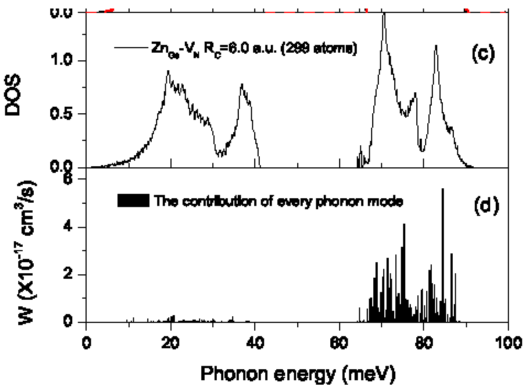

Figure 1, the phonon density of states (uper panel) and their contribution to the nonradiative recombination rate for a Zn_{Ga}-V_N impurity in GaN.

Accurate shallow impurity calculations: We have developed a procedure to calculate the shallow acceptor levels in semiconductors. This procedure combine local density approximation (LDA) large scale calculation (with patched electron potential, for 64,000 atom system) to converge the eigen energies with GW calculation to describe the central-cell potential. Compared to experiment, the calculated shallow impurity binding energy has an error of about 10 meV. We have studied Si:B, Si:Al, Si:Ga, Si:In, Si:Tl, GaP:Bi, GaAs:Si, GaAs:Ge, GaAs:Sn, GaAs:Mg, all shallow acceptor levels. The results are shown in Fig.2.

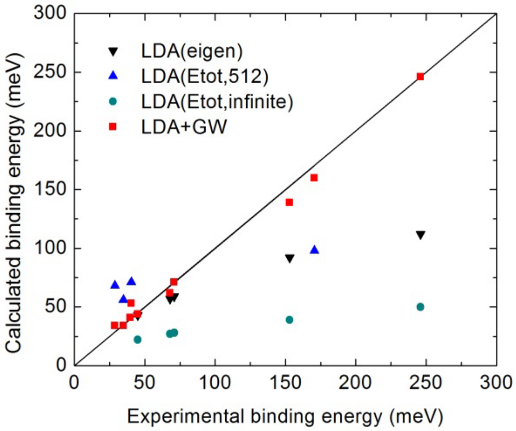

Figure 2, the calculated shallow acceptor binding energy compared with experimental binding energy. The LDA+GW are the current results, while other symbals represent results of othe conventional methods.

Ab initio non-adiabatic molecular dynamics (AB-NAMD): In AB-NAMD, the nuclei dynamics is carried out by Newton's law, while the electron evolution is described by the time dependent Schrodinger's equation. It is a powerful method to study carrier dynamics because it does not require any presumption of the underlying mechanisms of the carrier transport. The drawback for AB-NAMD is its high computational cost, due to the small time step (10^{-3}fs) one needs to use. We have developed a method which increases the time step of the computationally most expensive part to 0.5fs. We have also deployed the charge patching method, and an overlapping fragment method to solve the adiabatic states of the single electron Hamiltonian. Combining all these methods, we have simulated the carrier transport of a monolayer of thiophene ring molecules for 1 ps, which contains 4000 atoms.

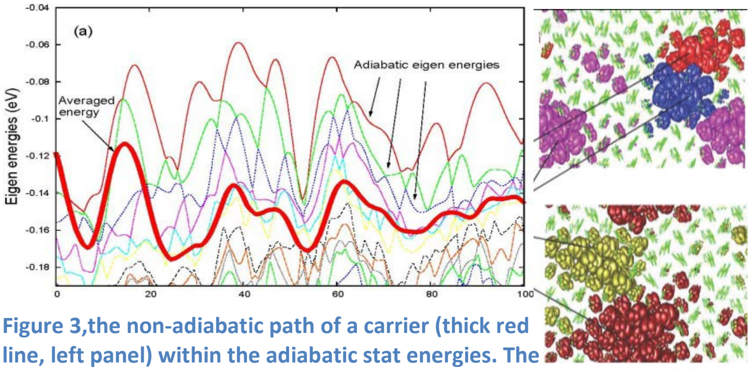

Figure 3,the non-adiabatic path of a carrier (thick red line, left panel) within the adiabatic stat energies. The adiabatic states are shown in the right side panels.

LS3DF atomic relaxation: LS3DF method is a divide-and-conquer DFT total energy method for nanosystem calculations. It divides a system into many small fragments, calculates each fragment quantum mechanically, while patching their charge densities to yield the charge density of the full system. The Poisson equation is solved for the full system, thus the long range Coulomb interaction has been taken into account. It uses a novel patching scheme, which cancels out the artificial boundary effects among different fragments. It is highly accurate, with typical total energy errors of about 10 meV/atom comparing to direct DFT calculations. Due to its divide-and-conquer scheme, it can be massively parallelized (e.g., scaled to 150,000 computer processors). Recently, we have calculated the atomic forces based on LS3DF method, found they are very close to direct DFT calculated force. We have successfully used the atomic forces to relax a Si quantum dots with 4000 atoms. The atomic relaxation is also helped by using an approximated Hessian matrix based on valence force field model.

GPU plane wave pseudopotential DFT calculation: We have implemented our plane wave pseudopotential (PWP) DFT code PEtot on GPU machine based on CUDA programming. This is aimed at overcoming the lack of scaling problem for large scale PWP DFT calculations. Our implementation indicated that GPU can be used to significantly speedup the PWP DFT calculation (e.g., by a factor of 20). However, the program needs to be redesigned, and sometime new algorithms need to be introduced.

Table 1, the number of CPU and GPU processors, and their computational times for 1 MD step of a 512 atom GaAs system.

No. of CPU core	512	1024	2048	4096
PEtot_CPU (time, second)	277	223	203	216
No. of GPU	32	64	128	256
PEtot_GPU(time, second)	31.6	20.8	13.2	11.4

Planned Activities: 2012-2013

We plan to further improve the AB-NAMD method. Currently, we use classical force field method to move the atoms, thus ignoring the polaron effects. We will incorporate the polaron effect in our calculation in the future. We will use this method to systematically study the carrier transport in 2D self-assembled monolayer molecules and to compare with experimental measurements. We will also use AB-NAMD to calculate the charge transport in nanosystems, including nanocrystals connected with linker molecules, or core-shell, and connected quantum dots. We will also use AB-NAMD to study carrier cooling in a nanosystem. Recently, we have developed a realistic ligand passivation model for PbS, PbSe quantum dots. We will investigate the surface defect states based on this surface passivation model. We will study the carrier nonradiative recombination via the surface defect states using our newly developed variational method for electron-phonon coupling constant calculations. We will carry out more shallow impurity calculations, especially use such calculations to explain many fine structures of bulk optical spectroscopy. We will use the LS3DF method to calculate the effects of stress on nanosystems, especially the change of their electronic structures. Finally, we will study the charge transports between connected quantum dots, or between quantum dots and connected molecules.

Publications

- A. Garcia-Lekue, L.W. Wang, "Self-consistent non-equilibrium transport using planewaves" Comp. Mat. Sci. 45, 1016 (2009).
- L.W. Wang, "Ab initio calculation of shallow acceptor levels in Si", J. Appl. Phys. 105, 123712 (2009) .
- N. Vukmirovic, L.W. Wang, "Electronic structure of disordered conjugated polymers: polythiophenes" J. Phys. Chem. B 113, 409 (2009).
- B. Sadtler, D.O. Demchenko, H. Zheng, S.M. Hughes, M.G. Merkle, U. Dahmen, L.W. Wang, A.P. Alivisatos, "Selective facet reactivity during cation exchange in cadmium sulfide nanorods", J. Am. Chem. Soc. 131, 5285 (2009).
- F. Tao, S. Dag, L.W. Wang, Z. Liu, D.R. Butcher, M. Salmeron, G.A. Somorjai, "Restructuring of hex-Pt(100) under CO gas environments: formation of 2-D nanoclusters", Nano. Lett. 9, 2167 (2009).
- L.W. Wang, "Computational challenges for nanostructure solar cells", Energy & Env. Sci. 2, 944 (2009).
- Y. Zhang, A. Mascarenhas, S.H. Wei, L.W. Wang, "Comparison of atomistic simulations and statistical theories for variable degree of long-range order in semiconductor alloys", Phys. Rev. B, 80, 045206 (2009).
- L.W. Wang, "Electronic structure calculations: divide and conquer for tractable computations", SciDAC review, number 14, Fall, page 22 (2009).
- N. Vukmirovic, L.W. Wang, "Chare carrier motion in disordered conjugated polymers: a multiscale ab-initio study", Nano Lett. 9, 3996 (2009).
- M.T. Sheldon, P.E. Trudeau, T. Mokari, L.W. Wang, A.P. Alivisatos, "Enhanced semiconductor nanocrystal conductance via solution grown contacts", Nano Lett. 9, 3676 (2009).
- X.W. Jiang, H.X. Deng, S.S. Li, J.W. Luo, L.W. Wang, "Quantum mechanical simulation of nanosized metal-oxide-semiconductor field effect transistor using empirical pseudopotentials: A comparison for charge density occupation methods", J. Appl. Phys. 106, 084510 (2009).
- Z. Zhao, J.C. Meza, B. Lee, H. Shan, E. Strohmaier, D.H. Bailey, L.W. Wang, "Large scale electronic structure calculations", J. Phys: Conf. Series, 180, 012079 (2009).
- A. Canning, J. Shalf, L.W. Wang, H. Wasserman, M. Gajbe, "A comparison of different communication structures for scalable parallel three dimensional FFTs in first principle codes", Proceed. Parco09, Lyon France (2009).
- S. Dag, L.W. Wang, "Packing structure of Poly(3-hexylthiophene) crystal: ab initio and molecular dynamics studies", J. Phys. Chem. B, 114, 5997 (2010).
- M.G. Vargniory, C. Yang, A. Garcia-Lekue, L.W. Wang, "Calculation of complex band structure for plane-wave nonlocal pseudopotential Hamiltonian", Comp. Mater. Sci. 48, 544 (2010).
- Y. Luo and L.W. Wang, "Electronic structures of CdSe/CdS core shell nanorods", ACS Nano. 4, 91 (2010).
- B. Lee, L.W. Wang, "Electronic structure of ZnTe:O and its usability for intermediate band solar cell", Appl. Phys. Lett. Appl. Phys. Lett. 96, 071903 (2010).
- I.R. Franchini, G. Bertoni, A. Falqui. C. Giannini, L.W. Wang, L. Manna, "Colloidal PbTe-Au nanocrystal heterostructures", J. Mat. Chem. 20, 1357 (2010).
- F. Tao, S. Dag, L.W. Wang, Z. Liu, D.R. Butcher, H. Bluhm, M. Salmeron, G.A. Somorjai, "Break-up of stepped Pt catalyst surfaces by high CO coverage", Science 327, 850 (2010).
- L.W. Wang, "Novel computational methods for nanostructure electronic structure calculations", Ann. Rev. Phys. Chem. 61, 19, (2010).
- N. Vukmirovic, L.W. Wang, "Quantum Dots: Theory", Book Chapter (in press).
- N. Vukmirovic, L.W. Wang, "Carrier heating in disordered conjugated polymers in electric field", Phys. Rev. B 81, 035210 (2010).
- D.H. Bailey, L.W. Wang, Z. Zhao, J. Meza, E. Strohmaier, B. Lee, "Tuning an electronic structure code". Book Chapter, in "Performance Science", Ed. D.H. Bailey, R. Lucas, 2010.
- I. Yamazaki, Z. Bai, H. Simon, L.W. Wang, K. Wu, "Adaptive projection subspace dimension for the thick-restart Lanczos method", Trans. Math. Soft. Vol.37, Number 3 (2010).
- A. Garcia-Lekue, L.W. Wang, "Plane-wave-based electron tunneling through Au nanojunctions", Phys. Rev. B 82, 035410 (2010).

- L.W. Wang, "On the relationship between random phase approximation and the GW calculations", Phys. Rev. B 82, 115111 (2010).
- S. Dag, L.W. Wang, "Atomic and electronic structures of nano and amorphous CdS/Pt interfaces", Phys. Rev. B 82, 241303(R) (2010).
- H.X. Deng, J. Li, S.S. Li, H. Peng, J.B. Xia, L.W. Wang, S.H. Wei, "Band crossing in isovalent semiconductor alloys with large size mismatch: First principles calculations of the electronic structure of Bi and N incorporated GaAs", Phys. Rev. B 82, 193204 (2010).
- M. G. Vergniory, J. M. Granadino, A. Garcia-Lekue, L.W. Wang, "Molecular conductivity switching of two benzene rings under electric field", App. Phys. Lett. 97, 262114 (2010).
- H.X. Deng, J. Li, S.S. Li, H. Peng, J.B. Xia, L.W. Wang, S.H. Wei, "Band crossing in isovalent semiconductor alloys with large size mismatch: First principle calculations of the electronic structure of Bi and N incorporated GaAs", Phys. Rev. B 82, 193204 (2010).
- D.H. Bailey, L.W. Wang, Z. Zhao, J. Meza, E. Strohmaier, B. Lee, "Tuning an electronic structure code", a chapter in "Performance Tuning of Scientific Applications", Editors: D.H. Bailey, R. Lucas, S. William (Chapman & Hall, CRC Computational Science Series, 2010).
- N. Vukmirovic, L.W. Wang, "Carrier hopping in disordered semiconducting polymers: How accurate is the Miller-Abrahams model?", App. Phys. Lett. 97, 043305 (2010).
- X.W. Jiang, S.S. Li, J.B. Xia, L.W. Wang, "Quantum mechanical simulation of electron transport in nanostructured devices by efficient self-consistent pseudopotential calculation", J. Appl. Phys. 109, 054503 (2011).
- N. Vukmirovic, L.W. Wang, "The density of states and wave function localization in disordered conjugated polymers: a large scale computational study", J. Phys. Chem. B 115, 1792 (2011).
- N. Vukmirovic, L.W. Wang, "Overlapping fragments method for electronic structure calculations of large systems", J. Chem. Phys. 134, 094119 (2011).
- S. Dag, S.Z. Wang, L.W. Wang, "Large surface dipole moment in ZnO nanorods", Nano Lett. 11, 2348 (2011).
- S. Xun, X. Song, H. Zheng, V.S. Battaglia, G. Liu, N. Vukmirovic, L.W. Wang, P. Olalde-Velasco, W.L. Yang, "Polymers with tailored electronic structure for ultra-high performance lithium battery electrodes" Advance Mat. 23, 4679 (2011).
- B. L.M. Hendriksen, F. Martin, Y. Qi, C. Mauldin, N. Vukmirovic, A. J. Katan, V. Altoe, S. Aloni, J.M.J. Frechet, L.W. Wang, M. Salmeron, "Electrical transport properties of oligothiophene based molecular films studied by current sensing atomic force microscopy", Nano Lett. 11, 4107 (2011).
- Y. Zhang, L.W. Wang, "Insights into the global electronic structure of semiconductor alloys through direct large scale computations for III-V alloys GaxIn1-xP", Phys. Rev. B 83, 165208 (2011).
- H. Zheng, J. Baker, T. Miller, B. Sadtler, A. Lindenberg, L.W. Wang, C. Kisielowski, A.P. Alivisatos, "Observation of transient structural transformation dynamics in a single Cu2S nanorod by TEM", Science 333, 206 (2011).
- J.M. Granadino-Roldan, N. Vukmirovic, M. Fernandez-Gomez, L.W. Wang, "The role of disorder on the electronic structure of conjugated polymers: the case of poly-2,5-bis(phenylethyny)-1,3,4-thiadiazole", Phys. Chem. Chem. Phys. 13, 14500 (2011).
- I-H. Chu, M. Radulaski, N. Vukmirovic, H.-P. Cheng, L.W. Wang, "Charge transport in a quantum dot supercrystal", J. Phys. Chem. C 115, 21409 (2011).
- L. Wang, W. Jia, X. Chi, Y. Wu, W. Gao, L.W. Wang, "Large scale plane wave pseudopotential density functional theory calculations on GPU cluster" SC11 Proceedings of 2011 International Conference for High Performance Computing, Networking, Storage and Analysis (ACM, New York, NY, 2011).
- W. Jia, Z. Cao, L. Wang, J. Fu, X. Chi, W. Gao, L.W. Wang, "The analysis of a plane wave pseudopotential density functional theory code on a GPU machine" Comp. Res. Comm. (in press)
- L.W. Wang, "High chalcocite Cu2S: A solid-liquid hybrid phase", Phys. Rev. Lett 108, 085703(2012)

Modeling Dynamically and Spatially Complex Materials: Accurate Classical Potentials to Mimic BCC Metal Properties

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Project Scope

A standard tool for calculations in condensed matter physics, material science, and chemistry is density-functional theory (DFT) – a computational methodology rooted in quantum mechanics. While DFT calculations are usually highly accurate and reliable, they are computationally expensive and therefore limited to studies of small systems over short times. On the other hand, molecular dynamics (MD) simulations based on classical inter-atomic potentials are much less computationally demanding, greatly extending materials simulations beyond the reach of DFT. Classical MD simulations are capable of studying diverse phenomena including plasticity, deformation under shock, atomic diffusion, and phase transformations. Vital to the success of MD simulations are high-quality potentials capable of mimicking the quantum mechanical interactions between atoms. Force-matching provides a bridge between accurate DFT and classical potentials by optimizing the potential parameters to forces, energies, and stresses computed by DFT for representative atomic configurations. Our potentials are constructed using the force-matching method and a fitting database containing a large number of forces from DFT-based MD simulations, as well as many DFT-computed physical properties. Fitting to force data from a variety of temperature and stress conditions creates potentials that are accurate over a large range of simulation conditions. Generating accurate potentials is an optimization problem in a high dimensional space. Our potentials are parameterized by splines, and the spline knots are optimized using a combination of simulated annealing and conjugate-gradient-like algorithms. Testing is the critical part of the fitting procedure. Rigorous and extensive tests for a wide range of properties properly gauge the quality of our potentials and lead to progressively better potentials during the iteration cycle of fitting. We assess the quality of our potentials by comparing a wide variety of computed properties to DFT calculations and experimental data: energy-volume curves for various crystal phases, elastic properties, point defects, low-index surface properties, phonons, thermodynamic behavior including melting, generalized-fault energies along major slip directions, the ideal shear, and the Peierls stress. All the testing procedures are automated by an efficient script, and results are presented in graphic/tabular forms. A significant amount of effort has been devoted to develop a systematic scheme that can produce accurate and reliable inter-atomic potentials. A cubic-spline-based modified embedded-atom method (MEAM) potential was developed for pure Ti [13] that accurately describes martensitic phase transformations between the hcp α, bcc β, and hexagonal ω phases. We have also developed an embedded-atom method (EAM) potential for pure Nb [11] and a MEAM potential for Mo [2] that accurately models a large variety of behavior, including structural and elastic properties, surface energies and relaxations, and melting.

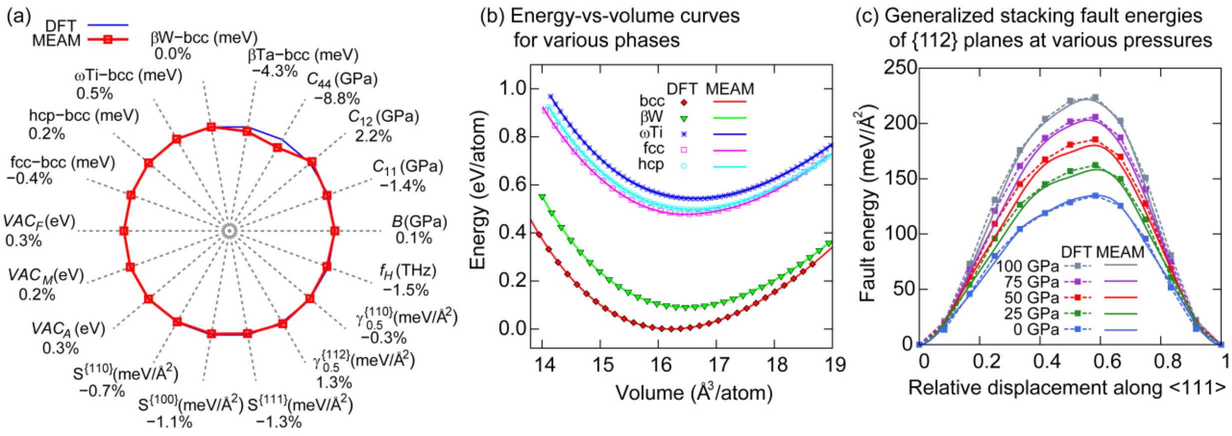

Figure 1: Examples of test results of one of our SW+MEAM potential for bcc W: (a) a radial plot for various properties, (b) energy vs. volume curves for bcc and four different meta-stable phases, and (c) generalized stacking fault energies of {112} planes along <111>. The classical potential reproduces DFT results for many properties with excellent agreement. In the radial plot (a), a circle is divided by 20◦, yielding 18 different radial directions. Each radial direction is associated with one of the physical properties: elastic constants, energies of various crystal phases, formation and migration energies of vacancy, low-index surface energies, gamma surface energies, and phonon frequency. DFT values are normalized in each property direction to form a regular octadecagon, represented by blue solid lines. Test results for classical potentials are normalized by DFT values in each direction, and represented by red connected squares.

Recent Progress

The most promising inter-atomic potentials for metals include EAM and MEAM potentials. EAM potentials are based on ideas from DFT and include effective many-body effects. MEAM potentials extend EAM potentials by additionally including explicit three-body interactions. We are developing EAM and MEAM potentials for the commercially important body-centered cubic (bcc) refractory metals (V, Nb, Ta, Mo, and W) in an effort to systematically study the behavior of the potentials under a variety of simulation conditions. This effort will provide insights into the capabilities of potentials for transition metals, produce accurate potentials for these metals, and provide a solid foundation for developing potentials for important alloy systems.

In addition to EAM and MEAM, we are also exploring a new format of spline-based classical potential that hybridizes both the Stillinger-Weber (SW) potential and the MEAM potential, which we currently address as SW+MEAM. By including the SW potential into the MEAM potential form we are adding more complexity and free parameters to the MEAM potential in the hopes that we are better able to mimic more quantum mechanical properties at a fraction of the computational cost. Our preliminary results for Mo and W show just that. The SW+MEAM potentials are able to reproduce the energy vs. volume curves for many low-lying metastable phases, and perform well in a battery of tests for various mechanical properties using DFT results as the benchmark in our comparisons, as can be seen in Fig. 1.

Developing a spline-based SW+MEAM using the previous fitting routine such as simulated annealing followed by a Powell least-squares minimization have become too computationally expensive to run on any current supercomputers. Also with the added complexity of the SW+MEAM functional form, finding a global minimum fit to large DFT database is proven to be too difficult for simulated annealing. A new optimizer is desperately needed with two goals in mind: (a) speed – fast optimizer that can quickly lead to a minima and (b) quality - optimizer that can consistently give the global minimum in a complex multidimensional space. Our preliminary results show a hybrid combination of the genetic algorithm and the Powell least-squares minimization routine satisfies both of these criteria. This new hybrid optimizer outperforms simulated annealing in every test case by at least an order of magnitude in speed. The hybrid optimizer is also capable of searching a more complex multidimensional space that we have seen simulated annealing consistently fails at. This new optimizer, we believe, is capable of computationally fitting long-range potentials that can better match DFT across a range of thorough tests that were previously impossible with any other classical potential fitting code.

Future Plans

The MEAM formalism is inherently a more complete description of complex materials than EAM since it explicitly includes a three-body bond-bending term. However, a thorough and systematic comparison of the two methods has not been conducted in the literature. Our initial comparisons of EAM potentials to MEAM potentials, both fit to the same data for a given metal, indicate that MEAM potentials can improve over EAM for some properties and generally agree better with experimental values and DFT calculations. We will conduct systematic comparisons between EAM and MEAM potentials over a wide range of properties.

Our success in constructing classical potentials for pure Ti and pure Nb motivates us to construct classical potentials for Ti-Nb alloys. Ti-Nb alloys undergo martensitic phase transformations leading to superelasticity. This, coupled with Nb's non-toxicity, makes Ti-Nb alloys promising materials for biomedical implants. Nb is also a major constituent of Gum Metal alloys - multicomponent bcc titanium alloys with exotic deformation properties. Ti-Nb serves as a tractable starting point for theoretical studies of Gum Metals. Classical potentials will be developed for use in molecular dynamics simulations to study the dynamics of phase transformations and deformation processes in Ti-Nb alloys.

The abundance of accurate and reliable classical inter-atomic potentials allows us to design some spin-off projects. Despite great advances in scientific computing results from many property simulations still remain unclear or controversial in materials science. One of them is the study of the low-temperature plasticity of bcc metals. Particularly, simulations for structures and dynamics of screw dislocations will be carried out. The DFT simulations for dislocations require large computational cells, and special boundary conditions to accommodate the long-range distortion. Hence, reported DFT results are scarce, and often problematic. Large-scale simulations with a large number of accurate inter-atomic potentials will lead to better understanding of plasticity of bcc metals. Studying phase diagrams including melting behaviors for some transition metals at high pressures and temperatures is another spin-off project that we can perform with good inter-atomic potentials.

Publications

1. "Magnetic states and optical properties of single-layer carbon-doped hexagonal boron nitride", Hyoungki Park, Amita Wadehra, John W. Wilkins, and Antonio H. Castro Neto, *Appl. Phys. Lett.* 100, 253115 (2012).
2. "Ab initio based empirical potential used to study the mechanical properties of molybdenum", Hyoungki Park, Michael R. Fellinger, Thomas J. Lenosky, William W. Tipton, Dallas R. Trinkle, Sven P. Rudin, Christopher Woodward, John W. Wilkins, and Richard G. Hennig, *Phys. Rev. B* 85, 214121 (2012).
3. "Energy landscape of silicon tetra-interstitials using an optimized classical potential", Yaojun A Du, Thomas A Lenosky, Richard G Hennig, Stefan Goedecker, John W Wilkins, *Phys. Status Solidi B* 248, 2050 (2011).
4. "A topological point defect regulates the evolution of extended defects in irradiated silicon", Hyoungki Park and John W. Wilkins, *Appl. Phys. Lett.*98, 171915 (2011).
5. "Accuracy of Quantum Monte Carlo Methods for Point Defects in Solids", William D. Parker, John W. Wilkins, and Richard G. Hennig, *Phys. Status Solidi B* 248, 267-274 (2011).
6. "Accurate electronic properties for (Hg,Cd)/Te systems using hybird density functional theory", Jeremy W. Nicklas and John W. Wilkins, *Phys. Rev. B* 84, 121308 (2011).
7. "Band offsets of semiconductor heterostructures: A hybrid density functional study", Amita Wadehra, Jeremy W Nicklas, and John W Wilkins, *Appl. Phys. Lett.* 97, 092119 (2010).
8. "Accurate ab-initio prediction of III-IV direct-indirect gap crossovers", Jeremy W Nicklas and John W. Wilkins, *Appl. Phys. Lett.* 97, 091902 (2010).
9. "Phase transformation in Si from semiconducting diamond to metallic beta-Sn phase in QMC and DFT under hydrostatic and anisotropic stress", R. G. Hennig, A. Wadehra, K. P. Driver, W. D. Parker, C. J. Umrigar, and J. W. Wilkins, *Phys. Rev. B* 82, 014101 (2010).
10. "Quantum Monte Carlo computations of phase stability, equations of state, and elasticity of high-pressure silica", Kevin P. Driver, R. E. Cohen, Zhingang Wu, R. Militzer, R. Lopez Rios, M. D. Towler, R. J. Needs, and J. W. Wilkins, *PNAS* 107, 9519-9524 (2010).
11. "Force-matched embedded-atom method potential for niobium", Michael R. Fellinger, Hyoungki Park, and John W. Wilkins, *Phys. Rev. B* 81, 144119 (2010).
12. "Relativity stability of extended interstitials in silicon", Hyoungki Park, and John W. Wilkins, *Phys. Rev. B* 79, 241203(R) (2009).
13. "Classical potential describes martensitic phase transformations between the α, β, and ω titanium phases", R.G. Hennig, T.J. Lenosky, D.R. Trinke, S.P, Rudin, and J.W. Wilkins, *Phys. Rev. B* 78, 054121(R) (2008)

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Theory of Hydrogen Storage in Complex Hydrides

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PROJECT SCOPE

We are developing a systematic, quantitative approach to designing novel materials with fast (de)hydrogenation kinetics using state-of-the-art first-principles density functional theory calculations based on microscopic models of nucleation, mass transport, and diffusion. One of our main objectives is to develop a comprehensive theoretical framework for describing the kinetics of phase transformations in multinary complex hydrides, including the nucleation and growth of product phases upon hydrogen release and uptake. This framework will fill a critical basic science area of need in the hydrogen storage field, providing an in-depth atomistic picture of the kinetics of phase transformations controlling the rate of hydrogen release from multicomponent complex hydrides.

The successful prediction of novel materials and reactions will also require development of more broadly applicable computational tools, which we are developing: (i) computational prediction of crystal structures of new materials, (ii) Monte Carlo methods to deduce stable interfaces (for nucleation kinetics), and (iii) the use of high-throughput computation and data mining tools to elucidate descriptors for materials properties.

RECENT PROGRESS

First Principles-Assisted Structure Solution

We have extended our earlier work on a symmetry-leveraging genetic algorithm (SLGA) designed to computationally solve crystal structures in a known space group. The enhanced approach, which we refer to as first principles-assisted structure solution (FPASS), now combines three elements to map an input diffraction pattern to a density functional-validated structure: 1) a computational structure optimization engine (a genetic algorithm acting on DFT total energies); 2) the target crystal's experimental candidate space group(s) and diffraction pattern; and 3) mined information on Wyckoff site occupancies in different space groups from the Inorganic Crystal Structure Database. FPASS is more robust and widely applicable than our first-generation SLGA, and we have successfully applied it to a wide variety of test cases: the hydrogen storage candidates MgNH and NH_3BH_3; Li_2O_2, relevant to Li-air batteries; the shape-memory alloy NiTi; and high-pressure silane, SiH_4.

Mass Transport in the $B_{20}H_{16}$ System

Using DFT calculations, we recently predicted that $B_{20}H_{16}$ should release 7 wt. % H2 at 20 °C and a pressure of 1 bar following: $B_{20}H_{16} \rightarrow 20B + 8H_2$. With this large hydrogen capacity and nearly ideal thermodynamic properties, this system is attractive for storage applications. However, there is no experimental data on the reaction kinetics. Following the methods of mass transport kinetics (developed by us, and initially applied to $NaAlH_4$ reactions), we have studied point defect energetics in both bulk $B_{20}H_{16}$ and B in order to gain insight into the mass transport kinetics. We find the defect formation energies in $B_{20}H_{16}$ are much lower than those in B, leading to large concentrations of defects in the former. In particular, we find that the lowest-energy defect is interstitial H_2 in $B_{20}H_{16}$. From this we conclude that mass transport is dominated by interstitial H_2 diffusion through $B_{20}H_{16}$.

The overall mass transport rate will be determined by the activation energy, $E_{act} = E_{form} + E_{mig}$, where the latter two terms described the defect formation and diffusion energetics, respectively. We have evaluated the formation energy and find that it is equal to 58 kJ/mol under dehydrogenation conditions and -6 kJ/mol under rehydrogenation conditions. We are in the process of evaluating the migration barrier; however, given the relatively low values of E_{form}, the activation energy is likely to be low enough that mass transport will occur relatively rapidly compared to other hydrogen storage systems.

Symmetry-Building Monte Carlo-Based Structure Prediction

Unconstrained structure prediction is unfeasible in even moderately sized systems. In reality, most crystals have higher than P1 symmetry, which sets constraints on some atomic coordinates and lattice vectors. These restraints reduce the number of crystallographic degrees of freedom and can be used to limit the search space during structure prediction. However, in cases where there exists no experimental information about the structure, these symmetries are a priori unknown.

We have developed a Monte Carlo-based structure prediction code that builds and leverages symmetry on the fly. Symmetry is treated in two steps: in the first, the symmetry is calculated to within some tolerance (e.g. 0.5 angstroms), after which the basis vectors and atomic coordinates are refined so that they exactly satisfy these symmetry requirements; secondly, subsequent trial moves are generated so that they do not violate any of the restrictions imposed by the set of symmetry operations. The symmetry-building step is treated as a Monte Carlo move so that it is attempted and accepted with some probability. In this way, the symmetry can be increased as the simulation proceeds (starting from no symmetry at all), simultaneously reducing the number of degrees of freedom that must be explored.

Monte Carlo Study of Nucleation in Hydrogen Storage Reactions

Recent work has focused on the study of mass transport as a possible rate-limiting step in hydrogen storage reactions. However, there is experimental evidence that nucleation may be rate-limiting in some cases; in the $MgH_2 + 2LiNH_2$ system, the activation energy has been observed to decrease on product seeding with $Li_2Mg(NH)_2$. In order to study the nucleation kinetics, we must first know which interfaces exist between the bulk and nucleus structures. Due to the complexity of structures of many metal hydrides, the number of possible interfaces (including relative orientations) between phases is too large to study exhaustively using first-principles methods.

We are developing a Monte Carlo-based code that will be used to search for possible interfaces found during nucleation. The code is built on classical potentials, which will be fit specifically to each system of interest. A search is then performed for the ground-state structure of the nucleus embedded in the bulk phase. From this, we can identify which interfaces are the most prevalent and therefore the lowest in energy. Finally, more accurate first-principles calculates can be carried out on this much smaller set of interfaces.

Modeling Dopant Solubility in Cubic Zirconia

A standard approach to understanding physical phenomena in materials is to search manually for clear interrelationships among properties, often by employing basic statistics such as linear regressions. The goal of such a search is to identify a *descriptor* variable that meaningfully explains a trend in another target property. But what if a materials data set is too large and/or chemically diverse to explain by straightforward human inspection or known descriptors? We present such a case by performing large-scale first-principles calculations to determine the solubility thermodynamics of 70 dopant cations in cubic zirconia. This data set, spanning three charge states and most non-synthetic metals in the periodic table, defies simple “manual” explanation, and is not captured by two established materials descriptors: cation size and *d*-band theory. To overcome these challenges, we employ advanced statistical methods [see Reshef et al., Science 334, 6062 (2011)] and data mining algorithms to cluster the dopants into distinct classes that behave similarly in zirconia.

In Figure 1, we give the results of X-means clustering [Pelleg and Moore, Proc. 17th Intl. Conf. Machine Learn. (2000)] on our collection of dopants. In this approach, we first enumerate a wide variety of properties of the dopants’ parent oxides (e.g., BaO, Fe_2O_3, ThO_2); these properties are both DFT-calculated (e.g., band gap) and empirical (e.g., electronegativity). Then, we use these properties as input to a clustering algorithm, which identifies groups of dopants that are *most alike each other*. These clusters, which should behave similarly in zirconia, form the basis of our subsequent solubility model.

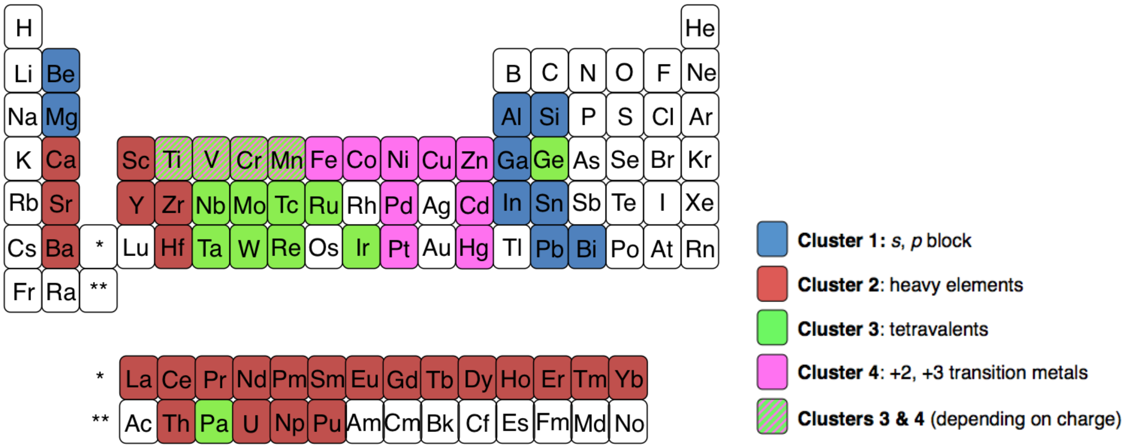

Figure 1. Results of our X-means clustering analysis, which we applied to data on the 70 dopant binary oxides in this study. The clustering algorithm identifies chemically meaningful relationships that appear on the periodic table, without supplying any human knowledge.

FUTURE PLANS

In the next year, we are planning to conduct an in-depth study of mass transport for the decomposition of magnesium borohydride, which will require calculations of defect energies and diffusion coefficients in magnesium borohydride, magnesium hydride, and magnesium closoborane. We are also planning to initiate studies of nucleation kinetics in sodium alanate to determine whether the nucleation of one of the product phases is a rate-limiting step in undoped samples.

We have concentrated during the present year on the development of a variety of novel methodologies: symmetry-constrained Monte Carlo, Monte-Carlo based nucleation code, symmetry-leveraged crystal structure solution, and high-throughput data mining schemes. It is anticipated that in the coming year, we will be extensively testing these novel methodologies on a wide variety of materials and hydrogen storage reactions.

PUBLICATIONS WITH ACKNOWLEDGED DOE SUPPORT

1. C. Kim, S.-J. Hwang, R. C. Bowman, Jr., J. W. Reiter, J. A. Zan, J. G. Kulleck, H. Kabbour, E.H. Majzoub, and V. Ozolins, "LiSc(BH4)4 as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density-Functional Theory Studies," to appear in Journal of Physical Chemistry C (2009).
2. Y.-S. Lee, Y. Kim, Y. W. Cho, D. Shapiro, C. Wolverton, and V. Ozolins, "Crystal structure and phonon instability of high-temperature β-Ca(BH4)2", Physical Review B 79, 104107 (2009).
3. V. Ozolins, E. H. Majzoub, and C. Wolverton, "First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H system," Journal of the American Chemical Society 131 (1), 230-237 (2009).
4. D. E. Farrell, D. Shin, and C. Wolverton, "First-principles molecular dynamics study of the structure and dynamic behavior of liquid Li4BN3H10", Phys. Rev. B 80, 224201 (2009).
5. V. Ozolins, A. R. Akbarzadeh, H. Gunaydin, K. Michel, C. Wolverton and E. H. Majzoub, "First-principles computational discovery of materials for hydrogen storage", Journal of Physics: Conference Series 180, 012076 (2009).
6. J. Yang, A. Sudik, C. Wolverton and D. J. Siegel, "High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery", Chem. Soc. Rev. 39, 656 (2010).
7. D. Farrell and C. Wolverton, "First-Principles Study of Vacancies and Hydrogen Interstitials Under Varied Chemical Conditions in $Li_4BN_3H_{10}$", Phys. Rev. B **85**, 174102 (2012).
8. Y. Zhang and C. Wolverton, "Crystal Structures, Phase Stabilities, and Hydrogen Storage Properties of Metal Amidoboranes", J. Phys. Chem. C **116**, 14224 (2012).
9. G. Grimvall, B. Magyari-Köpe, V. Ozolins, and K. Persson, *"*Lattice instabilities in metallic elements,*"* Reviews of Modern Physics **84**, 945–986 (2012).
10. D. Farrell and C. Wolverton, Structure and Diffusion in Liquid Complex Hydrides via Ab Initio Molecular Dynamics, (submitted to Phys. Rev. B, 2012).
11. Y. Zhang, Y. Wang, K. Michel, and C. Wolverton, "First-principles insight into the degeneracy of ground state $LiBH_4$ structures" (submitted to Phys. Rev. B, 2012).
12. B. Meredig and C. Wolverton, "A Hybrid Computational-Experimental Approach for Automated Crystal Structure Solutions" (submitted to Nature Materials, 2012).
13. X. Chen et al., "Structure Determination of an Amorphous Compound AlB_4H_{11}" (submitted to J. Amer. Chem. Soc., 2012).

Long Ranged Dispersive Interactions in Graphitic Nanostructures

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Main Thrust of the Project

Long ranged interactions, such as van der Waals and Casimir forces, are of fundamental importance for understanding the basic science of nanostructured graphitic materials. Such interactions are responsible for how different graphitic systems interact between each other and with other materials. The objective of this project is to investigate how unique properties stemming from the dimensionality, curvature, and honeycomb carbon atom arrangement influence the van der Waals/Casimir forces. For this purpose, analytical techniques with various degrees of approximations, capable of revealing various important contributions, are developed. The general strategy is to build a comprehensive theory that accommodates the important factors contributing to such dispersive interactions, and elucidate each one by studying limiting cases. Following this path, we are able to uncover an array of unusual functionalities of how graphitic interactions interact. Various ways to manipulate the magnitude and sign of van der Waals/Casimir force as well as practical devices are also found.

Van der Waals/Casimir Forces – Interactions of Collective Nature

Perhaps the simplest way to calculate van der Waals forces is to utilize the Lennard-Jones method. It is essentially a pairwise additive approximation relating the interaction to a set of constants which can be determined experimentally or calculated via *ab initio* methods. This approach is particularly attractive due to its simplicity and correct description of equilibrium configurations. We have utilized it for the prediction of new devices based on finite length carbon nanotubes, such as surface profiling and hot nanolithography applications [1, 2] – Fig. 1. However, the long ranged dispersive interactions are inherently of many-body character. A powerful way to investigate this point is to employ the discrete dipole method, which relies on taking each structure to be a collection of discrete dipoles. This is a unique

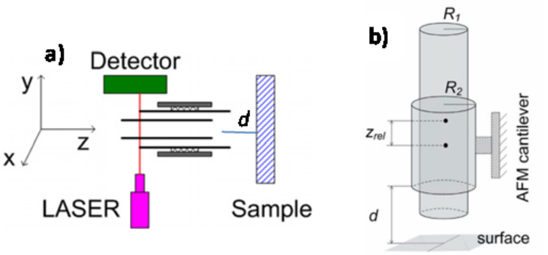

Fig. 1 ***a)*** *Surface profiling device based on oscillating double wall CNT;* ***b)*** *Double wall CNT for hot nanolithography. d is the distance between the stationary nanotube and the surface.* z_{rel} *is the distance between the centers of masses for the outer and inner tubes.*

method since it gives all many-body contributions to be exactly the same as the ones from quantum mechanical considerations [3].

Quantum Electrodynamical Approach and Graphitic Nanostructures Interactions

The discrete dipole method is an atomistic approach giving an exact solution for the many-body van der Waals energy, but it cannot be readily applied to extended objects or take into account the speed of light. In addition, the collective effects arising from the effective Coulomb interaction are also not included. To remedy these shortcomings, we have developed a Quantum Electrodynamics (QED) approach, which includes the specific boundary conditions and the collective nature of the electromagnetic fluctuations via the particular dielectric and magnetic response properties of the materials [4]. The difficulty here is obtaining a dyadic Green's function tensor that satisfies the Maxwell's equations for various geometries. Nevertheless, we are able to find a general solution for concentric carbon nanotubes, planar graphene sheets, and parallel graphene nanoribbons systems.

Significant efforts are devoted to obtaining the response properties of the interacting objects. This includes not only the response properties for the graphitic systems, but also other materials. For example, we utilize the random phase approximation (RPA) for carbon nanotubes. The nanotube electronic structure was calculated via in-house built nearest neighbor non-orthogonal tight binding model. For graphene, the optical properties are accounted for through its two-dimensional conductivity calculated with the Kubo formalism.

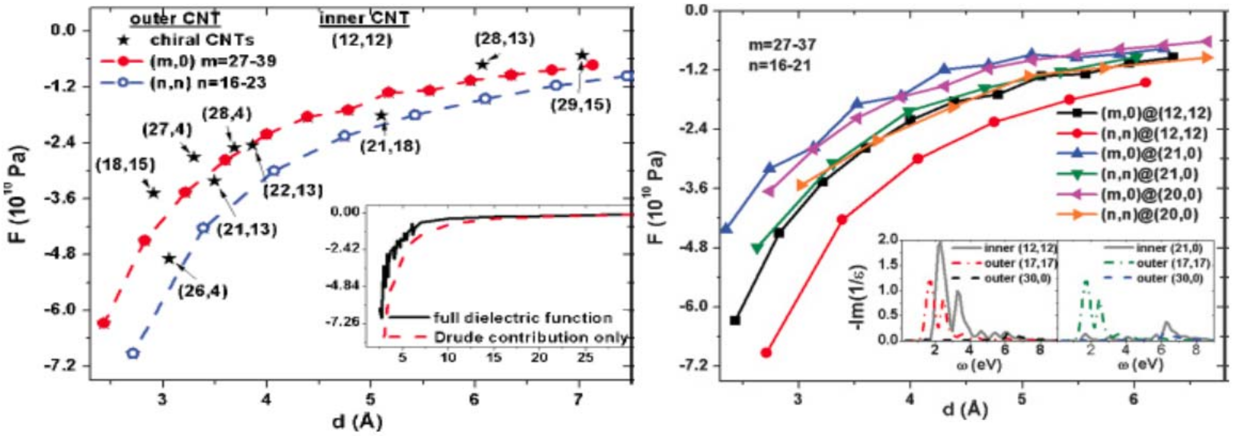

Fig. 2 *Casimir force of two concentric nanotubes vs. the inter-tube distance for* ***a)*** *(12,12) inner tube and different (n,m) chiralities of the outer one;* ***b)*** *CNTs with different chiralities.*

The QED approach clearly demonstrates the crucial importance of the collective low energy surface plasmon excitations of the carbon nanotubes at relatively close surface-to-surface separations within the concentric cylindrical geometry [5]. The dispersive attraction is dominated by the low energy (inter-band) plasmon excitations of both nanotubes. The key attributes determining the interaction are the existence of low frequency overlapping plasmons with strong and well pronounced peaks for both tubes. These results help us find a relationship between the strength of the interaction and the particular chiaralities of the nanotubes – Fig. 2. As the inter-tube separation increases, the plasmon effect diminishes and the collective excitations originating from the nanotube metallic or semiconducting nature do not influence the interaction in a profound way.

The dispersive interactions involving graphitic sheets has unusual functionalities as well. The van der Waals/Casimir graphene/graphene force is extremely temperature dependent. In the quantum limit (temperature $T=0$), the interaction is found to be $F = -3e^2/(32\pi d^4)$, showing that it does not depend on any quantum mechanical characteristics or the speed of light (e is the electron charge and d – the separation) [6]. F is also significantly reduced as compared to the force between two perfect metals given by $F_0 = -\hbar c\pi^2/(240d^4)$ ($\hbar$ is Plank's constant). The situation is very different when $T \neq 0$. Because of the linear wave vector dependence in the energy, the graphene thermal fluctuation length is significantly reduced. For regular dielectrics $\lambda_T = \hbar c/k_B T$ (k_B is Boltzmann constant), however, for graphene one finds that this length is ~$\lambda_T/200$. Thus even for low temperature ($T \geq 30\ K$), the Casimir force is described mainly by the thermal fluctuation contribution $F_T = -k_B T\varsigma(3)/(8\pi d^3)$ ($\varsigma(3)$ is Riemann zeta-function) [7].

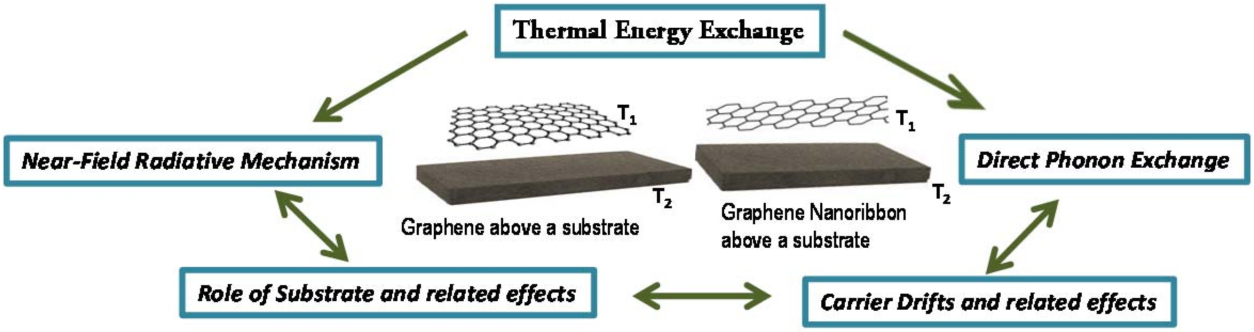

Fig. 3 Diagram of the main topics and systems to be investigated

Future Work – 2012-2013

Our work so far has been centered at situations when the interacting objects are at thermal equilibrium. Thermal exchange via electromagnetic radiation between objects held at different temperatures is a natural extension for the direction of this project. Understanding its science in terms of basic laws and functionalities is in the core of finding efficient ways of energy transfer management. Graphitic nanostructures offer a unique opportunity to investigate various aspects of this challenging problem. Their unusual properties not only promise discovering novel effects, but they are also relevant for future applications, especially in electronics, where heat exchange is an important factor.

The future development of our investigation will be on proximity thermal energy transfer and related effects in graphene/substrate and graphene nanoribbon/substrate systems – Fig. 3. Since graphitic nanostructures interact via long-ranged forces with other materials due to their chemically inert nature, near-field radiative and direct phonon exchange are the main mechanisms to be investigated here. The objective of the proposed work is to study the role of dimensionality, distance separations, types of substrates, and graphitic nanostructure characteristics in order to determine various regimes, where one or both processes are relevant. Of particular interest will be the response and phonon properties of the systems, since they are directly related to the long-ranged nature of these processes. Novel effects, such as piezoelectricity and magnetic response from metamaterials, will also be explored to tailor the energy exchange. In addition, the relative carrier motion and its role in these temperature dependent proximity processes as well as possible induced drag effects will be studied.

Efforts will be devoted to extend the previously developed QED approach in order to include temperature dependence and utilize scattering matrix techniques in order to account for more complicated than infinite planar geometries. We will continue building the fundamental understanding of response properties and relevant phonon properties of graphitic nanostructures and the substrate materials of interest, as well. The proposed directions will give us a platform not only to generalize the theoretical methods developed so far, but also to bring forward the basic science of energy transfer in graphitic nanostructures due to long-ranged interactions.

References:

1. A. Popescu, L.M. Woods, and I.V. Bondarev, *"A Carbon Nanotube Oscillator as a Surface Profiling Device",* Nanotechn. **19**, 435702 (2008), US Patent 8060943;

2. A. Popescu and L.M. Woods, *"Telescopic Hot Double Wall Carbon Nanotube for Nanolithography"*, Appl. Phys. Lett. **95**, 203507 (2009), Provisional Patent Application 09B090_Popescu;

3. Y. V. Shtogun and L.M. Woods, *"Many-Body van der Waals Interactions between Graphitic Nanostructures",* J. Phys. Chem. Lett. **1**, 1356 (2010);

4. L.M. Woods, A. Popescu, D. Drosdoff, and I.V. Bondarev, "*Dispersive Interactions in Graphitic Nanostructures*" (review), Chem. Phys., under review;

5. A. Popescu, L.M. Woods, and I.V. Bondarev, "*Chirality dependent carbon nanotube interactions*", Phys. Rev. B **83**, 081406 (R) (2011);

6. D. Drosdoff and L.M. Woods, "*Casimir forces and graphene sheets*", Phys. Rev. B **82**, 155459 (2010);

7. D. Drosdoff, L.M. Woods, A.D. Phan, and I.V. Bondarev, "Effects of spatial dispersion on the Casimir force between two graphene sheets", EPL, under review.

Density Functional Theory for Phase-Ordering Transitions

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Project Scope

This project is focused on theoretical developments for quantitative predictions of the microscopic structure, phase behavior, and dynamic responses of complex molecular systems from atomic constituents. The emphasis is on development and applications of the density functional theory (DFT) and its extensions to dynamic processes and non-equilibrium systems. On the one hand, we will formulate accurate free-energy functionals for systems at or near equilibrium and master equations for dynamic processes in systems far away from equilibrium, and calibrate the numerical performance of the new theoretical methods by using molecular simulation and/or experimental results. On the other hand, we pursue practical applications of these new theoretical tools for describing time-dependent processes of practical concerns; these include solvation and solvent-mediated potential of mean forces, self-assembly and phase transition in colloidal dispersions, structure and phase behavior of polymeric fluids, and ion transport in porous materials. Our long-term objective is to provide computational supports for understanding and reliable prediction of the phase behavior and the physicochemical properties of a wide variety of molecular systems. We expect that the theoretical tools will be important for design and optimization of industrial processes, in particular those pertinent to development of sustainable technologies for renewable energy production, storage and transmission.

Recent Progress (2011-2012)

Over the past 12 months, the research was mainly concerned with 1) application of the density functional theory to local-and-key interactions in colloidal systems; 2) solvent receding and drying transition near colloidal surfaces; 3) development of an efficient computational procedure to calculate direct correlation function of molecular solvents; 4) development of theoretical method for rapid prediction of solvation free energy.

1) Colloidal lock-and-key interactions

A conventional wisdom for controlling nanoparticle size and shape during the synthesis is that particle growth favors the direction of a facet with the highest surface energy. However, the particle solvation free energy, which dictates the particle stability and growth, depends not only on the surface area/free energy but also on other geometric measures such as the solvent excluded volume and the surface curvatures and their affiliated thermodynamic properties. In this work, we have studied the geometrical effects on the solvation free energies of non-spherical nanoparticles using morphometric thermodynamics and density functional theories. For idealized systems that account for only molecular excluded-volume interactions, morphometric thermodynamics yields a reliable solvation free energy when the particle size is significantly larger than the solvent correlation length. However, noticeable deviations can be identified in comparison with the microscopic theories for predicting the solvation free energies of small nanoparticles. The conclusion holds also for predicting the potential of mean force underlying the colloidal “key and lock” interactions. In comparison with the microscopic theories, morphometric thermodynamics requires negligible computational cost and thereby is very appealing for broad practical applications.

2) An efficient algorithm for computing the direct correlation functions of molecular fluids

Direct correlation function (DCF) plays an important role in liquid integral-equation theories and non-mean-field applications of the classical density functional theory. While for a simple fluid, the DCF can be easily calculated from the radial distribution function via the Fourier transform and/or, for special cases, can be derived from analytical expressions, computation of the site-site DCFs of a molecular fluid is more challenging due to numerical issues affiliated with solving the matrix integral equations. In this work, we developed a new theoretical method for accurate evaluation of the site-site DCFs of molecular fluids by combination of molecular simulation and analytical asymptotic analysis. The computational procedure entails four steps: 1) molecular simulation is used to calculate the site-site total correlation functions (TCFs) in real space; 2) the reference-interaction-site model (RISM) is used to calculate the site-site DCFs in Fourier space at large wave numbers; 3) asymptotic expressions are derived for the TCFs and DCFs in the limit of small wavenumbers; and 4) the site-site DCFs over the entire range are obtained by interpolation of the asymptotic results. The numerical procedure has been illustrated by application to bulk SPC/E water. Accurate evaluation of the site-site DCFs for water prepares a foundation for future applications of DFT to aqueous systems with atomic details.

3) Drying transitions at the surface of non-attractive particles

Solvent distribution near macroscopic substrates is pertinent to materials performance in solutions and a broad range of colloidal systems. Whereas current knowledge has been well advanced, quantification of the microscopic structure of the solvent near an extended surface remains a daunting theoretical challenge. Computational predictions are difficult in particular when solvation is competing with a surface phase transition or occurs near a surface with chemical or topological heterogeneity at a length scale much larger than the size of the solvent molecules. However, the problem is imperative for understanding hydrophobic phenomena near macroscopic substrates and for the rational design and fabrication of superhydrophobic materials. Despite much recent progress, a satisfactory solution is not yet attainable by microscopic theories or by molecular simulations. Interpretation of experimental results often hinges on phenomenological methods or mean-field approximations. In this work, we use a perturbative density functional theory (DFT) to examine the receding of a saturated solvent from a spherical cavity as the cavity radius varies from micro to macro length scales. In contrast to the mean-field predictions, the DFT calculations indicate that the solvent inhomogeneity remains microscopic even when the cavity radius approaches macroscopic limits, suggesting a first-order drying transition at non-attractive surfaces. Whereas the simple model is not intended to represent any specific system of practical concern, we expect that qualitatively the results are relevant to the solvent behavior in realistic systems.

4) Rapid prediction of solvation free energy

We have been developing an atomistic density functional theory (ADFT) as an alternative to molecular simulation for rapid and accurate computation of solvation free energies in an aqueous solvent. In the DFT calculation, the free-energy functional is formulated within the framework of the reference interaction site model (RISM) with a closure that accounts for multi-body correction effects based on the hypothesis of the universality of the bridge functional. With the site-site direct correlation functions of the pure water obtained from molecular simulation and the bridge functional derived from the modified fundamental measurement theory, ADFT enables rapid prediction of the solvation free energies from the atomic density profiles of the solvent molecules around the solute obtained from molecular simulation or from direct free-energy minimization. The new computational procedure is fully compatible with conventional force fields and can be easily integrated with standard simulation packages.

Future Plans (2012-2013)

The next-year research will be direct at 1) development of a theoretical framework for non-equilibrium mixtures and its application to ion transport in porous materials, and 2) investigation of the effects of the strength and range of colloidal forces on the kinetics of crystal growth and implementation of the time-dependent DFT for describing kinetic processes including crystal growth.

1) Ion transport

Much of the design and testing of materials for electric energy storage requires knowledge of ion and solvent transport properties at conditions far away from equilibrium. For example, charging and discharging of supercapacitors involve the transport of the cations, anions, and if in a solution their respective solvation shells, in porous materials. Whereas theoretical methods for predicting the structure and equilibrium properties of electric double layers are well-advanced, the transport properties remain difficult to be predicted by standard computational methods.

In a previous work, we have derived a set of self-consistent master equations for describing the time evolution of the microscopic structure (as represented by one-body densities), local flux distributions, local momentum fluctuations, and the two-body density correlation functions. After certain approximations, the new theoretical framework reduces to conventional non-equilibrium theories including the Vlasov equation, kinetic theories, the lattice Boltzmann method, and various versions of the dynamic or time-dependent density functional theory. While the previous work focused on one-component colloidal systems, we expect that similar theoretical concepts and mathematical equations can be established for multicomponent systems. Such a theory will be useful to describe ion transport in porous materials including organic electrolytes and ionic liquids that are commonly used in energy storage devices. A major goal of the planned research is thus to establish a theoretical framework for predicting ion transport in porous materials and validation of the new theoretical method with simulation/experimental data. The mathematical form of the equations in the new theory will be similar to conventional hydrodynamic and transport equations, for which algorithms have been in development for many years. This new, non-equilibrium theoretical framework, however, presents unique challenges stemming from the fact that the evolution equations for the two-body correlation effects couple, through a non-local pressure tensor, to the equations expressing conservation of mass, momentum, and energy. Algorithmic development will follow from analysis of the model and will extend from existing high-order discretization techniques for partial differential equations.

2) *Kinetics of colloidal crystallization*

Colloids display astonishing structural and dynamic properties that can be dramatically altered by modest changes in the solution condition or an external field. In principle, the kinetic pathways leading to formation of descried colloidal structures can be controlled either by a careful preparation of the initial non-equilibrium condition followed by a spontaneous bulk phase transition, by seeding with a supersaturated solution as in heterogeneous crystallization, or by using appropriate additives. Regrettably, theoretical prediction of the colloidal phase behavior remains challenging. In previous work, we have established reliable equations of state to predict the phase diagrams of colloidal dispersions (and protein solutions) from the colloidal forces. In addition, we have developed theoretical procedures to predict metastable states including formation of mesoscopic colloidal structures. The planned research aims to study the effects on colloidal forces on the kinetic pathways of phase transitions and on the kinetics of colloidal growth. For crystal growth near equilibrium, we plan to study the kinetic processes by using both molecular dynamic simulations and the dynamic density functional theory. A comparison of the results from different procedures yields valuable insights into the numerical performance of the theoretical method, which is useful for simulating crystal growth in complicated molecular systems that are beyond the reach of time-consuming simulation methods. To describe the kinetics of phase transition far away from equilibrium, we plan to use the newly developed master equations. A combination of theoretical and simulation studies will allow us to identify solutions conditions favoring formation of tailored colloidal structures including conditions favoring homogeneous crystal nucleation and growth.

Publications (2009-2012)

1. "Formation of lamellar structures from spherical particles", Z. Li and J. Wu, *Journal of Chemical Physics*, 130(16), 165102 (2009).
2. "Electrostatic regulation of genome packaging in human hepatitis B virus", T. Jiang, Z. G. Wang and J. Wu, *Biophysical Journal*, 96, 3065–3073, 2009
3. "Solvation of a Spherical Cavity in Simple Liquids: Interpolating between the Limits", J. Wu, *The Journal of Physical Chemistry B*, 113 (219), 6813-6818, 2009.
4. "Modeling microscopic morphology and mechanical properties of block copolymer/nanoparticle composites", J. Jin, J. Wu, and A. Frischknecht, *Macromolecules*, 42, 7537-7544, 2009

5. “Cluster formation and bulk phase behavior of colloidal dispersions”, T. Jiang and J. Wu, *Physical Review E*, 80, 021401, 2009.
6. “Anti-icing superhydrophobic coatings”, L. Cao, A. K. Jones, V. K. Sikka, J. Wu, and D. Gao, *Langmuir*, 25 (21), 12444–12448, 2009.
7. “Self-Similarity in Metal Chalcogenide Nanocluster Chemistry: Assembly of Supertetrahedral T5 Copper-Indium Chalcogenide Clusters into Super-Supertetrahedron of Infinite Order”, L. Wang, T. Wu, F. Zuo, X. Z., X. Bu, J. Wu, and P. Feng, *Journal of the American Chemical Society*, 132(10), 3283–3285, 2010.
8. “Density functional theory for predicting polymeric forces against surface fouling”, X. Xu, D. Cao and J. Wu, *Soft Matter*, 6(19), 4631-4646, 2010 (invited).
9. “Electrostatic origins of polyelectrolyte adsorption: Theory and Monte Carlo Simulations”, L. Wang, H. Liang, C. Wu and J. Wu, *Journal of Chemical Physics*, 133(4), 044906(13 pages), 2010.
10. “Equation of state for the phase behavior of polymers in carbon dioxide”, H. Y. Shin and J. Wu. *Industrial and Engineering Chemical Research*, 49 (16), 7678–7684, 2010.
11. “Entropic forces of single-chain confinement in spherical cavities”, Z. Jin, S. Zhao and J. Wu, *Physical Review E*, 82, 041805, 2010.
12. “A theoretical study of colloidal forces near amphiphilic polymer brushes”, E. R. A. Lima, T. Jiang and J. Wu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384, 115– 120 2011.
13. “Differential capacitance of planar electric double layers in ionic liquids from density functional theory”, J. Jiang, D. Meng and J. Wu, *Chemical Physics Letters*, 504, 153–158, 2011.
14. “Gaussian fluctuations in a single tethered DNA chain”, S. Zhao, J. Wu, D. Gao and J. Wu, *Journal of Chemical Physics*, 134, 065103, 2011.
15. “New theoretical method for rapid prediction of solvation free energy in water”, S. Zhao, Z. Jin and J. Wu, *Journal of Physical Chemistry B,* 115, 6971-6975, 2011.
16. “A hybrid method for studying multi-dimensional entropic forces”, Z. Jin and J. Wu, *Journal of Chemical Physics*, 115 (6), 1450–1460, 2011.
17. “Self-consistent equations governing the dynamics of non-equilibrium colloidal systems”, S. Zhao and J. Wu, *Journal of Chemical Physics*, 134, 054514, 2011.
18. “A perturbative density functional theory for square-well fluids”, Z. Jin, Y. P. Tang and J. Wu, *Journal of Chemical Physics*, 134 (17), 174702, 2011.
19. “Separation of ssDNA with a 10-nucleotide resolution under a stretching force in microfluidic channels”, J. Wu, S.L. Zhao, J. Wu and D. Gao, *Lab on Chip*, 11, 4036-4040, 2011
20. “Thermodynamic basis for the genome to capsid charge relationship in viral encapsidation”, C. L. Ting, J. Wu and Z.G. Wang, *PNAS*, 108(41) 16986-16991, 2011
21. “A classical density functional theory for interfacial layering of ionic liquids”, J. Wu, T. Jiang, D. Jiang, Z. Jin, D. Henderson, *Soft Matter*, 7, 11222-11231, 2011.
22. “A theoretical model for the dynamic structure of Hepatitis B nucleocapsid”, D. Meng, R. P. Hjelm, J. Hu, and J. Wu, *Biophysical Journal*, 101, 2476-2484, 2011.
23. “An efficient method for accurate evaluation of the site-site direct correlation functions of molecular fluids”, S. Zhao and J. Wu, *Molecular Physics*, 109(21), 2553-2564, 2011.
24. “Density functional study of the double layer formed by a high density electrolyte”, D. Henderson, S. Lamperski, Z. Jin, and J. Wu, *Journal of Physical Chemistry B*, 115, 12911-12914, 2011.
25. “Oscillation of Capacitance inside Nanopores”, D. Jiang, Z. Jin, and J. Wu, *Nano Letters*, 11, 5373-5377, 2011.
26. “Electrochemical properties of the double layer of an ionic liquid using a dimer model electrolyte and density functional theory”, D. Henderson, J. Wu, *Journal of Physical Chemistry B*, 116, 2520-2525, 2012.
27. “Shape Effect on Nanoparticle Solvation: A Comparison of Morphometric Thermodynamics and Microscopic Theories”, *Langmuir*, 28 (17), 6997–7006, 2012.
28. “Role of Polar Solvent in Dependence of Capacitance on Pore Size”, D. E. Jiang, Z. H. Jin, D. Henderson, J. Wu, *The Journal of Physical Chemistry Letters*, 3, 1727-1731, 2012

First Principles Investigations for Magnetic Properties of Innovative Materials

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Project scope

The goal of this project is to understand magnetic properties of innovative materials such as magnetic thin films, magnetic semiconductors, d0 magnets, graphene and topological insulators, by developing and using theoretical approaches based on the density functional theory. Manipulating strength and orientation of magnetization of different systems is probably one of the most active research subjects in condensed matter physics and materials science nowadays. We have performed extensive density functional simulations to investigate electronic, magnetic and transport properties semiconductors, oxides, nanowires, and thin films. Our results have been found useful by collaborators for the explanation of their important experimental data and, furthermore, we have also provided significant new insights and predictions for different material systems.

Recent major progress

Kondo effect in O_2/Au(110)

Kondo lattice systems can exhibit unusual many-body behaviors that result from the interplay between onsite Kondo screening and intersite coupling. In collaboration with Prof. W. Ho's group at University of California, Irvine, we used scanning tunneling microscopy to image the Kondo resonance in a nonconventional Kondo lattice formed by self-assembled oxygen (O_2) molecules, which are paramagnetic, on the gold reconstructed surface [Au(110)-1×2]. The interplay between the intermolecular coupling for molecules adsorbed along chains and the onsite Kondo effect leads to the coexistence of both local and nonlocal Kondo screening at the atomic level. The latter provides evidence for collective deconfinement of magnetization induced in Au, whereas the former shows local "hybridization" between the Kondo clouds of nearest-neighbor O2 molecules. Theoretical results in Fig. 1 were used to explain experimental findings for the formation of Kondo cloud. The Kondo signal is mostly strong at locations where O2-induced spin clouds start to overlap, as highlighted by white ellipses in Fig. 1D. Curves of the total density of states (DOS) in Fig. 1A show that the Au d band is well below the Fermi level and that states around EF are free- electron like. The 2p* orbitals of O2 have an exchange splitting of 2.5 eV, as indicated by the local density of states in Fig. 1B. The spin density at the Fermi level is mostly negative (antiparallel to the local magnetization of O2), a common ground-state feature of the Kondo liquid. The induced spin polarization in Au is rather delocalized (Fig. 1E), in good accordance to the uniform background Kondo signal observed in scanning tunneling microscope experiments of Ho's group.

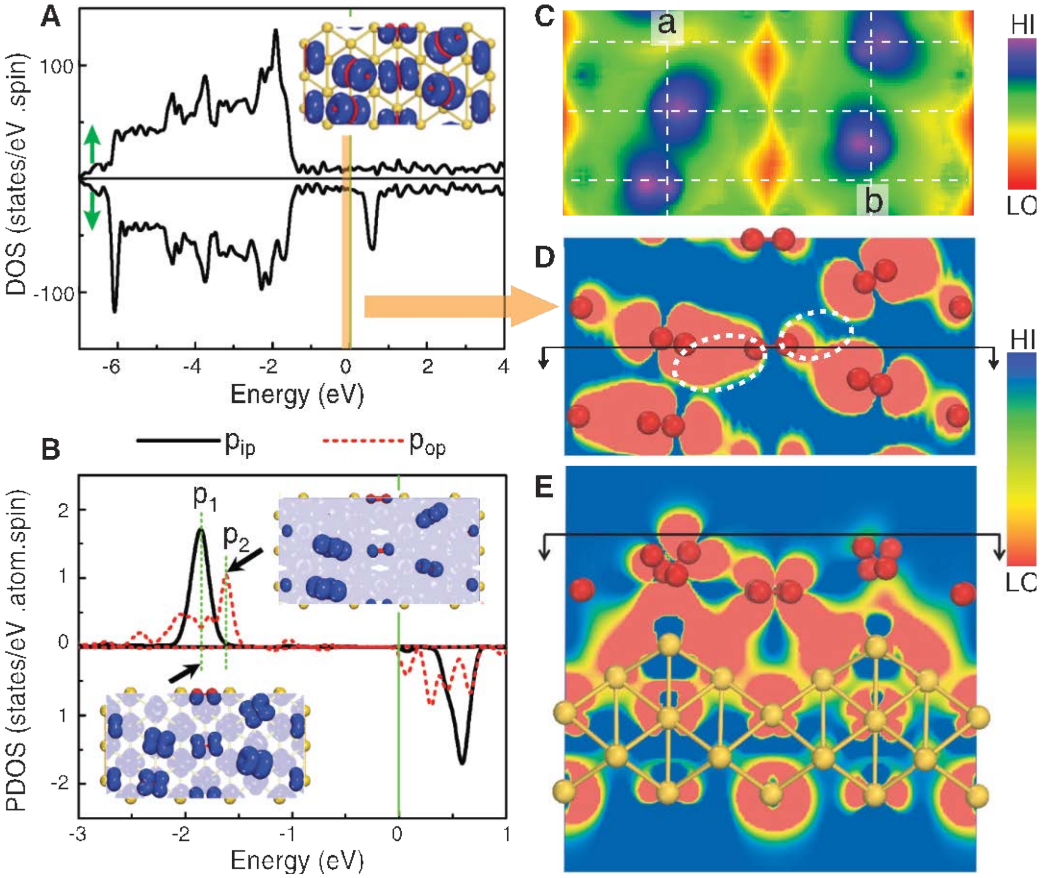

Fig. 1. (A) Total density of states. (Inset) Isosurfaces of total spin density of O2/Au(110). (B) Projected density of states at G point in O2 molecules of chain a. (Insets) Isosurfaces of energy-sliced charge densities for states within T0.05 eV around two peaks pointed out by arrows; pip and pop represent the projected DOS of in-plane and out-of-plane orbitals, respectively. Positive and negative values indicate states in the majority and minority spin channels, respectively. Fermi level is at 0. (C) Simulated STM topography based on the Tersoff and Hamann tunneling model, 3 Å above the topmost oxygen atom for states between 0 and 0.5 eV. (D and E) The top and side views, respectively, of the spin density for states within –0.25 eV to Ef [beige vertical bar in (A)]. The red color in (D) and (E) represents negative spin densities. The positions of the horizontal plane in (D) and the vertical plane in (E) are highlighted by the black lines in (E) and (D), respectively. The white dotted ellipses in (D) represent the lobes of Kondo enhancement.

2D Topological insulator state

The 2007 discovery of quantized conductance in HgTe quantum wells delivered the field of topological insulators (TIs) its first experimental confirmation. While many three-dimensional TIs have since been identified, HgTe remains the only known two-dimensional system in this class. Difficulty fabricating HgTe quantum wells has, moreover, hampered their widespread use. With the goal of breaking this logjam, we provide a blueprint for stabilizing a robust TI state in a more readily available two-dimensional material—graphene. Using symmetry arguments, density functional theory, and tight-binding simulations, we predict that graphene endowed with certain heavy adatoms realizes a TI with substantial band gap. For indium and thallium, our most promising adatom candidates, a modest 6% coverage produces an estimated gap near 80 K and 240 K, respectively, which should be detectable in transport or spectroscopic. We also introduce a new framework for engineering a two-dimensional spin-orbit coupling gap with impurity bands arising from heavy adatoms through graphene, in particular osmium and iridium. First principles calculations predict that the gaps generated by this means exceed 200 meV over a broad range of adatom coverage; moreover, tuning of the Fermi level is not required to enter the TI state. The mechanism at work is expected to be rather general and may open the door to designing new TI phases in many materials. Fig. 2 shows the calculated band structures of several graphene systems that have a large topological band gaps. The effects of external electric field and co-adsorption of Cu are also given.

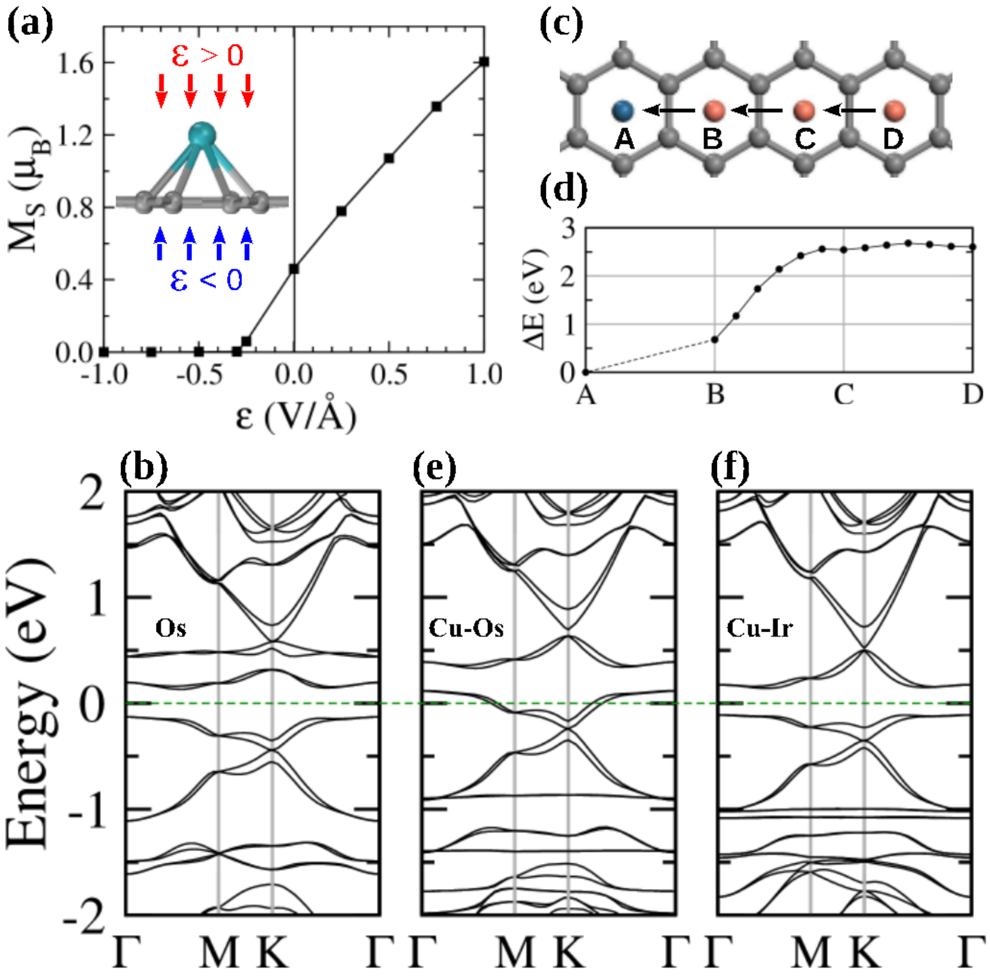

Fig. 2. (a) Magnetic moment Ms of Os/graphene versus external electric field ε applied perpendicular to the graphene sheet (see in- set for the direction of positive and negative ε). The moment disappears for ε → − , allowing a true topologi . Comparing to Fig. 3(a) one sees that the fields needed to restore time-reversal symmetry modify the band structure very little; in par- ticular a large gap remains at the Fermi level (green dashed line). (c) Possible diffusion path of a Cu atom beginning from position D and ending above an Os atom at position A. (d) Energy profile along this diffusion trajectory. The small diffusion barrier evident in (d) indicates that Cu-Os dimers should form quite efficiently. (e) Band structure for Cu-Os dimers on graphene at 6.25% coverage. Time- reversal symmetry is preserved here even at ε = 0, though the Fermi level now resides in the valence band. (f) Band structure Cu-Ir dimers on graphene at 6.25% coverage. This system preserves time-reversal symmetry, eliminates the shift in Fermi level, and also supports a large topological insulator gap.

Planned activities: 2012-2013

We have several research topics in the next year.

1. Explaining the unexpected enhancement of magnetization in Fe-Si amorphous alloys, in collaboration with F. Hellman's group in UC Berkeley.
2. Exploring new topological insulators and graphene states using adsorption and doping techniques with J. Alicea and experimentalists.
3. Investigating unusual Kondo effect in O_2/Au(110) and NO(Au(110), with W. Ho.
4. Investigating magnetism and magnetic anisotropy of transition metal phthalocyanine (TMPc) molecules on CuN and CuO substrates.
5. Studying magnetic ordering of Si_2Gd nanowires i=on Si(001) substrate for phase transitions.
6. Simulating Li segregation in Si nanowires for the deployment of anode materials in Li batteries.

Publications through 2011

1. Y. N. Zhang, F. Hanke, V. Bortolani, M. Persson, and R. Q. Wu, "Why sliding friction of Ne and Kr monolayers is so different on the Pb(111) surface", Phys. Rev. Lett., **106**, 236103 (2011).
2. J.S. Lee, J. T. Sadowski, H. Jang, J.H. Park, J. Hu, R.Q. Wu, J.Y. Kim and C.C. Kao, *"Magnetic Nanoparticles Trigger Spin Reorientation Transition in Ni/Fe/Ni/W(110)"*, Phys. Rev. B **83**, 144420 (2011).
3. Z. Y. Li, Z. Q. Yang, S. Qiao, J. Hu and R. Q. Wu, "Spin–orbit splitting in graphene on metallic substrates", J. Phys.: Condens. Matter **23**, 225502 (2011).
4. Y. Jiang, Y. N. Zhang, J.X. Cao, R. Q. Wu and W. Ho, *"Real-space imaging of Kondo screening in a two-dimensional Kondo lattice"*, Science **333**, 324 (2011).
5. C. Weeks, J. Hu, J. Alicea, M. Franz and R.Q. Wu, "Engineering a robust quantum spin Hall state in graphene via adatom deposition", Phys. Rev. X, 1, 021001 (2011).
6. D.D. Li, L. Zhao, R.Q. Wu, C. Ronning, and J.G. Lu, "Temperature Dependent Photoconductance of Heavily Doped ZnO Nanowires", Nano Research. 4, 1013 (2011).
7. Shengyong Qin, Tae-Hwan Kim, Wenjie Ouyang, Yanning Zhang, Hanno H. Weitering, Chih-Kang Shih, Arthur P. Baddorf, Ruqian Wu, and An-Ping Li, *"Metallic Conductance Stabilized by Interwire Coupling in Self-Assembled Quantum Wires"*, Nano Letters, 12, 938 (2012).
8. W.D. Xing, J. Hu, S.C. Kung, K. Donavan, W.B. Yan, R.Q. Wu, and R. Penner, "A Chemically-Responsive Nanojunction within a Silver Nanowire", Nano Letters, 12, 1729 (2012).
9. C. Antoniak, H. C. Herper, Y. N. Zhang, A. Warland, T. Kachel, F. Stromberg, B. Krumme, C. Weis, K. Fauth, W. Keune, P. Entel, R.Q. Wu, J. Lindner, and H. Wende, *"Induced magnetism on silicon in Fe3Si quasi-Heusler compound"*, Phys. Rev. B, **85**, 214432 (2012).
10. J. Hu, J. Alisea and R.Q. Wu, "Realization of Giant Topological Band Gap in Cu-Os/graphere", Phys. Rev. Lett. submitted.
11. J. Hu, and R.Q. Wu, *"Control properties of molecular magnet with electric field"*, Phys. Rev. Lett. submitted.

Quantum Mechanical Simulations of Complex Nanostructures for Photovoltaic Applications

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I. Project Scope

In this proposal, the PI will first address the excited-state problem within the DFT framework to obtain quasiparticle energies from both Kohn-Sham (KS) eigenvalues and orbitals; and the electron-hole binding energy will be computed based on screened Coulomb interaction of corresponding DFT orbitals. The accuracy of these approaches will be examined against many-body methods of GW/BSE and quantum Monte Carlo (QMC). The PI will also work on improving the accuracy and efficiency of the GW/BSE and QMC methods in electronic excitation computations by using better KS orbitals obtained from orbital-dependent DFT as inputs. Then an extended QMC database of ground- and excited-state properties will be developed, and this will be spot checked and supplemented with data from GW/BSE calculations. The investigation will subsequently focus on the development of an improved exchange-correlation (XC) density functional beyond the current generalized gradient approximation (GGA) level of parameterization, with parameters fitted to the QMC database. This will allow the ground-state properties of focus systems to be more precisely predicted using DFT. These new developments will then be applied to investigate a chosen set of complex nanostructures that have great potential for opening new routes in designing materials with improved transport, electronic, and optical properties for PV and other optoelectronic usages: (1) Hybrid interfaces between materials with distinct electronic and optical properties, such as organic molecules (conjugated polymers, e.g. P3HT) and inorganic semiconducting materials (Si and ZnO). Complicated interface structures, including interface bonding configurations, compositional and geometrical blending patterns, interfacial defects, and various sizes and shapes of inorganic nanomaterials, will be considered for the purpose of understanding the working mechanisms of present organic/nano PV systems and designing optimum interface structures for fast charge separation and injection. (2) Complex-structured semiconducting nanomaterials that could induce charge separation without pn- or hetero-junctions. The new methodology will allow the PI to investigate the performance of realistic semiconducting nanomaterials of internal (impurities, defects, etc.) and external (uneven surface, mechanical twisting and bending, surface chemistry, etc.) complexities on optical absorption and charge transport against charge trapping and recombination. Of particular interest is whether such structural complexity in a single material could even be beneficial for PV usage, for example, charge separation through morphology control.

II. Recent Progress

Plasmon-Pole Models in the GW approximation

The current state-of-the-art method of computing quasiparticle (QP) electronic excitations is the many-body perturbation theory using Green's functions within the GW approximation. However, there are two outstanding issues: (1) The accuracy of the GW method strongly depends on approximations involved in evaluating electronic screening (W) and the levels of the selfconsistency; (2) They are computationally extremely demanding, therefore very difficult to be applied to nanoscale materials with complex structures. In this investigation we focus on the effects of approximations of electron screening on accuracy of GW calculations. Four different plasmon-pole models (PPMs) have been proposed and widely used in constructing dynamic electronic screening, but their accuracy and applicability haven't been carefully examined. Based on analytical analyses, we find that for simple semiconductors such as Si and GaAs where valence electrons are largely delocalized, these PPMs behave very similarly to each other; but they become sharply distinct in materials with localized valence states. Our calculations show that even though the Hybertsen-Louie model predicts the most accurate band gap in a variety of materials compared with experimental data, it is the Godby-Needs model that better agrees with the direct numerical integration for electronic screening. Thus our study suggests that in order to systematically improve the GW method, one needs to access each individual approximation by comparing with accurate numerical results instead of comparing with experimental band gap directly, because the coexistence of many approximations hinders assessing the specific modeling. Now we are investigating how to solve the slow convergence problem in transition metal oxides.

Origin of the Variation of Exciton Binding Energy in Semiconductors

Excitonic effects are crucial to optical properties, and the exciton binding energy (E_b) in technologically important semiconductors varies from merely a few meV to about 100 meV. This large variation, however, is not well understood. We investigate the relationship between the electronic band structures and exciton binding energies in semiconductors, employing first-principles calculations based on the density functional theory (DFT) and the many-body perturbation theory using Green's functions (GW/BSE). Our results clearly show that E_b increases as the localization of valence electrons increases due to the reduced electronic screening, as exemplified by Si and ZnO in Fig. 1. Furthermore, E_b increases in ionic semiconductors such as ZnO because, contrary to the simple two-level coupling model, it has both the conduction as well as the valence band edge states strongly localized on anion sites. These trends are quantized by electronic structures obtained from the DFT; thus, our approach can be applied to understand the excitonic effects in complex semiconducting materials.

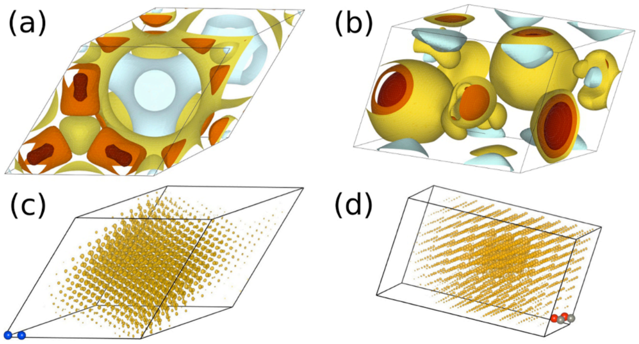

FIGURE 1. Isosurfaces of valence charge density (upper panels) and exciton distribution (lower panels), in Si (left panels) and in ZnO (right panels).

Electronic Band Structures of Graphene Nanomeshes

Recently, graphene has risen as a fascinating system in condensed matter physics for both fundamental science and practical applications, owing to its many unique and amazing properties originating from the massless Dirac fermions; however, the associated zero band gap has to be modified to allow a meaningful on-and-off ratio when used in field-effect transistors. Numerous attempts to open band gap have been made, among them, applying periodic potentials by surface-patterned modifications, such as graphene nanomeshes with periodic nanoscale perforation, are particularly promising; e.g., the field-effect transistors based on graphene nanomashes have been demonstrated with on-and-off ratios comparable to those of graphene nanoribbon devices. Extensive theoretical efforts have been spent to investigate such graphene structures, but the precise role of periodic perturbation on band gap opening remains unclear. Here we show that the band gap opening in graphene under periodic potentials can be accurately understood from mapping the discrete perturbative reciprocal lattice vectors onto Dirac points. If the lattice vectors of the periodic potential are linear combinations of those of the pristine graphene, which is often the case experimentally, then the modified graphene alternates between semimetal and semiconductor with a period of 3, with two thirds gapless and one third semiconducting, in contrast to graphene nanoribbons and carbon nanotubes. If the periodic potential is applied on some special patterns, all of the modified graphene can open up a sizable gap. These predictions are in excellent agreement with previous and present first-principles results for graphene nanomeshes, e.g, those GNMs plotted in Fig. 2, and periodically passivated or defected graphene. As well as revealing the fundamental physics involved, our finding indicates a cornucopia of possibilities of structural patterning and engineering graphene for realistic electronic and optical devices. We are also investigating the optical properties of graphene under such periodic perturbations.

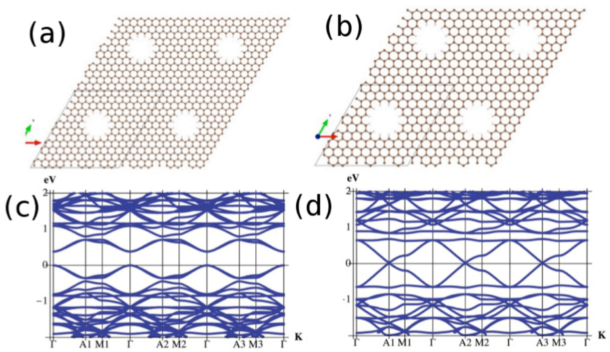

FIGURE 2. Lattice structure (upper panels) of two GNMs and their corresponding electronic structures (lower panels). The left GNM is a semiconductor, while the one on the right is semi-metallic.

An optimal size regime for oxidation resistant silicon quantum dots

First-principles computations have been carried out to predict that appropriately terminated silicon quantum dots with diameters in the range of 1.2–2 nm, as illustrated in Fig. 3, will offer a superb resistance to oxidation. This is because surface treatments can produce dangling-bond defect densities suf- ficiently low that dots of this size are unlikely to have any at all. On the other hand, these dots are large enough that surface curvature does not expose bonds that are vulnerable to oxygen attack. The absence of both surface defects and curvature-related vulnerabilities allows even very short passivating ligands to generate an effective barrier, an important consideration for charge and exciton transport within quantum dot assemblies. Our computations, which employ many-body perturbation theory using Green functions, also indicate that dots within this size regime have optical and electronic properties that are robust to small amounts of inadvertent oxidation, and that any such oxygen incorporation is essentially frozen in place.

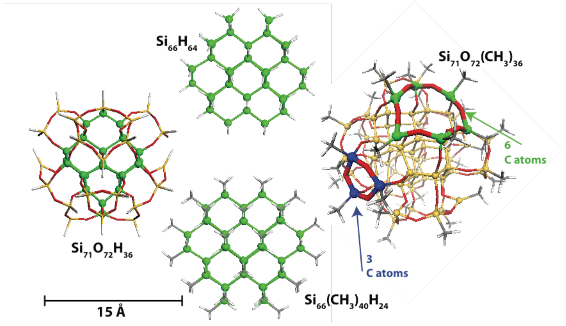

FIGURE 3: Small, quantum confined Si QDs illustrating passivation with H (top), CH3 + H (bottom) and siloxane networks (left and right). Si atoms are shown in tan, green and blue, O atoms are red, C atoms are gray, and H atoms are white.

First Principles Analysis of Charge Dynamics in Hybrid SiQD/P3HT Composites

The tunable energy levels and high carrier mobility of silicon quantum dots (SiQD) complement the strong visible range absorption of conjugated polymers and so offer a promising hybrid solar cell paradigm. However, the efficiencies of these composites are typically lower than those of their purely organic counterparts. A lack of understanding as to why this is so, and how it can be

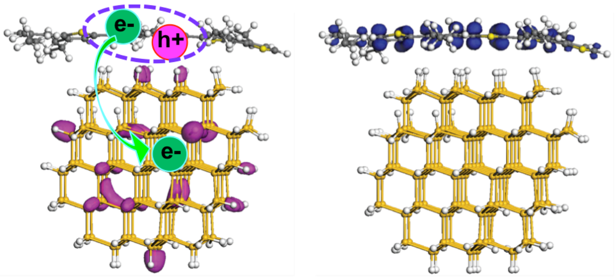

FIGURE 4. Schematic plotting of a Si quantum dot and the P3HT interface, in which the charge transfer dynamics is illustrated.

remedied, has motivated our theoretical study of a representative SiQD/P3HT system, as shown in Fig. 4. First principles computational tools were used to implement a new, non-adiabatic phonon assisted quantum tunneling model in order to quantify the charge separation and transport dynamics. The predicted charge separation rate is in good agreement with that measured experimentally, and it is much higher than the photoluminescence rate of the P3HT. This implies that excitons should be able to efficiently dissociate into free carriers. In addition, the charge hopping proceeds much more quickly than interfacial charge recombination, so a considerable fraction of free electrons and holes should be able to diffuse to the electrode based on the predicted carrier mobilities. In fact, the results indicate that P3HT/SiQD blends have the potential to out perform the widely used, purely organic, P3HT/PCBM architecture. We conclude that the low efficiency of current P3HT/SiQD solar cells originates from the high density of defects and a distribution of SiQD sizes. The influences of dangling bonds, oxidation, passivation and doping on the charge dynamics are analyzed from fisrt-principles to provide insights for improving the performance of these hybrid materials.

III. Planned Activities: 2012-2013

Method developments. (a) Implementing the new interpretation of the density functional theory for QP energies, and then testing its accuracy. (2) Assessing GW self-energy calculation procedures, so that large self-energy corrections in transition-metal oxides can be computed with much less conduction bands. (3) Combining our new DFT method with the GW approach. (4) Working on the possible density functional theory of excitations involving two-particle wave functions.

Method applications. (a) Graphene nanomeshes: [1] The exact energy gap using the GW method and our new development; [2] The optical absorption spectra and exciton binding energies of semiconducting GNMs by solving the Bethe-Salpeter equation (BSE); [3] Applying our new developments to study the electronic structures of GNMs. (b) Silicon nanowires and carbon nanotubes under twisting and bending. (c) The dynamics of electronically excited states: computationally designing novel interfacial nanostructures involving semiconducting QDs and molecular assembly for rapid charge transfer for PV applications.

IV. Publications

[1] "*Band Gaps in Graphene Nanomeshes*", William Oswald and Zhigang Wu, Phys. Rev. B **85**, 115431 (2012).

[2] "First principles analysis of the initial oxidation of Si(001) and Si(111) surfaces terminated with H and CH_3", Huashan Li, Zhibin Lin, Zhigang Wu, and Mark Lusk, J. Chem. Phys. **136**, 064507 (2012).

Laser-induced ultrafast magnetization in ferromagnets

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Project Scope

This program focuses on the emerging field of laser-induced femtosecond (fs) magnetization in ferromagnets or femtomagnetism with potential applications in magnetic recording. Our goal is to reveal the mechanism of ultrafast demagnetization and to train young researchers and students through active research and education. To achieve this goal, we use nickel as an example. We first compute the laser-induced spin and orbital momenta changes and establish the missing link between spin and orbital dynamics. Then we develop a new algorithm for two ultrafast x-ray based and element-specific techniques. This enables us to directly compare our theoretical results with experimental ones. Two immediate impacts from the proposed research are: (1) It reveals how the orbital degree of freedom and light polarization affect the magnetization change; (2) It establishes a new speed limit for the future magnetic recording.

Recent Progress

The magneto-optical Kerr effect (MOKE) is a powerful tool for studying changes in the magnetization of ferromagnetic materials. It works by measuring changes in the polarization of reflected light. However, because the conventional theoretical basis for interpreting a MOKE signal assumes measurement with continuous-wave light, its use for understanding high-speed magnetization dynamics of a material probed with femtosecond optical pulses has been controversial. Here we established a new paradigm for interpreting time-resolved MOKE measurements, through a first-principles investigation of ferromagnetic nickel. We found that the time-resolved optical and magnetic responses energetically follow their respective optical and magneto-optical susceptibilities. As a result, the one-to-one correspondence between them sensitively depends on the incident photon energy. In nickel, for photon energies below 2 eV the magnetic response is faithfully reflected in the optical response, but above 2 eV they decouple. By constructing a phase-sensitive polarization versus magnetization plot, we showed that for short pulses the magnetic signals are delayed by 10 fs with respect to the optical signals. For longer pulses, the delay shortens and the behavior approaches the continuous-wave response. This finally resolves the long-standing dispute over the interpretation in the time-resolved MOKE measurements and lays a solid foundation for understanding femtomagnetism. Figure 1 is our *Nature Physics* result, which shows how the magnetic and optical responses evolve with time.

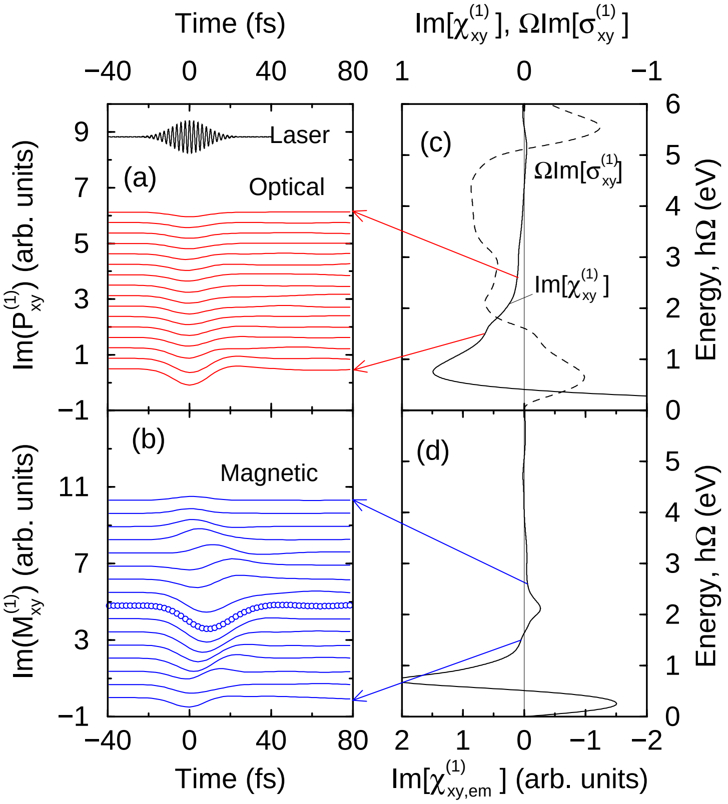

Figure 1: Magnetic and optical responses. (a) Time evolution of the first-order off-diagonal polarization as a function of incident photon energy. Inset: Laser pulse shape. The laser pulse duration is 12 fs, and laser field strength is 0.05 V/Å. (b) Off-diagonal magnetization change as a function of time. The empty-circle line denotes the result at $\hbar\omega = 2.0$ eV. The change with incident energy forms a ')' shape. (c) Off-diagonal susceptibility (solid line) and conductivity (dashed line) as a function of photon energy. Note the x-axis is the amplitude of the spectrum, and the y-axis is the photon energy. Two red arrows identify where the excitation energy is used in (a) and (b). (d) Magneto-optical susceptibility as a function of photon energy. This finding has been published in **Nature Physics**.

We further developed a microscopic theory of ultrafast spin linear reversal. This is directly motivated by a recent experiment (Vahaplar et al 2009 Phys. Rev. Lett. 103 117201) showing that a single femtosecond laser can reverse the spin direction without spin precession, or spin linear reversal (SLR), but its microscopic theory has been missing. Here we show that SLR does not occur naturally. Two generic spin models, the Heisenberg and Hubbard models, are employed to describe magnetic insulators and metals, respectively. We find analytically that the spin change is always accompanied by a simultaneous excitation of at least two spin components. The only model that has prospects for SLR is the Stoner single-electron band model. However, under the influence of the laser field, the orbital angular momenta are excited and are coupled to each other. If a circularly polarized light is used, then all three components of the orbital angular momenta are excited, and so are their spins. The generic spin commutation relation further reveals that if SLR exists, it must involve a complicated multiple state excitation. This research was published in Journal of Physics: Condensed Matter, Volume 23, page 206005 (2011).

Future Plans

We will focus on two fronts (a) the electron correlation effect, and (b) exchange interaction change due to the laser pulse and the fixed spin moment calculation. These two fronts are at the core of femtomagnetism and are extremely complicated since both spatial and temporal evolution are involved. Except our earlier study in a model system, no attempt has never been made before at the first-principles calculation level. We will start with time-dependent Hartree-Fock approximation to include the laser field in our Liouville equation. We will limit ourselves to much smaller numbers of k points. Otherwise, this problem becomes intractable. One key hurdle is how to parallelize the calculation as efficiently as possible.

For the exchange interaction change, we will start with the phonon excitation with different initial state preparation, similarly to our early investigations. By changing the atom position along those normal mode eigenvector directions, we will map out the essential change due to the phonon excitation.

Publications

1. G. P. Zhang, *Charge and spin responses under pump-probe excitations in comparison with single pump excitations*, Phys. Rev. B **85**, 224407 (2012).
2. Kirsten Middleton, G. P. Zhang, Michael R. Nichols, and Thomas F. George, *A comparative first-principles study of structural and electronic properties among memantine, amantadine and rimantadine*, Molecular Physics: An International Journal at the Interface between Chemistry and Physics **110**, 685-689 (2012).
3. M. S. Si and G. P. Zhang, *Hot spin spots in the laser-induced demagnetization*, AIP Advances **2**, 012158 (2012).
4. G. P. Zhang, G. Lefkidis, W. Hübner and Y. Bai, *Manipulating femtosecond magnetization in ferromagnets and molecular magnets through laser chirp*, J. Appl. Phys. **111**, 07C508 (2012).
5. G. P. Zhang, David A. Strubbe, Steven G. Louie and Thomas F. George, *First-principles prediction of optical second-order harmonic generation in the endohedral* N@C_{60} *compound*, Physical Review A **84**, 023837 (2011).
6. G. P. Zhang, *Microscopic theory of ultrafast spin linear reversal*, J. Phys.: Condensed Matter **23**, 206005 (2011).

7. G. P. Zhang, M. S. Si, and T. F. George, *Laser-induced spin protection and switching in a specially designed magnetic dot: A theoretical investigation*, Europhysics Letters **94**, 17005 (2011).

8. G. P. Zhang, G. Lefkidis, W. Hübner and Y. Bai, *Ultrafast demagnetization in ferromagnets and magnetic switching in nanoclusters when the number of photons is kept fixed*, J. Applied Physics **109**, 07D303 (2011). This paper has been selected for the April 2011 issue of Virtual Journal of Ultrafast Science.

9. M. S. Si and G. P. Zhang, *Resolving photon-shortage mystery in femtosecond magnetism*, J. Phys.: Condensed Matter **22**, 076005 (2010).

10. G. P. Zhang, Yihua Bai and T. F. George, *An energy- and crystal momentum-resolved study of laser-induced femtosecond magnetism*, Phys. Rev. B **80**, 214415 (2009).

11. Georgios Lefkidis, G. P. Zhang, and W. Hübner, *Angular momentum conservation for coherently manipulated spin polarization in photoexcited NiO: An ab initio calculation*, Phys. Rev. Lett. **103**, 217401 (2009).

12. G. P. Zhang, W. Hübner, Georgios Lefkidis, Yihua Bai, and T. F. George, *Paradigm of the time-resolved magneto-optical Kerr effect for femtosecond magnetism*, **Nature Physics 5**, 499 (2009). See also: News and Views by Bovensiepen, http://www.nature.com/nphys/journal/v5/n7/index.html.

13. G. P. Zhang, X. Sun and T. F. George, *Nonlinear optical response and ultrafast dynamics in* C_{60}, Journal of Physical Chemistry A **113**, (7), pp 1175-1188 (2009) (**Invited Centennial Feature Articles, cover page paper**).

14. T. Hartenstein, G. Lefkidis, W. Hübner, G. P. Zhang, and Yihua Bai, *Time-resolved and energy-dispersed spin excitation in ferromagnets and clusters under influence of femtosecond laser pulses*, J. Appl. Physics **105**, 07D305 (2009). This paper has been selected for the March 2009 issue of Virtual Journal of Ultrafast Science. http://www.vjultrafast.org

Project Title: Theory of Defects in Electronic Materials

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Project Scope:

This project will carry out theoretical development for accurate predictions of defects properties in electronic materials, and to perform, in parallel, cutting-edge research in defect physics, such as non-equilibrium doping, deep-level engineering, excited-state properties, and defect-defect interaction and correlation, using first-principles theoretical tools with balanced accuracy and computation efficiency. We will employ a comprehensive set of density functional theory (DFT) methods such as the local density approximation (LDA) and generalized gradient approximation (GGA)-based molecular dynamics (MD), the time-dependent DFT (TDDFT), and the hybrid functional methods, and the many-body GW quasiparticle perturbation theory for accurate prediction of defect properties in electronic materials. We will investigate accuracy and limitations of the hybrid functional methods for defect calculations, especially for localized states in wide gap semiconductors, and benchmark the results against the GW method. We will examine, for charged defects, the response of the screening charge to the defect and the effects of the artificially introduced compensating jellium background, with the aim of eliminating unphysical interactions. Non-equilibrium doping is an active research topic of high current interest. We will study radiation damage, with a focus on the electronic excitation effect associated with ion implantation, and develop a theory for the recently-emerged and promising optical hyperdoping method. We will push the frontier of *ab initio* defect study from mainly isolated point defects to strongly interacting and correlated defects, e.g., clustering, and from mainly ground-state properties to exited-state properties. We will also explore possible paths to lower dopant ionization energy in ultrawide gap materials.

Recent Progress:

(1) Dynamic Jahn-Teller Effect in Nitrogen Doped Diamond

Using a combination of first-principles calculations and vibronic interaction model analysis, we establish the presence of a dynamic Jahn-Teller (JT) effect in the 3E excited state for NV$^-$ center in diamond. Figure 1 shows the adiabatic potential energy surface (APES) for the NV$^-$ center, revealing three degenerate energy minima. The calculated APES is mapped to a quadratic JT Hamiltonian to obtain the JT stabilization energy and the tunneling splitting. We then diagonalize the vibronic Hamiltonian within the subspace spanned by the electronic doublet and the vibrational states of e phonon. Using these results, we calculate the temperature-dependent dephasing rate (W)

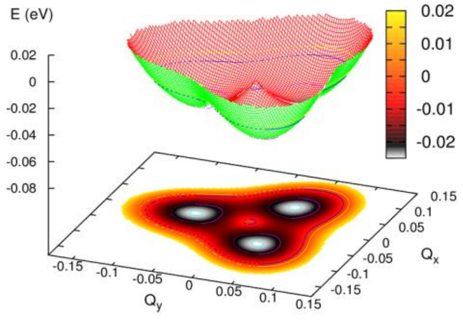

Figure 1.The adiabatic potential energy surface and its projection in (Q_x,Q_y) plane for the ^{3}E excited state of the NV$^-$ center in diamond. There equivalent energy minima can be clearly seen.

for the zero phonon linewidth in a two-phonon Raman model. The result agrees well with experiment. The calculated splitting of the first two vibronic states is also in good agreement with experiment.

(2) Athermal Effect driving Phase Change Memory

Phase change memory materials such as Ge2Sb2Te5 (GST) emerge as potential high-density memory materials to replace the current Flash Memory technology. A characteristic feature of the GST is the presence of an exceptionally large amount of lattice vacancies, as high as 20% for distorted RS crystal. The physics of the ultrafast and reversible (up to billion times) phase change is fascinating, but the microscopic origin for the change is complex and still unclear. In particular, the possible role of electronic excitation has not been considered. By taking electrons away from the bonding states and placing them in the antibonding states, excitation weakens the lattice. Figure 2 shows the atomic orbital-decomposed density of states along with real space charge. It reveals an inhomogeneous distribution of the states at different energies. States near the VBM have significantly more Ge s antibonding character than that of Sb. As a result, electronic excitations cause more Ge atoms to undergo coordination changes than Sb. This drives the amorphization as well as lowers the transition temperature considerably. For example, with a 9% excitation, amorphization takes place within only several picoseconds at a temperature of 300° below the melting point. It leads to a one order of magnitude smaller diffusion coefficient than that of normal melting and an amorphous structure with fewer unfavorable bonds. These effects are beneficial to reversibility and durability.

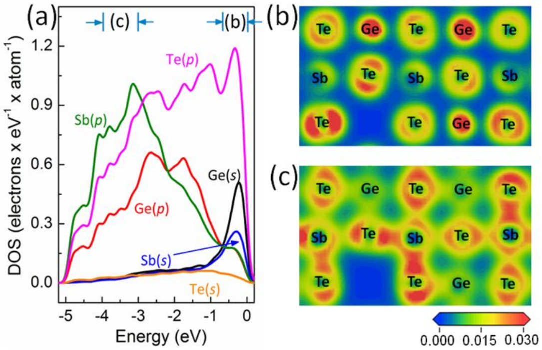

Figure 2. (a) Decomposed density of states for GST near the valence band maximum (E_{VBM} = 0) and (b) and (c) the corresponding charge distributions in the energy windows shown in panel (a).

(3) Regulating Doping of Topological Insulators

The discovery of three-dimensional (3D) topological insulators in pnictogen chalcogenides (Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3) has spurred tremendous interest. The surface states of the TIs have a linear dispersion near the Fermi energy, giving rise to Dirac fermion (DF) behavior for charge carriers. These DFs are robust, as they are protected by time-reversal symmetry. The difficulty, though, is the high concentration of intrinsic defects in these materials. By introducing large amount of free carriers, defects pin the Fermi level outside bulk band gap and shadow the electronic responses of the DFs. In collaboration with an experimental group, we have carried out a systematic study of the physical properties of native defects and have identified the major defects in these materials. Our findings have assisted experimental regulation of native defects to achieve desirable Fermi level positions. We have also studied transition metal impurities. Figure 3 shows an example for Fe at Bi site.

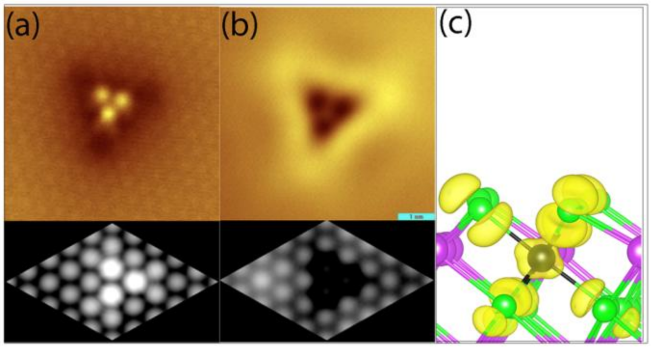

Figure 3. (a) and (b) Experimental (top) and simulated (bottom) STM images for Fe on Bi2Te3(111) surface at -0.4 V and +0.4 V bias. The simulated images are obtained from Fe_{Bi}, whose atomic structure is shown in (c) along with the partial charge density plot corresponding to the -0.4 V bias.

The results are also in good agreement with experiment.

Future Plans (2012-2013):

(1) Understanding hybrid functionals for defect calculations

Recently, various hybrid functionals (e.g., PBE0, HSE, and B3LYP) have been proposed for solid state physics with the promise of a better description of the exchange–correlation effects of many-electron systems, resulting in more faithful predictions of electronic and structural properties of materials. Often the success of a hybrid functional is measured by how well it can reproduce the electronic properties (e.g., the band gap) of the system under investigation. In some cases, it can also produce structural properties better than the widely used LDA and GGA. The same rationale applies to the study of defects in semiconductors. Strictly speaking, however, the fundamental quantities for defects (e.g., the defect formation and transition energies) cannot be derived from single-particle energy levels but have to be calculated using the so-called ΔSCF scheme. The intrinsic non-locality of the hybrid functional and over-localization of the wavefunction, combined with other approximations used today for defect studies, can severely limit the accuracies of the calculated results. We propose to apply the GW quasiparticle and hybrid functional methods together to investigate the applicability and limitations of the latter over a range of semiconductors with small to large band gaps.

(2) Electronic effect in radiation damage

To date, most theoretical studies of radiation damage are based on the Born-Oppenheimer approximation assuming electronic ground state. We note however that the high-energy particles can also excite ground state electrons into their excited states. Such an electronic excitation can act as a heat bath of energetic particles to significantly alter the energy transfer to ions and hence the defect creation. When ionic motions are fast, electrons may not respond instantaneously. Therefore, nonadiabatic electronic dynamics could be important for radiation damage. Here, we propose to study the electronic effect in radiation damage by using time-dependent density functional theory (TDDFT). We will first consider graphene as we already have some experience with this material. We will then move on to the effect by B implantation in Si. The objective is to develop a theory on how electronic effect will alter Frenkel-pair creation and damage propagation in these materials. In particular, we will consider the electron dynamics caused by fast ion beams.

(3) Native defects and clusters in copper zinc tin disulphide

In collaboration with researchers at IBM, we investigate native defects in Cu_2ZnSnS_4 (CZTS), which is an earth-abundant photovoltaic semiconductor. Unlike binary or ternary semiconductors, CZTS contains four elements, three of which are cations. Previous theoretical calculation has focused on Cu-deficient defects in this material. Different chemical compositions such as cu-rich, however, cannot be simply excluded. For example, in spite the large error bars, a recent experiment has indicated that active regions in CZTS could be Cu-rich and Sn-deficient. Yet, the growth condition for producing good quality CZTS is clearly Cu-deficient. Our research is designed to resolve this dilemma. An emphasis will be on the formation of defect clusters. While we will use the hybrid functional to calculate defect formation energy, we will use simulated annealing within the GGA to prescreening the potential low-energy clusters.

List of key publications (2010-2012)

1. B.-C. Shih, Y. Xue, M. L. Cohen, S. G. Louie, and P. Zhang, “Quasiparticle Band Gap of ZnO: High Accuracy from the Conventional G0W0 Approach”, Phys. Rev. Lett. 105, 146401 (2010).
2. P. Dev and P. Zhang, “Unconventional magnetism in semiconductors: Role of localized acceptor states”, Phys. Rev. B 81, 085207 (2010).
3. P. Dev, H. Zeng, and P. Zhang, “Defect Induced Magnetism in Nitride and Oxide Nanowires: Surface Effects and Quantum Confinement”, Phys. Rev. B 82, 165319 (2010).
4. T.-L. Chan, H. Kwak, J.-H. Eom, S. B. Zhang, and J. R. Chelikowsky, “Self-purification in Si nanocrystals: An energetics study”, Phys. Rev. B 82, 115421 (2010).
5. D. Han, D. West, X.-B. Li, S.-Y. Xie, H.-B. Sun, and S. B. Zhang, “Impurity doping in SiO2: Formation energies and defect levels from first-principles calculation”, Phys. Rev. B 82, 155132 (2010).
6. L. Wang, Y. Y. Sun, K. Lee, D. West, Z. F. Chen, J. J. Zhao, and S. B. Zhang, “Stability of graphene oxide phases from first-principles calculations”, Phys. Rev. B (Rapid Comm.) 82, 161406 (2010).
7. P. Wang, Z. Liu, F. Lin, G. Zhou, J. Wu, W. Duan, B.-L. Gu, and S. B. Zhang, “Optimizing photoelectrochemical properties of TiO2 by chemical codoping”, Phys. Rev. B 82, 193103 (2010).
8. X. Q. Liu, X. B. Li, L. Zhang, Y. Q. Cheng, Z. G. Yan, M. Xu, X. D. Hans, S. B. Zhang, Z. Zhang, and E. Ma, “New Structural Picture of the Ge2Sb2Te5 Phase-Change Alloy”, Phys. Rev. Lett. 106, 025501 (2011).
9. X.-B. Li, X. Q. Liu, X. Liu, D. Han, Z. Zhang, X. D. Han, H.-B. Sun, and S. B. Zhang, “Role of electronic excitation in the amorphization of Ge-Sb-Te alloys”, Phys. Rev. Lett. 107, 015501 (2011).
10. T. L. Chan, D. West, and S. B. Zhang, “Limits on passivating defects in semiconductors: the case of Si edge dislocations”, Phys. Rev. Lett. 107, 035503 (2011).
11. T. A. Abtew, Y. Y. Sun, B.-C. Shih, P. Dev, S. B. Zhang, and P. Zhang, "Dynamic Jahn-Teller effect in NV center in diamond", Phys. Rev. Lett. 107, 146403 (2011).
12. G. Wang, X.-G. Zhu, Y.-Y. Sun, Y.-Y. Li, T. Zhang, J. Wen, X. Chen, K. He, L.-L. Wang, X.-C. Ma, J.-F. Jia, S. B. Zhang, Q.-K. Xue, “Topological Insulator Thin Films of Bi2Te3 with Controlled Electronic Structure”, Adv. Mater. 23, 2929 (2011).
13. W. Xie, Y. Y. Sun, S. B. Zhang, and J. E. Northrup, “Structure and sources of disorder in poly(3-hexylthiophene) crystals investigated by density functional calculations with van der Waals interactions”, Phys. Rev. B 83, 184117 (2011).
14. T.-L. Chan, S. B. Zhang, and J. R. Chelikowsky, “Charged dopants in semiconductor nanowire under partially periodic boundary conditions”, Phys. Rev. B 83, 245440 (2011).
15. S. Qi, F. Jiang, J. Fan, H. Wu, S. B. Zhang, G. A. Gehring, Z. Zhang, and X. Xu, “Carrier-mediated nonlocal ferromagnetic coupling between local magnetic polarons in Fe-doped In2O3 and Co-doped ZnO”, Phys. Rev. B 84, 205204 (2011).
16. Y. Zhang, X. Yuan, X. Sun, B-C. Shih, P. Zhang, and W. Zhang, “Comparative Study of Structural and Electronic Properties of Cu-based Multinary Semiconductors”, Phys. Rev. B 84, 075127 (2011).
17. Y. Jiang, Y. Y. Sun, M. Chen, Y. Wang, Z. Li, C. Song, K. He, L. Wang, X. Chen, Q.-K. Xue, X. Ma, and S. B. Zhang, “Fermi-level tuning of epitaxial Sb2Te3 thin films on graphene by regulating intrinsic defects and substrate transfer doping”, Phys. Rev. Lett. 108, 066809 (2012).
18. B.-C. Shih, Y. Zhang, W. Zhang, and P. Zhang, “Screened Coulomb Interaction of Localized Electrons in Solids from First-principles”, Phys. Rev. B 85, 045132 (2012).
19. D. West, Y. Y. Sun, S. B. Zhang, T. Zhang, X. Ma, P. Cheng, Y. Y. Zhang, X. Chen, J. F. Jia, and Q. K. Xue, “Identification of magnetic dopants on the surfaces of topological insulators: Experiment and theory for Fe on Bi2Te3(111)”, Phys. Rev. B (Rapid Comm.) 85, 081305 (2012).

Magnetization dynamics at elevated temperatures

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Project Scope

This project aims at establishing a theoretical framework for modeling and predicting magnetization dynamics of magnetic nanosystems at elevated temperatures. Fast magnetization dynamics excited by external perturbations such as laser pumping and high current heating involves physics on the time scale of picoseconds and femtoseconds, several orders of magnitude faster than conventional nanosecond magnetization dynamics of nanomagnets. This proposed research consists of two broadly defined objectives. The first is to identify physical processes responsible for the femtosecond dynamics by using the quantum kinetic Bloch approach. The key physics is how highly non-equilibrium electrons excited by external sources transfer their energy and angular momenta to spins and lattice via electron-spin interaction and spin-orbit coupling. The second object is to establish an effective description for ensemble magnetization so that the picosecond magnetization dynamics can be modeled by an effective dynamic equation at high temperatures where the conventional Landau-Lifshitz-Gilbert equation fails. The program intends to deliver a number of numerical algorithms and codes for applications in various systems.

Project Progress

1. Laser induced demagnetization at high temperatures

Laser-induced demagnetization is theoretically studied by explicitly taking into account interactions among electrons, spins and lattice. Assuming that the demagnetization processes take place by the thermalization of the sub-systems, the adiabatic temperatures of each subsystems are introduced and determined by explicitly calculating the energy transfer between the thermalized interacting subsystems. These energy transfers are accounted for through electron-magnons and electron-phonons interaction, which govern the demagnetization time scales. By properly treating the spin system in a self-consistent random phase approximation, we derive magnetization dynamic equations for a broad range of temperature. The dependence of demagnetization on the temperature and pumping laser intensity is calculated in detail. In particular, we show several salient features for understanding magnetization dynamics near the Curie temperature. For example, while the critical slowdown in dynamics occurs, we find that an external magnetic field can restore the fast dynamics. In Fig. 1, we show how a large laser intensity can slow down the spin dynamic to a few nano-seconds for otherwise femtosecond dynamics.

2. Generalized Bloch equation for magnetization dynamics

By using the quantum kinetic approach with the instantaneous local equilibrium approximation, we propose an equation that is capable of addressing magnetization dynamics for a wide range of temperatures. The equation reduces to the Landau-Lifshitz equation at

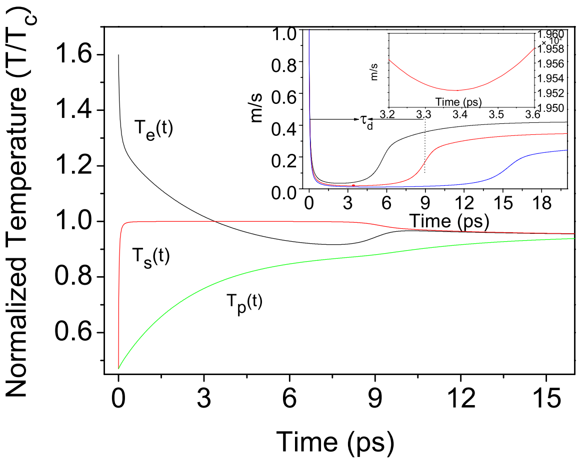

FIG. 1: Time evolution of three temperature for a large laser-fluence case $T_e(0) = 1.6T_c$. The critical slowing down of the spin system is identified as the plateau in the figure. The insert defines a slowdown time τ_d. The smaller insert panel shows the magnified region in the vicinity of the maximum spin temperature. (Figure from Publication [1])

low temperatures and to the paramagnetic Bloch equation at high temperatures. Near the Curie temperature, the magnetization reversal and dynamics depend on both transverse and longitudinal relaxations. We further include the stochastic fields in the dynamic equation in order to take into account fluctuation at high temperatures. Our proposed equation overcomes the non-analytic damping coefficients in the Laudau-Lifshitz-Bloch (known as LLB) equation and may be broadly used for modeling laser pump-probe experiments and heat assisted magnetic recording. In Fig. 2, we show how the improved equation differs from the conventional Landau-Lifshtz when the temperature is higher than the Curie temperature.

Planned Activities

In the next year, we continue to execute and expand our proposed research. Two research directions are described below.

First, we will study laser induced femtosecond spin dynamics beyond the adiabatic limit. Up until now, we have focused the magnetization dynamics adiabatically, namely, one can define temperatures for each electronic systems although different subsystems have their own time-dependent temperatures. Such adiabatic assumption is no longer valid when the initial electronic excitations are ultra-fast, of the order of femtoseconds. In fact, recent experiments have already indicated that the initial spin dynamics play key roles for the evolution of the non-equilibrium spin states to the eventual equilibrium states. Thus, it is needed to develop theory without the adiabatic approximation. The approach we are taking is the quantum kinetic theory where the density matrix of particles follows kinetic Bloch equation without assuming the smallness of non-equilibrium density to the equilibrium value. Since the microscopic Hamiltonian of the interactions for transitional metal-based ferromagnts are relatively known, we can solve the equation in various conditions relevant to experiments. We hope that our research would advance our fundamentally understanding of physics of demagnetization and remagnetization at femtosecond time scale.

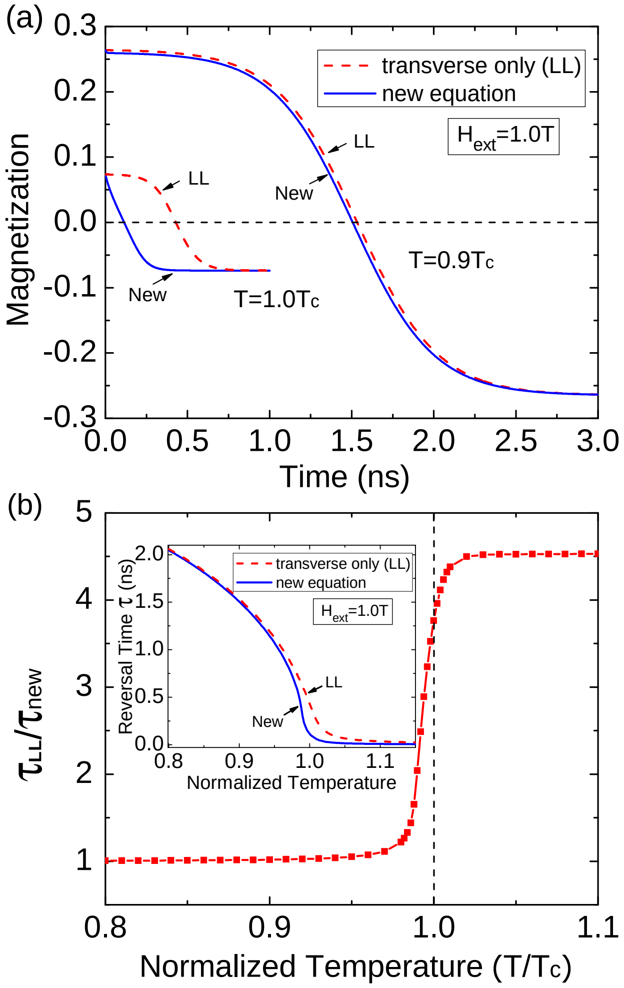

FIG. 2: a) The time dependence of magnetization reversal when a reversal magnetic field is applied at $t > 0$ for the temperature $T = 0.9T_c$ and $T = 1.0T_c$ as indicated. The blue (solid) and red (dashed) curves were obtained by our new proposed equation and by the the conventional Landau-Lifshitz equation, respectively. b) the reversal times and their ratio as a function of the temperature obtained from a). The parameters are: spin relaxation time $\tau_s = 1.0$ ps, spin $S = 1/2$, the anisotropy constant $K = 0$, and the external field $H = 1.0$ T.

The second research direction we are taking is on the application of the improved Landau-Lifshitz equation we have just proposed a few months ago (we name it the generalized Bloch equation). In micromagnetic modeling of magnetization dynamics, the most popular method is based on either the atomistic Landau-Lifshitz (a-LL) equation or Landau-Lifshitz-Bloch equation which is derived from the a-LL equation. Even though the a-LL equation is known to have severe fundamental problems, it continues to be a main tool in explaining and predicting experimental phenomena. We will take two distinct steps to evaluate the effectiveness of our proposed effective equation in replacing the a-LL model: 1) by using the known microscopic interactions, we determine the relaxation parameter in our generalized Bloch equation, and 2) we will carry out extensive simulations for various systems. The simulation will start with simple bulk ferromagnetic metals and gradually adding complexities such as the finite size effect and multi-composite materials (e.g., ferrimagnetic materials). Our goal is to provide a better simulation tool based on the improved equation which overcomes the shortcomings in the existing a-LL model.

Publications

1. A. Manchon, Q. Li, L. Xu and S. Zhang, Theory of laser-induced demagnetization at high temperatures, Phys. Rev. B **85**, 064408 (2012) (10 pages).
2. L. Xu and S. Zhang, Electric field control of interface magnetic anisotropy, J. Appl. Phys. **111**, 07C501 (2012).
3. L. Xu and S. Zhang, Magnetization dynamics at elevated temperatures, accepted for publication in Physica E (2012) (9 pages).
4. A. Manchon and S. Zhang, Spin Torque Effects: Theory, to appear as Chapter 8 of the book entitled: Spin Transport and Magnetism in Electronic Systems (K10210), Taylor & Francis Group, edited by E. Y. Tsymbal and I. Zutic, to appear in 2012.
5. S. Zhang, Voltage control magnetization, to appear as a chapter of the book entitled: Spin current, A SERIES ON SEMICONDUCTOR SCIENCE AND TECHNOLOGY, Oxford University Press, edited by S. Maekawa *et al.*, to appear in 2012.

Tailoring Magnetism and Spin in Quantum Dots

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PROJECT SCOPE

Magnetic doping of semiconductor nanostructures such as quantum dots (QDs) provides an interesting interplay of interaction effects in confined geometries and novel opportunities to control the ordering of carrier spin and magnetic impurities at the nanoscale. However, owing to the computational complexity of including even a small number (~10) of magnetic impurities, there is a greater need to apply various approximations schemes to describe magnetic QDs. Unfortunately, a widely used mean-field approximation neglects the thermodynamic spin fluctuations and shows serious problems, including spurious phase transitions, when applied to such small magnetic systems. These difficulties impede the progress in understanding of the fundamental properties and the potential applications of magnetic QDs. To systematically address this situation, our main objectives are: (i) to develop a comprehensive framework suitable to study the interplay of many-body effects and quantum confinement in small magnetic systems; (ii) to explore novel possibilities to control the ordering of magnetic impurities and carrier spin in QDs, as well as to provide proposals for their experimental implementation.

RECENT PROGRESS

Robust Magnetic Polaron Formation in (II,Mn)VI Quantum Dots

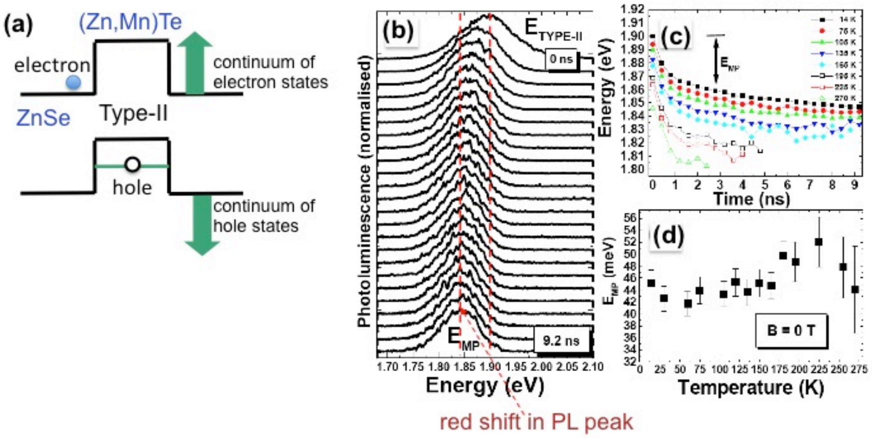

Fig. 1 (a) Type-II band alignment in the (Zn,Mn)Te/ZnSe QDs. (b) Temporal evolution of the PL at 14 K. (c) Time dependence of the photoluminescence (PL) peak from 14 to 270 K. (d) Temperature dependence of the magnetic polaron formation energy (E_{MP}).

The formation of a magnetic polaron (MP) can be viewed as a cloud of localized impurity spins, aligned through exchange interaction and is typically considered a low-temperature phenomenon ($T < 30$ K) and binding energy $E_{MP} < 20$ meV [1]. In collaborations with experimentalists at U. Buffalo, we explored paths to overcome those limitations and provide a theoretical explanation for robust MP formation. The previous QDs with Type-I band alignment (the position of a conduction band minimum and valence band maximum coincide) were not suitable to promote high-temperature magnetism and we turned to Type-II QDs (Fig. 1). Our dots have a strong spatial separation between electrons and holes leading to much longer radiative lifetimes — the carriers have more time to align nearby Mn-spins, combined with a strong Mn-hole overlap. The MP formation leads to the energy lowering and a red shift in the photoluminescence (PL). Our time-resolved PL measurements, reveal a striking difference from the previous results in epitaxial

Type-I QDs : 1) MP formation persists to a much higher *T*, in Fig. 2 (c) (> 200 K, vs ~ 30 K for Type-I QDs). 2) E_{MP} in Fig. 2 (c) is 2-3 times larger than in Type-I QDs. 3) weak *T*-dependence in Fig. 2 (d) is very different from the rapid decay in Type-I QDs. Our theoretical model [1] has explained these findings. We have incorporated subtleties of the Type-II QDs and proposed a prominent role of the Mn-Mn aniferromagnetic coupling on MP formation, leading to a weak *T*-dependence of the transverse magnetic susceptibility and thus to the weakly dependent $E_{MP}(T)$.

Predictions of Closed-Shell Magnetism in Quantum Dots

We have proposed a new concept of magnetic bipolaron and an unexpected possibility of magnetic ordering in closed-shell QDs [2]. Predictions of magnetic properties of QDs are usually guided by knowledge of their shell structure, a ubiquitous feature in small systems of interacting particles such as atoms, nuclei, and QDs. According to a theorem by Wigner, the ground state of any non-magnetic two-electron system, including a two-electron QD, is a spin-singlet. Thus, it is widely expected that closed-shell Mn-doped QDs do not allow magnetic ordering. However, on the example of a two-particle system, we show, that the Mn-doping alters the magnetic properties of closed-shell QDs. Surprisingly, we find a pseudosinglet (PS) ground state (total spin zero realized with two different Bohr radii), which allows ordering of Mn spins that could be interpreted as the two-particle analog of magnetic polaron, which we term magnetic bipolaron.

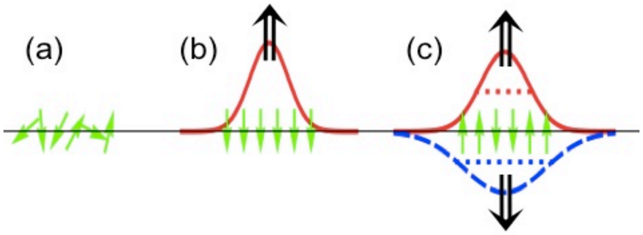

Fig. 2 Emergence of magnetic bipolarons. (a) Without carriers, Mn spins (green arrows) are randomly oriented. Black arrows show carrier's spin projection associated with the orbitals. (b) With one carrier MP forms. Mn spins align in one direction. (c) Two carriers assemble in a PS state, forming a magnetic bipolaron. The sign of the Mn-spin projection depends on the sign of the carrier-spin density [2].

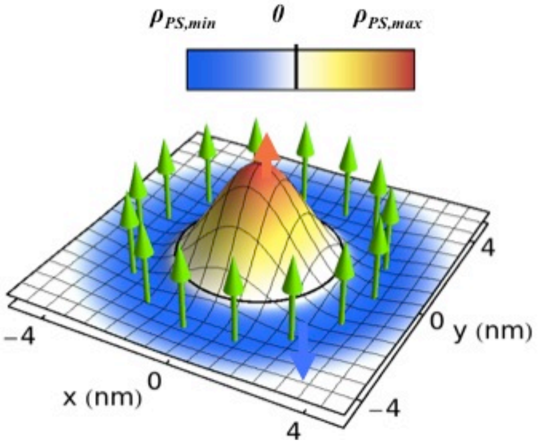

Fig. 3 Spin corral. Colored surface: The hole-spin density ρ_{PS} of PS. Black circle indicates vanishing $\rho_{PS.}$ Green arrows: Mn spins, placed to maximize the stability of the ferromagnetic alignment. Red and blue arrows: The more probable hole-spin projections at two positions [2].

We envision a possibility for a formation of spin corral, illustrated in Fig. 3. Suitable radial placement on Mn atoms leads to the periphery by intentionally introducing Mn in the material surrounding the dot. In epitaxial CdSe/(Zn,Mn)Se Type-I QDs Mn can be created only at the periphery by intentionally introducing Mn in the material surrounding the dot. In colloidal QDs radial segregation of impurities occurs during the growth, desirable for the implementation of spin corral. The placing of individual Mn ions with STM is another promising path to realize the spin corral.

We predict that the PS existence can be experimentally verified for a homogeneous distribution of Mn in QDs, e.g., as a blue shift of interband PL with magnetic field B applied along the growth axis. With increasing B, all the Mn spins will tend to align antiparallel to it, destroying the PS magnetization profile. Thus, PS should increase its energy, while evolving towards the ordinary singlet. This effect could be observed in Type-II QD, strong exchange coupling in these QDs is seen as MP formation [1].

Monte Carlo Simulations of Electrical Control of Ferromagnetism in Quantum Wells

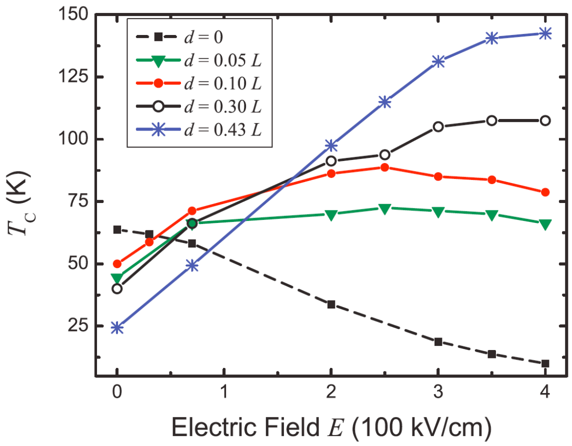

Fig. 4 Dependence of Curie temperature T_C on electric field for various off-center displacements d for a thin magnetic layer from the center of a quantum well having a width L [3].

We have developed detailed Monte Carlo simulations [3] revealing that the electrical-control of ferromagnetism in (Ga,Mn)As, a can lead to a reversible switching of ferromagnetism with $\Delta T_C > 100\ K$ [Fig. 4], an order of magnitude larger range than in the state-of-the art experiments. The key consideration is the proper optimization of the sample geometry. We have chosen GaAs quantum well in which we have altered the position of the thin magnetic layer (Mn-doped) resulting in a high degree of control of T_C. The use of electric field for a reversible electrostatic doping is particularly suitable since it does not alter the level of disorder, while providing important clues about the ordering, including the possibility of the impurity-band formation and localization effects. The attainable electric field can also strongly modify materials properties in other systems such as high-temperature superconductors, manganites, and single-molecule devices [4].

Other Topics

We have also explored other possibilities to control spin and magnetism in semiconductor nanostructures. One of them pertains to magnetic anisotropy, extensively studied in bulk dilute magnetic semiconductors, but largely overlooked in magnetic QDs where it could play an important role, in transport phenomena, formation of MPs, control of magnetic ordering, non-volatile memory, and quantum bits. We have shown that tuning the confinement allows a control of magnetic easy axis in QDs in ways not available in bulk dilute magnetic semiconductors [5]. We have also explored the implications of spin-dependent properties in QDs on lasers [6-8] and considered different possibilities to use thermal gradients and inhomogeneous magnetization to optimize transport properties [8-11]. With E. Tsymbal (U. Nebraska), the PI has co-edited a comprehensive book of Spin Transport and Magnetism which includes an overview by Albert Fert, 2007 Nobel Laureate in Physics and several topics conducted under this project:
http://www.amazon.com/Handbook-Transport-Magnetism-Evgeny-Tsymbal/dp/143980377

FUTURE PLANS

We plan to investigate several peculiar effects for magnetic ordering in QDs. For certain hole densities p we expect a reentrant T-dependence of the magnetization: it disappears for some temperature range and reappears at higher T. Some hints for such an unusual behavior could be seen already inferred from Fig. 1(d), where the magnetic polaron binding energy may increase with T. Our preliminary results show that such a reentrant scenario is indeed possible, not just in the mean-field approximation (MF), but also with the fluctuation approach (FA), when the statistical spin fluctuations are correctly taken into account. However, multiple transition temperatures in a MF description of are not physical in small system such as QDs which are clearly not in a thermodynamic limit. FA should therefore lead to a qualitative changes and removal of such spurious transitions. We expect that an experimental realization of a reentrant magnetism is feasible in QDs with thermally changing occupancy (it is not enough to consider a single QD occupancy as in the usual MP description). Our related results are given in Fig. 5. We will study PL of such QDs as the nonmonotonic *T*-dependence of E_{MP} should also be reflected in nonmonotonic trends for the PL peak and intensity to yield clear experimental signatures for our predictions. We will explore how the magnetic bipolarons [2] (neglected in Fig. 5 for double QD occupancy) would modify the reentrant magnetism. We will develop Monte Carlo simulations to further corroborate the prospect for reentrant magnetism and other effects of multiple QD occupancies.

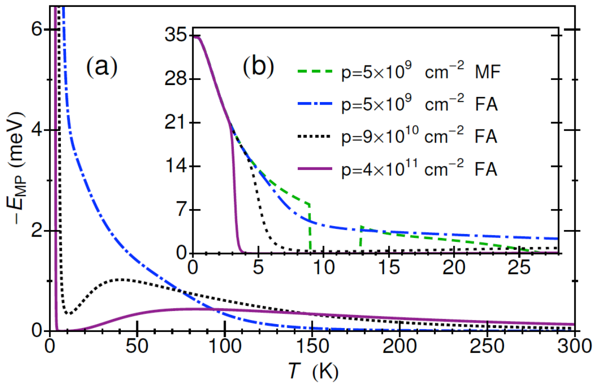

Fig. 5 (a) Reentrant magnetism in the fluctuation approach (FA) for p=5 x 10^9, 9 x 10^{10}, 4 x 10^{11} cm^{-2}. Comparison of the FA and the mean field (MF). FA (dot-dashed) shows no reentrant magnetism predicted for p=5 x 10^9 cm^{-2} (dashed).

It is known that in that the interplay of confinement and Coulomb interactions in nonmagnetic quantum dots can lead to strongly correlated phases differing qualitatively from the Fermi liquid behavior. We will explore how the presence of magnetic impurities in QDs can provide additional opportunities to study correlation effects and the resulting ordering in carrier and impurity spin. For this investigations it will be crucial to accurately treat the effects of Coulomb interactions so we will compare several different methods: from the exact diagonalization and Monte Carlo studies to the more intuitive variational approaches. We expect to establish how the correlations could be enhanced by the Mn-impurities and which experimental probes would be suitable to identify the corresponding signatures of strongly correlated phases.

We made a substantial progress in proving that for the open-shell QDs the spin-ordered states of Mn impurities with spontaneously broken time-reversal symmetry persist at all *T*. For the single-carrier dots these states are MPs. Our method accounts for thermodynamic spin fluctuations using the steepest descent integration with proper elimination of the Goldstone modes. We intend to demonstrate that the correct choice of the saddle point is crucial for avoiding spurious phase transitions, common artifacts of the mean-field approach to the nanoscale magnetic systems.

List of Papers Supported by this DOE Award

1. I. R. Sellers, R. Oszwaldowski, V. R. Whiteside, M. Eginligil, A. Petrou, I. Zutic, W. –C. Chou, W. C. Fan, A. G. Petukhov, S. J. Kim, A. N. Cartwright and B. D. McCombe, Robust Magnetic Polarons in Type-II (Zn,Mn)Te/ ZnSe Magnetic Quantum Dots, Phys. Rev. B **82**,195320 (2010).
2. R. Oszwaldowski, I. Zutic, and A. G. Petukhov, Magnetism in Closed-Shell Quantum Dots: Emergence of Magnetic Bipolarons, Phys. Rev. Lett. 106, 177201 (2011).
3. E. Dias Cabral, M. A. Boselli, R. Oszwaldowski, I. Zutic, and I. C. da Cunha Lima, Electrical Control of Magnetic Quantum Wells - Monte Carlo Simulations, Phys. Rev. B **84**, 085315 (2011).
4. I. Zutic and J. Cerne, Chameleon Magnets, Science 332, 1040 (2011).
5. K. Vyborny, J. E. Han, R. Oszwaldowski, I. Zutic, and A. G. Petukhov, Magnetic Anisotropies of Quantum Dots, Phys. Rev. B **85**, 155312 (2012).
6. R. Oszwaldowski, C. Gothgen, I. Zutic, Theory of Quantum Dot Spin-Lasers, Phys. Rev. B **82**, 085316 (2010).
7. J. Lee, R. Oszwaldowski, C. Gothgen, and I. Zutic, Mapping Between Quantum Dot and Quantum Well Lasers: From Conventional to Spin Lasers, Phys. Rev. B **85**, 045314 (2012). Editors Suggestion and selected for a Viewpoint in Physics
8. J. Sinova and I. Zutic, The New Moves of the Spintronics Tango, Nature Materials **11**, 368 (2012).
9. B. Scharf, A. Matos-Abiague, I. Zutic, J. Fabian, Theory of Thermal Spin-Charge Coupling in Electronic Systems, Phys. Rev. B **85**, 085208 (2012). Editors Suggestion.
10. I. Zutic and H. Dery, Taming Spin Currents, Nature Materials **10**, 647 (2011).
11. I. Zutic and J. Lee, Spin Twists in a Transistor, Science **337**, 307 (2012).
12. E. Y. Tsymbal and I. Zutic (Editors), Handbook of Spin Transport and Magnetism (Chapman and Hall/CRC Press, New York, 2011), 39 chapters and approximately 800 pages.

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