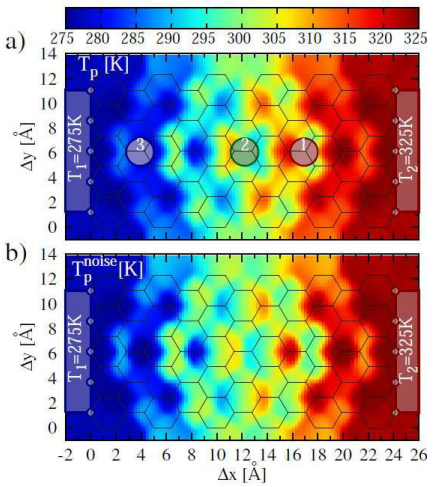
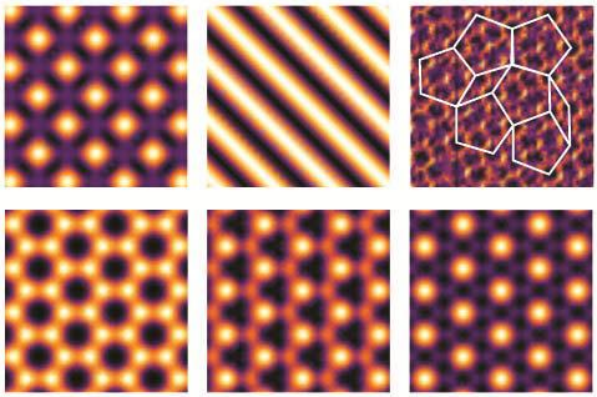
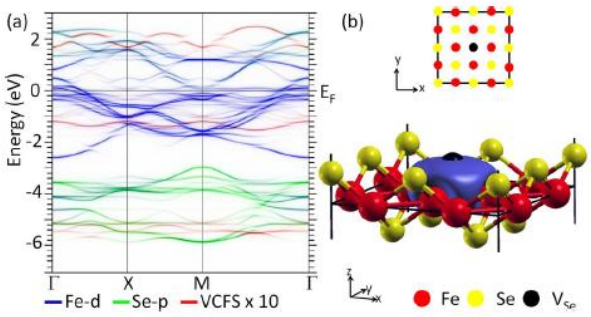
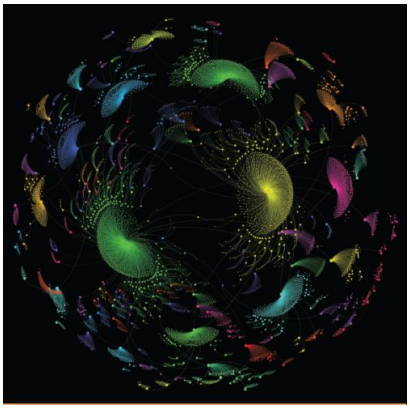
Theoretical Condensed Matter Physics
Principal Investigators' Meeting
August 11-13, 2014
Gaithersburg, Maryland









Office of Basic Energy Sciences
Division of Materials Sciences and Engineering

U.S. DEPARTMENT OF ENERGY | Office of Science

On the Cover

Top left: Local temperature in graphene nanoribbon. J. Meair, J.P. Bergfield, C. A. Stafford, and Ph. Jacquod, Arχiv:1306.6345 (2013).

Top right: Real-space spin and total density plots for various ordered crystalline and quasicrystalline states in cold atom systems. S. Gopalakrishnan, I. Martin, and E. A. Demler, Phys Rev Lett 111, 185304 (2013).

Bottom left: Band structure for Se vacancy in FeSe monolayer. T. Berlijn, Hai-Ping Cheng, P. J. Hirschfeld, and Wei Ku, Phys Rev B 89, 020501R (2014).

Bottom right: Network graph containing all 7,410 DFT-predicted convex hull phases in Open Quantum Materials Database. From Cover, JOM, November 2013.

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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 second TCMP Principal Investigators' meeting, held August 11–13, 2014 in Gaithersburg, 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.

The TCMP program emphasizes strongly correlated materials, materials discovery, non-equilibrium transport, ultrafast response, and fundamental research in materials related to energy technologies. Ongoing research includes strongly correlated electron systems, quantum phase transitions, computational and data driven materials design, magnetism, superconductivity, optical response, semiconductors, thermoelectric materials, and neutron and photon scattering. Computational techniques include quantum Monte Carlo, improvements to density functional theory, extensions of dynamical mean field theory, density matrix renormalization group, self-consistent GW calculations and field theoretical approaches.

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 biennial 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 Tammy Click, Verda Adkins-Ferber, and Tim Ledford 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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AGENDA

2014 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 10, 2014

*****Arrival, Dinner on Your Own*****

MONDAY, AUGUST 11, 2014

7:00 – 8:30 am	*****Breakfast*****
8:30 – 9:00 am	Jim Davenport, Program Manager, Theoretical Condensed Matter Physics *TCMP Program Overview*
Session I	**Superconductivity** Chair: Matthias Graf, Los Alamos National Laboratory
9:00 – 9:30 am	Andrey Chubukov, University of Wisconsin *Search for Exotic Superconductivity in Fe-Pnictides*
9:30 – 10:00 am	Victor Galitski, University of Maryland *Strong Correlation Effects and Fluctuations in Topological Kondo Insulators*
10:00 – 10:30 am	*****Break*****
10:30 – 11:00 am	Eun-Ah Kim, Cornell University *Charge and Spin Order in High Tc Superconductors*
11:00 – 11:30 am	Srinivas Raghu, Stanford University *Unconventional Pairing: Role of Band Structure Effects and Screening*
11:30 – 12:15 pm	Linda Horton, Director, Materials Sciences and Engineering Division *BES Program Updates*
12:15 – 1:00 pm	*****Working Lunch***** *Overview of Poster Session I: Presenters with Highlights*

Session II	**Materials Discovery** Chair: Hai-Ping Cheng, University of Florida
1:00 – 1:30 pm	Priya Vashishta, University of Southern California *Self-Healing Nanomaterials and Hydrogen-on-Demand: Multimillion-Atom Reactive Molecular Dynamics Simulations*
1:30 – 2:00 pm	Lin-Wang Wang, Lawrence Berkeley National Laboratory *Charge Transfer and Carrier Dynamics in Nanostructures, Defects and Organic Systems*
2:00 – 2:30 pm	Christopher Wolverton, Northwestern University *Accelerating Materials Discovery with Data-Driven Atomistic Computational Tools*
2:30 – 3:00 pm	Alex Zunger, University of Colorado *Three Challenges in Discovery-Level Materials Theory*
3:00 – 3:30 pm	***Break***
Session III	**Oxides** Chair: Olle Heinonen, Argonne National Laboratory
3:30 – 4:00 pm	Laurent Bellaiche, University of Arkansas *Switching Magnetic Ordering by an Electric Field in Multiferroics*
4:00 – 4:30 pm	Inna Ponomareva, University of South Florida *Static and Dynamic Properties of Complex Ferroics from Atomistic Simulations*
4:30 – 5:00 pm	Jerry Bernholc, North Carolina State University *Electronic Structure and Electron Transport in Carbon-Based Nanosystems*
5:00 – 5:30 pm	Fernando Reboredo, Oak Ridge National Laboratory *Applications of Ab Initio Quantum Monte Carlo Methods to Strongly Correlated Oxides and Magnetic Materials*
6:00 – 7:30 pm	***Working Dinner*** *Scientific Highlights of the Day: Discussion and Input from Attendees*
7:30 – 9:30 pm	***Poster Session I***

TUESDAY, AUGUST 12, 2014

7:00 – 8:00 am	***Breakfast***
Session IV	**Exotic States** Chair: Jainendra Jain, Pennsylvania State University
8:00 – 8:30 am	Duncan Haldane, Princeton University *Incompressibility and Geometry of Fractional Quantum Hall States*
8:30 – 9:00 am	Senthil Todadri, Massachusetts Institute of Technology *Are Non-Fermi Liquids Stable to Cooper Pairing?*
9:00 – 9:30 am	Alexei Tsvelik, Brookhaven National Laboratory *Composite Order in the Pseudogap Phase of the Cuprates: A Condensation of Coupled CDWs*
9:30 – 10:00 am	Sasha Balatsky, Los Alamos National Laboratory *Novel Superconducting States at Surfaces and Interfaces*
10:00 – 10:30 am	***Break***
Session V	**Magnetism** Chair: Donna Sheng, California State University, Northridge
10:30 – 11:00 am	Leon Balents, University of Califonia, Santa Barbara *Nodal Semimetal and Quantum Criticality in the Pyrochlore Iridates*
11:00 – 11:30 am	Alexander Chernyshev, University of California, Irvine *Disorder, Dynamics and Transport in Quantum Magnets*
11:30 – 12:00 pm	Eugene Chudnovsky, City University of New York *Random Fields, Topology, and Glassy States of Matter*
12:00 – 12:30 pm	Christopher Henley, Cornell University *Quasicrystals from the Bottom Up: Where Are the Atoms and Why?*
12:30 – 1:15 pm	***Working Lunch*** *Overview of Poster Session I: Presenters with Highlights*

Session VI	**Electrons and Phonons** Chair: Yuli Lyanda-Geller, Purdue University
1:15 – 1:45 pm	Murray Daw, Clemson University *New Insights and Methods for Calculating Vibrational Mode Lifetimes in Insulators*
1:45 – 2:15 pm	Andrew Millis, Columbia University *Calculating the Correlated Electron Physics of Real Materials*
2:15 – 2:45 pm	Kostya Matveev, Argonne National Laboratory *Decay of Fermionic Quasiparticles in One-Dimensional Quantum Liquids*
2:45 – 3:15 pm	Samuel Trickey, University of Florida *Density Functionals for Hot Matter*
3:15 – 3:45 pm	***Break***
Session VII	**Semiconductors** Chair: Mei-Yin Chou, Georgia Tech
3:45 – 4:15 pm	Philip Allen, Stony Brook University *Size-Dependent Effects in Phonon Thermal Conductivity*
4:15 – 4:45 pm	Walter Lambrecht, Case Western Reserve University *Electrons, Phonons and Excitons in Halide Perovskites*
4:45 – 5:15 pm	Shengbai Zhang, Rensselaer Polytechnic Institute *Defects in Emerging Electronic Materials*
5:15 – 5:45 pm	Igor Zutic, University at Buffalo *Unconventional Spin and Orbital Ordering in Semiconductor Nanostructures*
6:15 – 7:30 pm	***Working Dinner*** *Scientific Highlights of the Day: Discussion and Input from Attendees*
7:30 – 9:30 pm	***Poster Session II***

WEDNESDAY, AUGUST 13, 2014

7:00 – 8:00 am	***Breakfast***
Session VIII	**Optical Properties** Chair: Charles Stafford, University of Arizona
8:00 – 8:30 am	Igor Bondarev, North Carolina Central University *Plasmon Nanooptics with Pristine and Hybrid Nanotube Systems*
8:30 – 9:00 am	John Rehr, University of Washington, Seattle *Cumulant Expansion Methods for Multi-electron Excitations and Satellites in X-ray Spectra*
9:00 – 9:30 am	David Singh, Oak Ridge National Laboratory *Materials Theory*
9:30 – 10:00 am	Lilia Woods, University of South Florida *Casimir Interactions in Graphene Systems: A Novel Perspective of a Ubiquitous Force*
10:00 – 10:30 am	*** **Break***
Session IX	**Non-Equilibrium & Time Dependence** Chair: Guoping Zhang, Indiana State University
10:30 – 11:00 am	Claudio Chamon, Boston University *Non-equilibrium Steady State Design of Electronic Material Properties*
11:00 – 11:30 am	James Freericks, Georgetown University *Theoretical Description of Ultrafast Pump/Probe Experiments in Electron-Phonon Coupled Systems*
11:30 – 12:00 pm	Michel van Veenendaal, Northern Illinois University *Nonequilibrium Dynamics in Photoinduced Systems*
12:00 – 12:30 pm	Emanuel Gull, University of Michigan *Bold-Line Quantum Monte Carlo on the Real-Time Contour: Combining Analytical and Numerical Methods*
12:30 – 1:00 pm	**Wrap-up, debriefing, evaluation** *Meeting Feedback, Suggestions for Future Meetings*

TCMP PI Meeting

Poster Session I, Monday 7:30 – 9:30 PM

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

2. **Harold Baranger,** Duke University
   Environmental Entanglement Caused by a Qubit: Multi-Polaron Ansatz for the Spin-Boson Model

3. **Nick Bonesteel**, Florida State University
   Gauge Fluctuations and Interlayer Coherence in Bilayer Composite Fermion Metals

4. **Kieron Burke and Steve White**, University of California Irvine
   Studying Failures of DFT with DMRG

5. **Garnet Chan**, Princeton University
   Seriously Realistic Correlated Materials

6. **Hai-Ping Cheng,** University of Florida
   Electron Transport Across Graphene Side-Contact Junctions by a Plane-Wave Multiple Scattering Method

7. **Piers Coleman**, Rutgers University
   Possible Internal d-Wave Structure of s± Pairs in Iron-Based Superconductors

8. **Rafael Fernandes**, University of Minnesota
   Origin of Electronic Nematicity and Its Impact on the Superconductivity of Iron-Based Materials

9. **Liang Fu,** Massachusetts Institute of Technology
   Topological Crystalline Insulators

10. **Yuli Lyanda-Geller**, Purdue University
    New Topological Charge Density Patterns and Melting Transitions in Quantum Hall Systems

11. **Leonid Glazman**, Yale University
    Dynamics of Quasiparticles in Superconducting Weak Links

12. **Francois Gygi**, University of California, Davis
    High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

13. **Eric Heller**, Harvard University **and Mario Borunda**, Oklahoma State University
Quantum Optimal Control in Nanostructures

14. **Michael Hermele**, University of Colorado
New Parameter Regimes and States of Matter in Strongly Correlated Quantum Systems

15. **Peter Hirschfeld**, University of Florida
Impurity Induced States in Superconducting $Bi_2Sr_2CaCu_2O_{8+\delta}$

16. **Kai-Ming Ho**, Ames Laboratory
Development of Methods for Crystal Structure Prediction and Material Discovery

17. **Jainendra Jain**, Pennsylvania State University
Fractional Angular Momentum in Ultra-Cold Atomic Systems

18. **Paul Kent**, Oak Ridge National Laboratory
Developments in Ab Initio Quantum Monte Carlo

19. **Wei Ku**, Brookhaven National Laboratory
Effects of Disordered Impurities in Fe-Based Superconductors

20. **Patrick Lee**, Massachusetts Institute of Technology
Properties of Majorana Bound States: Poisoning Time and Other Issues

21. **Robert Markiewicz**, Northeastern University
Electronic Structure, Spectroscopy and Correlation Effects in Novel Materials

Poster Session II, Tuesday, 7:30 – 9:30 PM

1. **Mei-Yin Chou**, Georgia Tech
Computational Studies of the Electronic Properties of Few-Layer Graphene

2. **Sumit Mazumdar**, University of Arizona
Metal-Intercalated Polycyclic Aromatic Hydrocarbons and Superconductivity: Role of Molecular Valence 3

3. **Eugene Mishchenko**, University of Utah
Attraction-Repulsion Transition in the Interaction of Adatoms and Vacancies in Graphene

4. **Jeffrey Neaton and Lin-Wang Wang**, Lawrence Berkeley National Laboratory
Theory of Materials at LBNL

5. **Danny Perez**, Los Alamos National Laboratory
   Multiscale Accelerated Dynamics

6. **Talat Rahman and Duy Le**, University of Central Florida
   Single-Layer Transition Metal Dichalcogenides: Good Old Materials with Tunable Novel Properties

7. **Peter Riseborough**, Temple University
   The Competition between Neel and Hidden Order in URu_2Si_2

8. **Sashi Satpathy**, University of Missouri
   Two-Dimensional Electron Gas and the Rashba Effect at a Polar Surface: The $KTaO_3$ (100) Surface

9. **Pedro Schlottmann**, Florida State University
   Phase Separation and FFLO Phases in Ultra-Cold Gas of Fermionic Atoms with Attractive Potential in a 1D Trap

10. **Donna Sheng**, California State University, Northridge
    Entanglement and Topological Characterization of Bilayer System

11. **Charles Stafford**, University of Arizona
    Local Thermodynamics of a Quantum System Far from Equilibrium

12. **Uwe Täuber and Michel Pleimling,** Virginia Tech
    Non-equilibrium Relaxation and Aging Scaling of Magnetic Flux Lines in Disordered Type-II Superconductors

13. **Giovanni Vignale**, University of Missouri, Columbia
    Density Functional Theory of Thermoelectric Phenomena

14. **Valerii Vinokur**, Argonne National Laboratory
    Fluctuations and Coherence in Quantum Mesoscopic Systems

15. **Art Voter**, Los Alamos National Laboratory
    Hyperdynamics at Extreme Scales

16. **Cai-Zhuang Wang**, Ames Laboratory
    Gutzwiller Density Functional Theory for First-Principles Calculation of Strongly Correlated Electron Systems

17. **Ruqian Wu**, University of California, Irvine
    Chern Half Metals: The Case of Graphene with Co or Rh Adatoms

18. **Zhigang Wu**, Colorado School of Mines
    Electronic and Optical Properties of Graphene with Periodic Defects

19. **Guoping Zhang,** Indiana State University
    Laser-Induced Ultrafast Demagnetization and Spin Switching in Femtomagnetism: Passage through Exchange Interaction and Exchange Splitting

20. **Shufeng Zhang,** University of Arizona
    New Insights of Spin Pumping from Time-Dependent Linear Response Approach

Theory and Computation for Semiconductor Catalysis and Solar Water Splitting

Principle investigator: Philip B. Allen
Department of Physics and Astronomy
Stony Brook University, Stony Brook, NY 11794-3800
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Project Scope

The aim is improved theoretical understanding of processes by which solar energy can be captured at catalytic interfaces (e.g. the semiconducting GaN/water interface) to drive the reaction $2H_2O \rightarrow 2H_2 + O_2$. Computation (primarily density functional theory) provides the method to simulate processes, and to interact with experiment. The material chosen for study is the wurtzite-structure alloy of GaN with ZnO, apparently stable over the full concentration range x of $Ga_{1-x}Zn_xN_{1-x}O_x$. We study structure and thermodynamics of clean and wet surfaces of this alloy. We ask how alloying affects the photo-absorption spectrum and carrier mobility. We study bulk and surface carrier traps and their importance for photo-catalysis. We generalize the USPEX evolutionary structure-predicting algorithms, to enhance predictability of thermodynamically relevant surface and interface structures. We study perovskite-structure polar materials, of the $CaTiO_3/SrTiO_3/BaTiO_3$ family. Their interfaces with water offer new ways to tune the photochemistry. We study pure water and ice in order to improve the microscopic density-functional description (including van der Waals interactions) and to quantify the importance of quantizing the high energy vibrations (particularly the OH stretch.) We study thermal conductivity of these materials. We particularly address the difficult problem of thermal conduction size effects seen in heat management of small systems and relevant to photocatalysis.

Recent Progress

GaN (10-10)/water interface.

The clean non-polar (10-10) surface of GaN has a complicated and important chemical interaction with water. Our Brookhaven collaborators Kharche and Muckerman (KM) have recently published a paper revising a result found previously by Stony Brook colleagues Wang and Fernandez-Serra (WF). Working closely with Kharche and Fernandez-Serra, we confirm that the KM results are more realistic than the WF results. We trace the discrepancy to slow equilibration (long memory of initial conditions.) It has been a valuable exercise to compare results from different researchers using different initial conditions, different system geometries, and different software packages. To our surprise, our most recent simulations (and those of WF) have very odd surface vibrational properties inconsistent with the unpublished details of KM. Our "progress" sometimes seems like a "random walk." In this case, the final outcome, not yet determined, may be to locate a well-hidden bug in a standard software package.

Surface structures

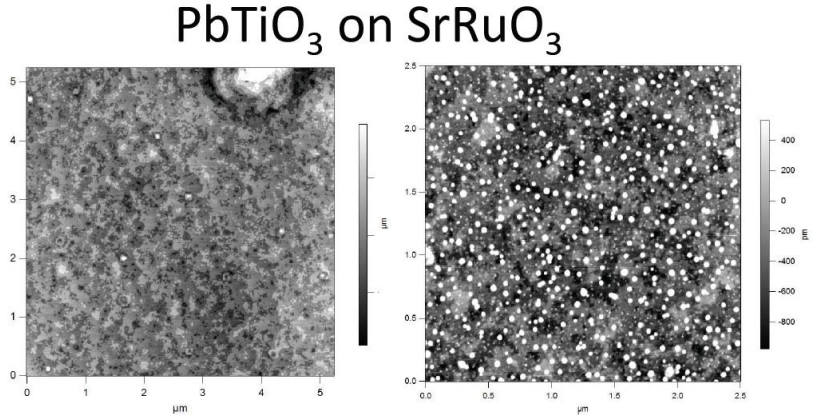
The (0001) surface of ZnO has a particularly carefully studied structure. When oxygen and hydrogen are present, the variety of states identified so far is dauntingly large and complex. We have found a very interesting additional candidate where, in the presence of hydrogen, a zinc vacancy forms; a ZnH_3 complex is built above the vacancy (which is occupied by a fourth hydrogen. This is part of a project to develop a surface-structure prediction capability for the computer codes of the USPEX suite.

Alloy theory

Our earlier work showed that the alloy $Ga_{1-x}Zn_xN_{1-x}O_x$ has a stable ordered x=0.5 phase (consisting of alternating GaN and ZnO layers with (0001) stacking.) However, the ion mobility below 1000K is very small, strongly inhibiting the ordering, which is predicted to occur only below 800K. It is believed that experimental samples of this alloy, used for water splitting, have only short-range order. Using our "cluster-expansion" parameters for this alloy, we have made Monte-Carlo predictions of the short-range compositional order. Density-functional theory (DFT) on 432-atom supercells gives us relaxed coordinates and local bond lengths, showing dramatic local bond-length changes, amounting to almost ±10% deviations from the ordered wurtzite bond lengths. Nearest neighbor bond-lengths can be classified by local environment, but farther neighbors cause significant statistical fluctuations from the mean for a given local environment.

Photocatalysis on perovskite superlattice surfaces.

In collaboration with the Dawber lab, ferroelectric films of $PbTiO_3$ have been tested for



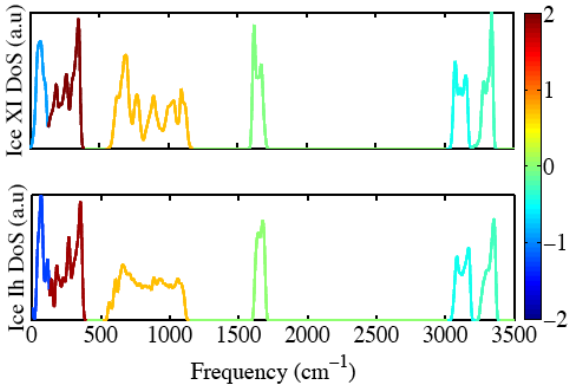
A PbTiO3 film before and after photo-excitation under $AgNO_3$ solution. Dots are metallic silver precipitates.

photocatalytic activity using aqueous $AgNO_3$ solution. Weak ultraviolet illumination is used for a short time. The photo-holes cause water oxidation ($2H_2O + 4h^+ \rightarrow 4H^+ + O_2$) on the $PbTiO_3$/water interface. The photo-electrons reduce the Ag+ ions, which deposit as hemispheres of metallic silver on the $PbTiO_3$ surface. The volume of Ag deposited

then measures the efficiency of oxidation. It is apparent that $PbTiO_3$ works well as a water oxidation catalyst under ultraviolet light.

Nuclear quantum effects in ice and water.

Quantized nuclear motions of the protons in ice and water alter the physics and the photochemistry. D_2O ice has a larger lattice constant than H_2O ice. This anomaly happens because compressing the OH--O distance softens the covalent OH bond while strengthening the non-covalent H--O hydrogen bond. This softens the OH stretch frequency and makes the lattice prefer to shrink to maximize the advantage of reduced zero-point energy. The reversed sign (shrinking instead of expanding) is a specific signature of H-bonding. We have computed the zero point and thermal shifts of the bulk modulus of ice. These are large because of the weak intermolecular bonding. There



A DFT calculation (using a "van der Waals functional") of vibrational density of states of ordered (above) and disordered ice. The color scale indicates the value of the Gruneisen constant that determines zero point and thermal expansion.

exists a significant literature on temperature dependence of bulk modulus. Previous theory consists only of an ad hoc formula, which we find to be wrong. The correct formula for thermal and zero-point corrections to the bulk modulus is

$$B = B_0 - \frac{1}{V_0}\sum_Q n_Q(n_Q+1)\frac{(\hbar\omega_Q\gamma_Q)^2}{k_BT} + \frac{1}{V_0}\sum_Q \hbar\omega_Q\left[\gamma_Q\left(1+\frac{B_0'}{B_0}\right)-\gamma_Q'\right]$$

Here B_0 and V_0 are "frozen lattice" values, n_Q is the Bose function, γ_Q is the Gruneisen constant, and primes indicate dimensionless volume derivatives ($B_0'=VdB_0/dV$.) This new result is being tested against numerical results.

Future Plans (for the next year)

- Alloys: a bond-valence model will be tested to account for the average local environment effect in $Ga_{1-x}Zn_xN_{1-x}O_x$. Optical properties, vibrations, and hot carrier relaxation will be studied.

- $PbTiO_3$-based ferroelectric photocatalysis: band gap tuning by multilayering and alloying will attempt to allow visible light to be used for water splitting. Biasing the ferroelectric as a way to tune the catalytic efficiency will be tested.

- Thermal conductivity will be studied for ice, water, and interfaces of water with crystalline GaN and H_2O.

- I expect to evolve new methodologies for analysis of size effects in thermal conductance. These are based on improving the understanding of the non-locality of thermal conductance $\kappa(\vec{r},\vec{r}')$. This should allow significant improvements in non-equilibrium molecular dynamics simulations, both for nanosystems and for the bulk limit. Theory will be developed to improve the analysis of "transient thermal grating" spectroscopy, a new technique containing information about phonon mean free paths and their influence on finite systems.

Publications (2013-2014)

P. B. Allen, T. Berlijn, D. A. Casavant, and J. M. Soler, "Recovering hidden Bloch character: Unfolding electrons, phonons, and slabs," Phys. Rev. B **87**, 085322:1-10 (2013); erratum Phys. Rev. B 87, 239904 (2013).

Q. Zhu, Li Li, A. R. Oganov, and P. B. Allen, "Evolutionary Method for Predicting Surface Reconstructions with Variable Stoichiometry," Phys. Rev. B **87**, 195317:1-8 (2013).

P. B. Allen, "Improved Callaway model for Lattice Thermal Conductivity," Phys. Rev. B **88**, 144302:1-5 (2013).

Jian Liu, Luana S. Pedroza, Carissa Misch, Maria V Fernández-Serra, and Philip B Allen, "Temperature and composition dependence of short-range order and entropy, and statistics of bond length: the semiconductor alloy $(GaN)_{1-x}(ZnO)_x$," J. Phys. Condensed Mat. **26**, June 17. 2014 (in press).

P. B. Allen, "Size Effects in Thermal Conduction by Phonons," http://arxiv.org/abs/1405.5105, accepted (July, 2014) for Phys. Rev. B, pending minor modifications.

Electron interaction effects in nanosystems

Principal Investigator: Anton Andreev
Physics Department, University of Washington, Seattle, WA 98195

Program scope

The research program aims to develop theory of electron transport in nanosystems with strongly correlated carriers. The work is organized around the following themes.

Theory of electron transport beyond the Fermi- and Luttinger- liquid paradigms. Charge carriers in high mobility semiconductor nanostructures often form strongly correlated liquids in which the energy of Coulomb repulsion U exceeds the Fermi energy, ε_F. In this case there is a wide and largely unexplored interval of temperatures, $\varepsilon_F < T < U$, in which the Fermi-liquid (or Luttinger liquid in one-dimension) description is inapplicable but the liquid remains strongly correlated. Part of the research program focuses on development of theory of electron transport in one- and two- dimensional high mobility systems in the regime where the Luttinger- or Fermi- liquid description becomes insufficient or inadequate. This work will advance our understanding of electron transport in semiconductor nanostructures with strong Coulomb repulsion between the charge carriers.

Transport phenomena in non-centrosymmetric media. Another part of the research program aims to develop theory of transport phenomena in non-centrosymmetric (and/or time reversal non-invariant) conductors and superconductors. This includes theory of linear and circular photogalvanic effect and the Kerr effects in chiral magnets and superconductors, 2) photogalvanic effect in monolayers of transition metal dichalcogenides, 3) theory of spin and charge transport in normal metal/p-wave superconductor structures with the chiral $p_x + ip_y$ symmetry of the order parameter.

Recent Progress

1. *Equilibration of spin-degenerate one-dimensional electron liquid in the Wigner crystal regime* [with K. A. Matveev and A. Klironomos]. Understanding of the microscopic mechanism of equilibration of one-dimensional electron liquids is an important theoretical problem. Equilibration processes affect transport properties of clean quantum wires, Coulomb drag etc. At low temperature equilibration of one dimensional liquids proceeds in two distinct stages: i) equilibration of the gas of particle-hole excitations to some equilibrium state characterized by a velocity u, and ii) slow relaxation of the velocity u to the value dictated by the total momentum of the liquid. The latter stage of equilibration involves electron backscattering processes. Equilibration of one-dimensional quantum liquids has attracted much attention recently. It has been previously studied in the weak interaction regime, where it

proceeds via three body collisions. At strong interactions, where the electrons form a one-dimensional Wigner crystal, a microscopic theory of equilibration processes was constructed only for a spin-polarized electron liquid. Consideration of the spin-degenerate case represents a much more difficult problem, and requires analysis of scattering processes of both spin and charge excitations in the electron liquid. In the limiting case of strong interactions (which is realized at low electron densities) the electron liquid may be viewed as one-dimensional Wigner crystal with antiferromagnetic spin-exchange between the nearest neighbors on the Wigner lattice. The charge excitations correspond to phonons of the Wigner crystal and the spin-excitations are spinons in the Heisenberg chain. In this approximation the Hamiltonian of the system is integrable, and equilibration is absent.

We studied the leading perturbations breaking integrability of the system and their effect on equilibration dynamics. They consist of i) the anharmonic interactions between phonons in the Wigner crystal, ii) coupling between spin and charge excitations, and iii) spin exchange processes between next nearest neighbors in the spin chain. We have obtained the corresponding perturbations to the Hamiltonian and determined the dependence of their strength on the electron density (in units of the inverse Bohr radius). The study of next nearest neighbor exchange processes required numerical work. We also analyzed the effects of these perturbations on equilibration dynamics. This enabled us to evaluate the equilibration rate for spin degenerate electron liquids at strong interactions and determine the temperature dependent correction to the quantized conductance of clean quantum wires. The manuscript reporting the results of this work was recently accepted to Phys. Rev. B, see also arXiv:1406.1762.

2. *Theory of Coulomb drag in the hydrodynamic regime* [with S. Apostolov and A. Levchenko]. We developed a theory of Coulomb drag in ultraclean double layers with strongly correlated carriers. In the regime where the equilibration length of the electron liquid is shorter than the interlayer spacing the main contribution to the Coulomb drag arises from hydrodynamic density fluctuations. These fluctuations consist of plasmons, which are driven by fluctuating longitudinal stresses, and diffusive modes that are caused by temperature fluctuations and ensuing thermal expansion of the electron liquid. We expressed the drag resistivity in terms of the kinetic coefficients of the electron fluid. Our results are nonperturbative in interaction strength and do not assume Fermi-liquid behavior of the electron liquid. This theory is relevant for Coulomb drag measurements in clean semiconductor nanostructures with strong Coulomb interactions. The results of this work were published in Phys. Rev. B **89**, 121104(R) (2014).

3. *Electron transport in normal metal/p-wave superconductor junctions* [A. Keles and B. Spivak]. We developed a theory of low temperature electron transport in p-wave superconductor-insulator-normal metal junctions. In diffusive metals the p-wave component of the order parameter decays exponentially at distances larger than the

mean free path *l*. At the superconductor-normal metal boundary, due to spin-orbit interaction, there is a triplet to singlet conversion of the superconducting order parameter. The singlet component survives at distances much larger than *l* from the boundary. It is this component that controls the low temperature resistance of the junctions. As a result, the resistance of the system strongly depends on the angle between the insulating boundary and the **d**-vector characterizing the spin structure of the triplet superconducting order parameter. We also analyzed the spatial dependence of the electric potential

in the presence of the current, and show that the electric field is suppressed in the insulating boundary as well as in the normal metal at distances of order of the coherence length away from the boundary. This is very different from the case of the normal metal-insulator-normal metal junctions, where the voltage drop takes place predominantly at the insulator.

The results of this work were published in Phys. Rev. B **89**, 014505 (2014). This paper was selected as Editor's suggestion.

4. *Theory of disordered unconventional superconductors* [with A. Keles, B. Spivak, and S. Kivelson]. In contrast to *s*-wave superconductivity, which by Anderson theorem is robust with respect to disorder, unconventional superconducting state is very sensitive to disorder is easily driven to a normal state. In the vicinity of the transition between superconducting and normal states the superconducting state consists of superconducting islands connected by Josephson links. It was shown by Kivelson and Spivak that for *d*-wave superconductors the Josephson junction model reduces to the Mattis model. In this work we extended the theory to *p*-wave materials and studied the role of spontaneous breaking of time reversal symmetry in the superconducting state. The Mattis model arises as a leading approximation in the distance between the islands. We studied corrections to the Mattis model and stability of the superconducting phase with respect to perturbations to the Mattis model Hamiltonian. The manuscript on this work was submitted for publication to JETP, see also arXiv:1405.7090.

Future plans

- *Coulomb drag in the collisionless-to-hydrodynamic crossover region*. Most theoretical treatments of Coulomb drag in clean bilayer systems focused on the collisionless regime, where the mean free path due to intralayer electron-electron scattering exceeds the interlayer distance. In our recent work (Ref. 2 below) we studied Coulomb drag in the collision-dominated hydrodynamic regime. We are currently working on the theory of Coulomb drag in the crossover region between the collisionless and the hydrodynamic regime. This theory is being developed assuming applicability of the Fermi-liquid theory.

- *Resonant photovoltaic effect in dichalcogenides.* We are working on the theory of photovoltaic effect in semiconductor dichalcogenide monolayers in the regime where the frequency of radiation is below the band gap but is nearly resonant with the exciton absorption line.
- *Magnetooscillations of transport and thermodynamic quantities in singly connected conductors* [with I. Aleiner and V. Vinokur]. Quantum interference pattern of electron trajectories depends sensitively on the magnetic field. This sensitivity underlies many magnetotransport phenomena in disordered conductors at weak fields. In the metallic regime magnetotransport effects are governed by statistics of magnetic field fluxes threading the trajectories of diffusing electrons. The latter depend sensitively on the proximity to the sample boundary. Our preliminary results show that this sensitivity results in oscillatory dependence of equilibrium and transport phenomena in singly connected conductors connected to superconducting leads. This may explain oscillations in magnetoconductance of singly connected SNS junctions in the resistive state that were observed in recent transport experiments in D. Shahar's group.

List of publications 2014

1. "Electron transport in p-wave superconductor-normal metal junctions" A. Keles, A. V.Andreev, and B. Z. Spivak Phys. Rev. B **89**, 014505 (2014).
2. "Hydrodynamic Coulomb drag of strongly correlated electron liquids", S. S. Apostolov, A. Levchenko, and A. V. Andreev, Phys. Rev. B **89**, 121104(R) (2014).
3. "Vortex lattices in dipolar two-component Bose-Einstein condensates", N. Ghazanfari, A. Keles, M. O. Oktel, Phys. Rev. A¨ **89**, 025601 (2014).
4. "Theory of disordered unconventional superconductors", A. Keles, A. V. Andreev, S. A. Kivelson, B. Z. Spivak, arXiv:1405.7090, submitted to JETP.
5. "Scattering of charge and spin excitations and equilibration of a one-dimensional Wigner crystal", K. A. Matveev, A. V. Andreev, A. D. Klironomos, arXiv:1406.1762, accepted to Phys. Rev. B.

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. Recently we begin investigation of the possible multiband superconducting state at the STO/LaAlO interfaces.

Recent Progress

Progress has been focused on two areas. The 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 more phenomenological strongly correlated models. In parallel, we are developing theory of novel orders that can capture tendencies for inhomogeneous domain structures in correlated matter with a shift in research toward interfaces. Progress is organized around (1) methods development and (2) applications or detailed model studies.

Methods Development

We continued the development of ab-initio methods with correlation effects and corresponding downfolded effective tight-binding models. We focused on the DMFT and FLEX approximations for electron correlations to be combined with ab-initio electronic structure calculations for predictions of spectral properties in ARPES or for downfolded tight-binding Hamiltonians. In parallel we developed lattice Bogoliubov-de Gennes (BdG) solvers for nanoscale defects within the scenario of the Swiss Cheese model and relevant for

interfaces, which can be viewed as extended two-dimensional defects. The BdG methods were applied to pnictides for studies of ARPES, LDOS and penetration depths.
In an unrelated effort, we applied our expertise on defects and disorder to solid helium and the possibility of intrinsic quantum inhomogeneity of states.

Applications

Integrated with the development of methods, we studied various materials and model systems. Specific examples are given below.

Effective low-energy theories and inelastic spectroscopies of emergent states

Stability of Weyl metals and Dirac materials: We investigated the effects of bulk impurities on the electronic spectrum of Weyl semimetals, a recently identified class of Dirac materials[1]. Using a T -matrix approach, we studied resonant scattering due to a localized impurity in tight-binding versions of the continuum models recently discussed by [Burkov, Hook, and Balents, Phys. Rev. B 84, 235126 (2011)], describing perturbed four-component Dirac fermions in the vicinity of a critical point. The impurity potential is described by a strength g as well as a matrix structure. Unlike the case in d-wave superconductors, where a zero energy resonance can always be induced by varying the scalar and/or magnetic impurity strength, we find that for certain types of impurity, the Weyl node is protected and that a scalar impurity will induce an intragap resonance over a wide range of scattering strength. A general framework was developed to address this question, as well as to determine the dependence of resonance energy on the impurity strength.

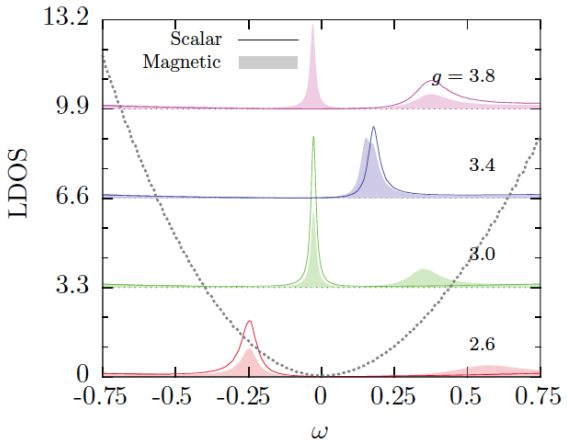

Figure 1: Resonance LDOS at nearest-neighbor site [x,y,z] = [0,0,1] by scalar and magnetic impurities. Solid curves: scalar impurity. Shaded curves: magnetic scattering. LDOS values with different g couplings are plotted on different baselines.

Inelastic electron tunneling spectroscopy at local defects in graphene. We addressed local inelastic scattering from the vibrational impurity adsorbed onto graphene and the evolution of the local density of electron states near the impurity from a weak to strong coupling regime. For weak coupling the local electronic structure is distorted by inelastic scattering developing peaks or dips and steps. These features should be detectable in the inelastic electron tunneling spectroscopy d^2I/dV^2 using local probing techniques. In the strong coupling limit, a local negative U center forms in the atoms surrounding the impurity site. For those atoms, the Dirac cone structure is fully

destroyed, that is, the linear energy dispersion as well as the V-shaped local density of electron states is completely destroyed. We further considered the effects of the negative U formation and its evolution from weak to strong coupling. The negative U site effectively acts as a local impurity such that sharp resonances appear in the local electronic structure. The main resonances are caused by elastic scattering off the impurity site, and the features are dressed by the presence of vibrationally activated side resonances. Going from weak to strong coupling, changes the local electronic structure from being Dirac-cone-like including midgap states, to a fully destroyed Dirac cone with only the impurity resonances remaining.

Designed states at interfaces - topological states engineering

Proximity-induced unconventional superconductivity in topological insulators. We studied and classified the proximity-induced superconducting pairing in a topological insulator (TI)-superconductor (SC) hybrid structure for SCs with different symmetries. The Dirac surface state gives a coupling between spin-singlet and spin-triplet pairing amplitudes as well as pairing that is odd in frequency for p-wave SCs. We also found that all SCs induce pairing that is odd in both frequency and orbital (band) index, with oddness in frequency and orbital index being completely interchangeable. The different induced pairing amplitudes significantly modified the density of states in the TI surface layer enabling the engineering of topological states.

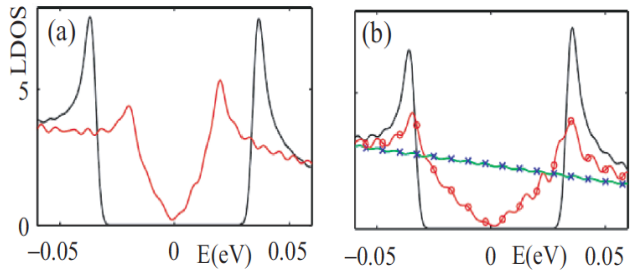

Figure 2: LDOS (states/eV/unit cell) in the TI surface state as a function of energy for a spin-singlet SC (a) with s-wave (black) and d-wave (red) symmetries and for a spin-triplet SC (b) with p-wave A_{1u} (green line), A_{2u} (black line), $B_{1u/2u}$ (red line with circles), and $E_{2u,+/-}$ (blue crosses) symmetries. The Dirac point is found at higher energies due to doping from the SC. Ripples are due to finite k-point sampling.

Future plans

For the next two years, we plan to continue our studies of topological states engineering by focusing in particular on competing interactions at interfaces and emergent states and continue develop ab-initio electronic structure calculations for the correlated materials. The following topics will be investigated:

Modeling of local electronic properties and superconductivity in the presence of strain: Emergent superconductivity can propagate by an increase in the overall carrier density at the interface. This can be due to strain, defects, and dislocations that produce a fundamental shift in the carrier density at the interface. We will use the lattice BdG theory with strain effects

incorporated through ab-initio derived hopping parameters to study local electronic properties.

Modeling of mesoscale magnetic structures with strain:
An intimately connected emergent phenomenon in complex oxide interfaces is the observation of small mesoscale structures. For example, magnetic domains spread "randomly" throughout the $SrTiO_3$ – $LaAlO_3$ interface. We will investigate possible origins of these magnetic domains. We will also investigate the effects of magnetic and electron-lattice interactions in the formation of superconducting state at interface. We believe the superconductivity at the interface is a multiband phenomenon with two superconducting gaps forming within a certain doping range.

Publications

(2013-2014)

1. Dirac Materials; T. Wehling, A Black Schaffer, A.V. Balatsky, Advances in Physics (in press, 2014).
2. Electronic transport properties of different phases of $CaFe_2As_2$: Fermi-surface reconstruction and complex phase equilibria; K. Gofryk , B. Saparov, T. Durakiewicz, M. J. Graf, A. S. Sefat, Physical Review Letters 112, 186401 (May 2014).
3. Evolution of Fermi surface topology in doped 122 iron pnictides; L. Pan, J. Li, Y.-Y. Tai, M. J. Graf, J.-X. Zhu, C. S. Ting, Physical Review B 88, 214510 (Dec 2013).
4. Odd-frequency superconducting pairing in multiband superconductors; A. M. Black-Schaffer, A. V. Balatsky, Physical Review B 88, 104514 (Sep 2013).
5. Comment on "Giant plasticity of a quantum crystal"; C. Zhou, C. Reichhardt, M. J. Graf, J.-J. Su, A. V. Balatsky, I. J. Beyerlein, Physical Review Letters - Comment **111**, 119601 (Sep 2013).
6. Plastic response of dislocation glide in solid helium under dc strain rate loading; C. Zhou, J.-J. Su, M. J. Graf, C. Reichhardt, A. V. Balatsky, I. J. Beyerlein, Physical Review B 88, 024513 (Jul 2013).
7. Engineering three dimensional topological insulators in Rashba-type spin-orbit coupled heterostructure; T. Das and A.V. Balatsky, Nature Commun. 4, 1972 (Jun 2013).
8. Proximity-induced unconventional superconductivity in topological insulators; A. M. Black-Schaffer, A. V. Balatsky, Physical Review B 87, 220506(R) (Jun 2013).
9. Inelastic electron tunneling spectroscopy at local defects in graphene; J. Fransson, J.-H. She, L. Pietronero, A. V. Balatsky, Physical Review B 87, 24504 (Jun 2013).
10. Mapping between finite temperature classical and zero temperature quantum systems: quantum critical jamming and quantum dynamical heterogeneities; Z. Nussinov, P. Johnson, M. J. Graf, A. V. Balatsky, Physical Review B 87, 184202 (May 2013).
11. Field-angle-resolved anisotropy in superconducting $CeCoIn_5$ using realistic Fermi surfaces; T. Das, A. B. Vorontsov, I. Vekhter, M. J. Graf, Physical Review B 87, 174514 (May 2013).
12. Stability of Weyl metals under impurity scattering; Z. Huang, T. Das, A. V. Balatsky, D. P. Arovas, Physical Review B 87, 155123 (Apr 2013).
13. Self-consistent spin-fluctuation spectrum and correlated electronic structure of actinides; T. Das, J.-X. Zhu, M. J. Graf, Journal of Materials Research 28, 659 (Mar 2013), (Invited Feature Paper).

Theory of Fluctuating and Critical Quantum Matter

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Project Scope

Our work centers on the theory of phenomena in electronic materials materials involving strong quantum fluctuations, which arise due to frustration, exotic interactions (especially those originating from spin-orbit coupling), and proximity to quantum critical points. The projects are divided roughly into two areas: phases of frustrated quantum magnets, and quantum critical points in itinerant systems with frustrated or exotic interactions. All components are connected both to specific experiments and materials, and to general issues at the forefront of the theory of correlated quantum matter.

Recent Progress

Quantum spin ice

The rare earth insulating pyrochlores, $A_2B_2O_7$ are a wide class of minerals where A is a magnetic rare earth ion and B is non-magnetic. Some pyrochlores, such as $Yb_2Ti_2O_7$ and $Pr_2Zr_2O_7$, have rare earth electrons which behave like quantum S=1/2 spins. These materials offer the possibility for observing exotic quantum phases. Our group has worked for several years on developing models for the quantum dynamics of spins in these materials, solving their phase diagrams, and searching for exotic ground states.

Using symmetry considerations, we derived a universal model Hamiltonian for insulating rare earth pyrochlores, and vetted this by several detailed comparisons with experiment. This model generalizes the classical spin ice Hamiltonian which describes $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ to the quantum case, hence the name quantum spin ice. We have been developing new techniques to find the ground state and T>0 phase diagram. Initial work introduced a new slave particle representation and an approximate solution in a limited quadrant of phase space using a gauge Mean Field Theory (gMFT), and revealed two distinct so-called U(1) Quantum Spin Liquid (QSL) phases [1]. We have since extended the methodology to tackle other important regimes. For the parameters appropriate to non-Kramer's ions such as Pr^{3+}, we showed the possibility of formation of not only a U(1) QSL but also a fully gapped Z_2 QSL, and also demonstrated a dramatic stabilization

of the U(1) QSL under certain conditions [2]. We also applied the gMFT treatment to T>0, and found that an "entropy collapse" pre-empts the usual symmetry breaking mechanism for the thermal transitions, which explains the very low transition temperatures in these compounds [3].

Order by Disorder

The same model Hamiltonian mentioned above describes *all* rare earth pyrochlores with dipolar doublets, including ones that are not in the quantum spin ice category. The material $Er_2Ti_2O_7$ is an example of an easy-plane antiferromagnet which we have understood in detail. It provides in fact the most robust example to date of the phenomena of quantum order-by-disorder, in which a classical degeneracy is weakly broken by quantum zero point fluctuations. Our quantitative calculations explained inelastic neutron scattering, susceptibility, and specific heat data, and predicted a very small energy gap [4]. This has since been confirmed in experiment, with a magnitude very close to our prediction.

Kagome Spin Liquid

We determined the universal patterns of dimer order in odd-circumference kagome cylinders with a 2d spin-liquid ground state [5]. This is in excellent agreement with DMRG calculations from Steve White's group, and gives further evidence for the nature of the spin liquid ground state in this canonical model of quantum magnetism.

Quantum Criticality in Pyrochlore Iridates

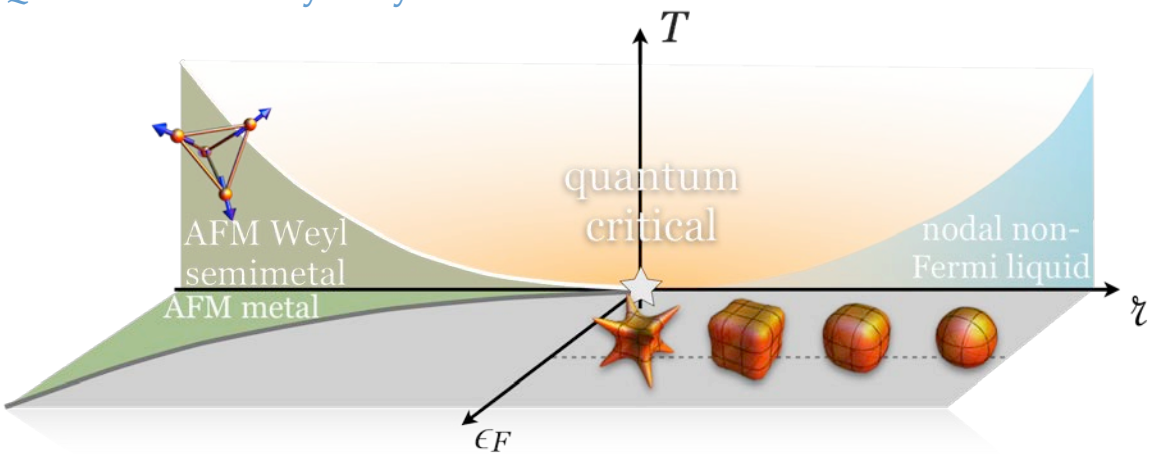

Figure 1: Phase diagram and novel quantum criticality in the pyrochlore iridates.

Quantum criticality is a pervasive and fascinating correlation phenomena in quantum materials. It arises typically in two forms: (1) in insulators, for which standard methods of statistical mechanics are usually applicable, and the criticality itself is often similar to that of a classical thermal phase transition, and (2) in metals, where the enormous number of low energy electronic excitations near the Fermi surface modifies the behavior in an

essentially non-classical way. We have discovered that in strongly spin-orbit coupled systems, a third possibility emerges naturally: in a semi-metal with a point-like Fermi node, the low energy electronic excitations are still significant but less numerous than in a metal. There is considerable evidence for this situation in the pyrochlore iridates.

We have formulated and solved a non-trivial model for such nodal quantum criticality in these compounds, using renormalization group and large N methods [6]. It predicts a broad quantum critical regime and strong renormalization of both quasiparticle and collective modes: a new strongly coupled universality class for quantum criticality. Moreover, perturbations of the critical point allow one to potentially access a wide range of other interesting phases, including a Weyl semimetal, topological insulator, and a non-Fermi liquid phase. Some of these phases are also discussed in our recent review article [7].

Future Plans

Entangled and fluctuating phases of frustrated magnets

We plan new **numerical calculations for quantum spin** ice, to make the phase diagram more quantitative. We are also motivated by recent experimental progress in identifying highly frustrated quantum spin-1/2 antiferromagnets with novel ground states, including candidate QSLs. Two notable examples are herbertsmithite and volborthite, both of which have kagome-lattice like structures. An understanding of their highly suppressed or even absent ordering is still lacking, in our view due largely to a very limited understanding of interactions in these materials. We will sharpen this understanding by modeling the full **magnetization process** versus field magnitude and orientation, by an iterative process of proposing and refining models, and calculating their properties by DMRG and many body analytic methods, and comparison to experiment. Apart from QSLs, there is a strong prospect of finding other "hidden orders" such as **spin nematic** and spin density wave states. We will also work on **double perovskites**, where there are unconventional spin-1/2 frustrated systems in three dimensions, for which spin-orbit coupling plays an essential role. We aim specifically to understand the phase transitions in Ba_2NaOsO_6, which may exhibit an **spatial nematic** phase similar to what is seen in the Fe-based superconductors.

Itinerant quantum criticality in frustrated systems

We plan to continue to apply the group's expertise in frustrated magnets to conducting systems with a frustrated magnetic component. This includes the **pyrochlore iridates** discussed above, for which we plan to more precisely characterize the electronic structure using a combination of *ab initio* calculations and a collaboration with ARPES experimentalists. We will also calculate transport and spectral properties of this system as quantitatively as possible. The next extension is to doping these materials, which provides a natural way to tune between nodal criticality and the Fermi surface case, as well as to tune to the critical point itself. This means of tuning may perhaps be more

accessible, and more robust to effects of disorder. We also have begun to study several **quasi-kagome heavy fermion materials**, which exhibit quantum critical points. Here we will begin by characterizing the order parameters, and then develop field theoretic models and new theoretical approaches to them.

Publications under DOE support

[1] Savary, Lucile, and Leon Balents. "Coulombic quantum liquids in spin-1/2 pyrochlores." *Physical review letters* 108, no. 3 (2012): 037202.

[2] Lee, SungBin, Shigeki Onoda, and Leon Balents. "Generic quantum spin ice."*Physical Review B* 86, no. 10 (2012): 104412.

[3] Savary, Lucile, and Leon Balents. "Spin liquid regimes at nonzero temperature in quantum spin ice." *Physical Review B* 87, no. 20 (2013): 205130.

[4] Savary, Lucile, Kate A. Ross, Bruce D. Gaulin, Jacob PC Ruff, and Leon Balents. "Order by Quantum Disorder in $Er_2Ti_2O_7$." *Physical review letters* 109, no. 16 (2012): 167201.

[5] Ju, Hyejin, and Leon Balents. "Finite-size effects in the Z_2 spin liquid on the kagome lattice." *Physical Review B* 87, no. 19 (2013): 195109.

[6] Savary, Lucile, Eun-Gook Moon, and Leon Balents. "A New Type of Quantum Criticality in the Pyrochlore Iridates." *arXiv preprint* arXiv:1403.5255 (2014).

[7] Witczak-Krempa, William, Gang Chen, Yong Baek Kim, and Leon Balents. "Correlated Quantum Phenomena in the Strong Spin-Orbit Regime." *Annu. Rev. Condens. Matter Phys*. 5, no. 1 (2014): 57-82.

Electronic Structure, Spectroscopy and Correlation Effects in Novel Materials

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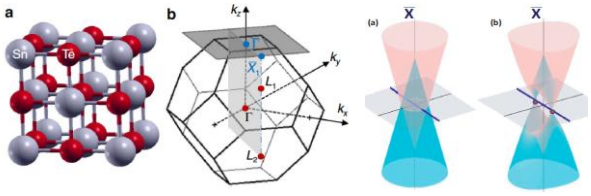
Project Scope

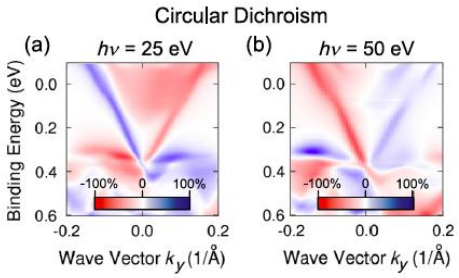
The present research project concerns theoretical studies of electronic structure, spectroscopic response, and correlation effects in a wide variety of novel materials of current interest. Our overarching goal is to undertake realistic modeling of various highly resolved spectroscopies of materials for 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, positron annihilation spectroscopies, and work on neutron scattering and optical spectra. Specific systems considered are cuprates, pnictides, topological insulators, manganites, magnetite, nano-particles, and 2D ultrathin films beyond graphene. 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

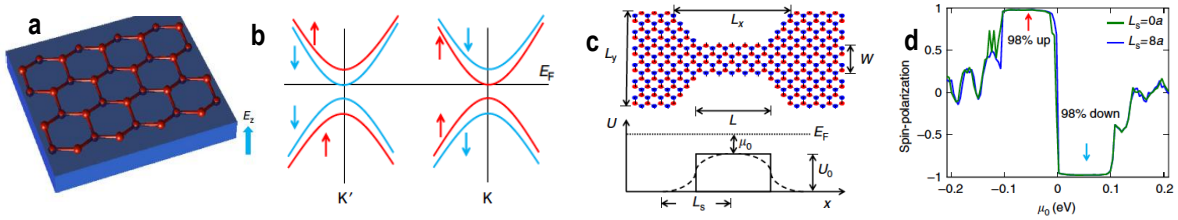
Predicting New Classes of Topological Insulator Materials, Spin Textures of Topological States [Nature Commun. 3, 982 (2012); PRB 87, 235317 (2013); Science 341, 1496 (2013); Nature Commun. 3, 1192 (2012); PRL 110, 216801 (2013); PRB 88, 165129 (2013); Nature Phys. 8, 616 (2012); Nano Lett. 13, 1915 (2013)]: The figure highlights our theoretical prediction that the SnTe system can be expected to harbor a topological crystalline insulator (TCI) phase, a new kind of topological phase in which topological surface states are protected by the mirror symmetry of the crystal lattice. Our prediction was verified subsequently by three experimental groups independently, providing thus the first and currently the only materials realization of a TCI system. We have clarified the complex Dirac cone structure in SnTe (based on our first-principles results) as a pair of interacting Dirac cones (see figure). The Fermi surface undergoes a Lifshitz transition as one goes above or below the Dirac points with complicated evolution of spin textures. In contrast to BiSe/Te, which contains a single Dirac cone located at the center of the [111] surface plane, SnTe supports an even number of Dirac cones protected by the mirror symmetry on surfaces symmetric about the [110] mirror planes with distinct associated Chern numbers. We note that the aforementioned predicted structure of Dirac states has been verified via ARPES and STS/STM experiments.



In connection with determining spin-textures via ARPES measurements, we have shown with the example of Bi_2Te_3 topological insulator (TI) that the dichroic signal (difference between the ARPES intensity for right and left circularly polarized photons) reverses sign as a function of photon energy, which is in accord with the corresponding measurements (see figure). These results leave no doubt that circular dichroism (CD) in the TIs cannot, in general, provide a robust basis for probing the spin textures of the Dirac states, which are of key importance for understanding the nature of TIs and their applications, and that realistic first-principles modeling of the spectra including effects of the final states and the ARPES matrix element are essential for interpreting the CD spectra properly. An analysis of CD spectra based on free-electron final states is fundamentally limited in its reach.

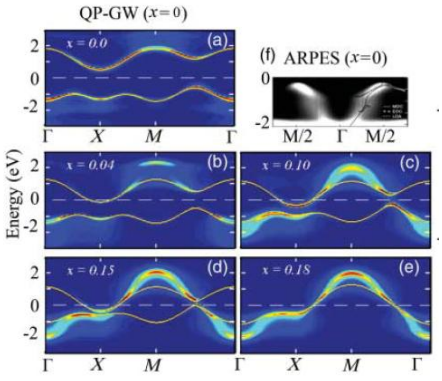


2D Thin Films Beyond Graphene, Spintronics and Other Applications [Nature Commun. 4, 1500 (2013); App. Phys. Lett. 104, 032410 (2014); App. Phys. Lett. 104, 173104 (2014); Nano Lett. 14, 2505 (2014); Nature Nanotech. 9, 111 (2014); PRB 88, 165301 (2013); App. Phys. Lett. 102, 022424 (2013)]: The figure below highlights some of our results with the example of a pristine silicene sheet in the low-buckled honeycomb structure, and shows how the buckling of the structure, in sharp contrast to the flat structure of graphene, allows breaking of the inversion symmetry of the lattice by an external electric field, yielding a band gap and a spin-polarized band structure controllable by a perpendicular



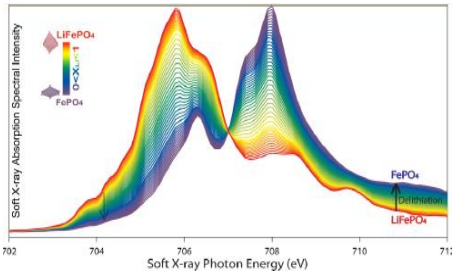
electric field. Our first-principles computations show that field-gated silicene possesses two gapped Dirac cones with nearly 100% spin polarization, see panel (b). On this basis we propose the design of a spin-filter, see panel (c), which would enable the spin-polarization of an output current to be switched electrically, without the need to switch external magnetic fields. Our quantum transport calculations, see panel (d), indicate that our design will be highly efficient (nearly 100% spin-polarization) and robust against weak disorder and edge imprefections. Our analysis further shows that 2D-silicene harbors a rich phase diagram with external electric and magnetic fields in which it goes from a band insulator, to a quantum anomalous Hall insulator, to a valley polarized metal, to a spin valley polarized metallic phase.

A Comprhensive 'Beyond LDA,' GW-Approximation Based Scheme for Modeling the Doping- and temperature-Dependent Electronic Spectra of the Cuprates within the Intermediate Coupling Scenario [Advances in Physics (2014, a major review); PRB 85, 064510 (2012); PRB 85, 075104 (2012); PRB 85, 144526 (2012); PRB 85, 214504 (2012); PRB 85, 224535 (2012); PRB 86, 024511 (2012); Nature Materials 12, 707 (2013); Science 9, 608 (2014)]: Our 'beyond LDA,' intermediate coupling scheme is based on obtaining self-energy corrections to the one-particle Green's function by applying the GW-approximation to the 'uncorrelated,' material-specific LDA-derived spectrum. The only essential parameter involved is the value of the on-site Coulomb energy *U* (Hubbard parameter) at half-filling. We refer to this scheme as a quasi-particle GW or QP-GW scheme. The basic nature of the resulting electronic spectrum of the cuprates can be understood with the example of normal state NCCO and how electronic correlations modify the spectrum for the simple case of a single band under the combined influence of the self-energy corrections and the anti-ferromagnetic order (as the simplest model of the pseudogap).



The figure above shows how the electronic spectrum splits into four distinct pieces. The undoped (x=0) system is seen to be gapped with upper and lower magnetic bands, each of which splits into two parts with electron doping, a low energy coherent part and a higher energy incoherent part, the two parts being connected by the crossover energy scale of the high energy kinks or 'waterfalls' above and below the Fermi energy. With increasing doping from half-filling, small Fermi surface (FS) pieces appear, which yield a large FS in the overdoped system. We have demonstrated the efficacy of our QP-GW model by showing that it captures a great deal of the salient features of the available spectroscopic data on electron as well as hole doped cuprates from ARPES, STM/STS, neutron scattering, inelastic light scattering, optical and other experiments.

Inelastic X-Ray Scattering for Advanced Characterization of Li-battery Materials [JACS 134, 13708 (2012)]: The figure highlights results from our joint theory-experiment Fe L-edge XAS (X-ray absorption spectroscopy) study of the Fe-phosphate material. The spectrum is seen to consist of two distinct features. The feature on the left hand side of the figure increases uniformly in intensity with increasing Li content, while the feature on the right hand side simultaneously undergoes a decrease in intensity. Our modeling of the electronic structure, including multiplet effects, gives insight into the evolution of Fe-3d valence states and how these states are redistributed during the lithiation and delithiation cycles, as charge is transferred between the Li and Fe in the presence of crystal field effects produced by the deformation of FeO_6 octahedra. Our analysis clearly reveals the two-phase nature of the $LiFePO_4$ (LFP) as a cathode material, and allows us to adduce that the shape of the L-edge consists of two distinct associated signals, which can be used to accurately fingerprint the Li content in a sample of LFP of unknown composition.



Planned activities

Highlights of ongoing/planned activities are: (1) Modeling/analysis of spin-textures of topological states in 2D and 3D topological materials and the associated ARPES and STS/STM spectra. (2) New topological materials prediction to expand the menu of available materials, especially the TCIs, where the current choice is limited to just the (Pb,Sn)Te/Se class. (3) Thin film materials beyond graphene, especially those with large spin-orbit coupling, their topological phases, and their quantum transport characteristics in the presence of external electric and magnetic fields. (4) Modeling/analysis of the doping and temperature dependencies of the electronic spectra of the cuprates with focus on the deeply underdoped regime using our comprehensive beyond LDA intermediate coupling scheme, and extensions of this scheme to encompass multi-orbital Fe-based superconductors. (5) Generalizations of our work on realistic modeling of STS/STM spectra of homogeneous phases to treat STS/STM spectra of defects and impurities in the cuprates, including relativistic generalizations for handling TI materials. (6) Modeling electronic structures of ordered and disordered phases of various Li-battery materials, and the associated inelastic x-ray scattering spectra (Compton, XAS, XES, RIXS) to develop the potential of these techniques as unique, in situ, in time advanced characterization tools with the capability to probe closed electrochemical cells. (7) Modeling of K-, L- and M-edge RIXS spectra of cuprates and extensions of our methodology for treating dissipation effects and time-domain problems.

Selected Publications (2012-)

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3. 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,

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8. H. Lin, T. Das, Y. Okada, M. C. Boyer, W. D. Wise, M. Tomasik, B. Zhen, E. W. Hudson, W. Zhou, V. Madhavan, C.-Y. Ren, H. Ikuta, and A. Bansil: "Topological Dangling Bonds with Large Spin Splitting and Enhanced Spin Polarization on the Surfaces of Bi_2Se_3" Nano Letters 13, 1915 (2013).
9. M. R. Scholz, J. Sánchez-Barriga, J. Braun, D. Marchenko, A. Varykhalov, M. Lindroos, Y. J. Wang, H. Lin, A. Bansil, J. Minár, H. Ebert, A. Volykhov, L. V. Yashina, and O. Rader: "Reversal of the Circular Dichroism in Angle-Resolved Photoemission from Bi_2Te_3," Physical Review Letters 110, 216801 (2013).
10. Y. Okada, D. Walkup, H. Lin, C. Dhital, T.-R. Chang, S. Khadka, W. Zhou, H.-T. Jeng, M. Paranjape, A. Bansil, Z. Wang, S. D. Wilson, and V. Madhavan: "Imaging the evolution of metallic states in a correlated iridate," Nature Materials 12, 707 (2013).
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18. M Neupane, S-Y Xu, R Sankar, N Alidoust, G Bian, C Liu, I Belopolski, T-R Chang, H-T Jeng, H Lin, A. Bansil, F. Chou, M. Z. Hasan: "Observation of a three-dimensional topological Dirac semimetal phase in high-mobility Cd_3As_2," Nature Communications 5, 3786 (2014).
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20. Timo Saari, Cheng-Yi Huang, Jouko Nieminen, Wei-Feng Tsai, Hsin Lin, and Arun Bansil: "Electrically tunable localized tunneling channels in silicene nanoribbons," Applied Physics Letters 104, 173104 (2014).

Quantum Phases of Nanosystems: Dissipation, Interactions, and Non-Equilibrium Phenomena

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Project Scope

This project concerns the intersection of three major themes: First, *open quantum systems* have received increasing attention because of both fundamental interest in the decoherence induced when a quantum system interacts with its environment and the relevance to processes of societal relevance such as photosynthesis and energy capture. Second, *quantum simulation* of strongly interacting systems as a way of producing exotic states of matter is being pursued in a variety of settings. Third, *non-equilibrium quantum systems* are being studied for the qualitatively new phenomena that they exhibit. The focus in this project is on how dissipative nanoscale systems can demonstrate and elucidate these three themes by making use of the increasing control that is experimentally possible.

The building block here is a quantum dot coupled to a dissipative electromagnetic environment. Several experimental groups are actively pursuing this platform, including G. Finkelstein here at Duke with whom we collaborate. We have recently shown that this system can emulate resonant tunneling in an interacting one-dimensional Luttinger liquid, and can support strong-coupling fixed points naturally described by Majorana fermions.

The plan for the present project is to further explore possibilities for producing exotic quantum states and phenomena by using quantum dot(s) coupled to dissipative electromagnetic environment(s). One goal, for instance, is to study more complicated open quantum systems (several dots or leads, spin effects, different kinds of environment) in order to survey the kind of physics possible. Another goal is investigate systems described by multiple Majorana modes.

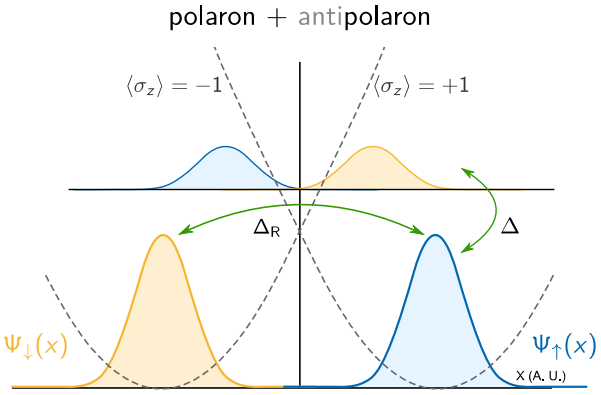
Recent Progress

Stabilizing Spin Coherence Through Environmental Entanglement

[Pubs. 10 & 12]

The coupling of a quantum object to a macroscopic reservoir plays a fundamental role in understanding the complex transition from the quantum to the classical world. While quantum information stored in the quantum subsystem alone is lost during the interaction with the unobserved reservoir degrees of freedom, it is in principle preserved in the entangled many-body state of the global system. The nature of this complete wavefunction has received little attention, especially regarding entanglement among the reservoir states, but is becoming accessible experimentally. We have recently uncovered a simple emerging structure of the wavefunctions in open quantum systems.

Figure 1. Intuitive physical picture behind polaron and antipolaron formation. The wavefunction for a single oscillator mode is shown (blue and gold curves correspond to the ↑ and ↓ projections, respectively). The main weight of the wavefunction is carried by the polaronic components (the two large lower lobes), but their overlap is exponentially small, Δ_R (horizontal green arrow). An enhanced tunneling energy is achieved through the emergence of reduced weight antipolarons (the two small upper lobes), with an energy gain proportional to the bare scale Δ (vertical green arrow). [From Pub. 12.]



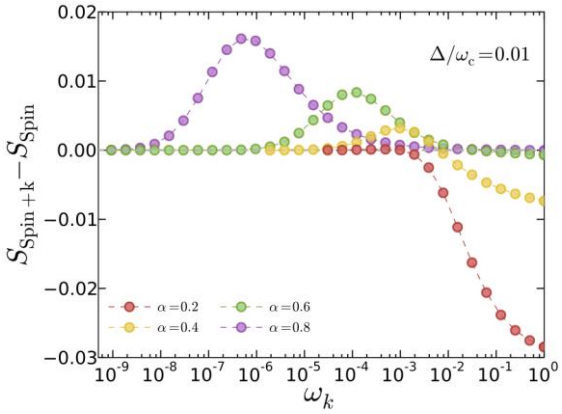


Figure 2. Excess entanglement ρ^2-entropy of the subsystem (qubit plus given oscillator k-mode) with the rest of the environment. The figure displays NRG results for four values of dissipation α = 0.2, 0.4, 0.6, 0.8, showing a qualitative change of behavior in the strong dissipation regime, α > 0.5. The large and positive entropy excess is built from the entanglement generated by multi-polaronic components.

We focus on the spin-boson model (a quantum two-level system coupled to a continuum of harmonic oscillators) as a paradigmatic open quantum system, and develop a systematic variational coherent state expansion for its many-body ground state. Energetic constraints at the heart of this technique are understood in terms of polarons (displacements of the bath states in agreement with classical expectations) and antipolarons (counter-displacements due to quantum tunneling), as shown in Fig. 1. These non-classical properties of the environment stabilize the quantum coherence of the spin.

The entanglement among the different environmental modes is investigated by looking at a spectroscopic signature of the bipartite entanglement entropy between a given environmental mode and all the other modes. We observe a drastic change in its behavior for increasing dissipation, see Fig. 2, indicative of the entangled nature of the environmental states. In addition, the entropy spreads over a large energy range at strong dissipation, a testimony to the wide entanglement window characterizing the underlying Kondo state. Comparisons to numerical renormalization group calculations and to the Bethe Ansatz solution demonstrate the rapid convergence of our variational multi-polaron expansion, suggesting that it should be useful for dissipative models of greater complexity, as relevant for numerous systems of interest in quantum physics and chemistry.

Tunable Quantum Phase Transitions and Majorana Quantum Criticality Realized By Dissipative Resonant Tunneling [Pubs. 9 & 11]

We extended our work on conduction through a resonant level connected to dissipative environments, motivated by experiments here at Duke. Previously [4,8], we used a mapping to a Luttinger liquid-type model to show that this system exhibits a

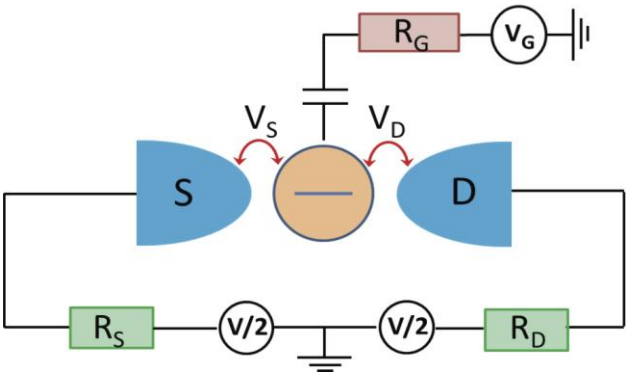


Figure 3. Schematic of a spinless quantum dot coupled to two conducting leads and a gate. The source and drain junctions are characterized by tunneling amplitudes V_S and V_D, as well as capacitances C_S and C_D. The dot-leads system is symmetrically biased by a voltage V through the lead resistances R_S and R_D. The gate is capacitively coupled to the dot (capacitance C_G) through a resistance R_G. We consider the simplified situation in which $C_S = C_D \equiv C$ and $R_S = R_D \equiv R/2$.

quantum phase transition (QPT) from a two-channel Kondo like state to one-channel Kondo behavior. Recently, we have carried out two extensions. First, we analyzed the case when two dissipative environments are coupled to the resonant level, one to the gate and the other to the source and drain leads [9]. Second, we calculated the conductance perturbatively around an exactly solvable limit, showing that the striking experimental result of linear dependence on temperature is an indirect signature of the presence of a decoupled Majorana fermion zero mode [11].

In the case of a resonant level coupled to two dissipative baths, one is produced by the resistive source and drain leads, and a second is connected to a gate potential that shifts the energy of the resonant level (see Fig. 3). While coupling a resonant level to one or the other type of bath has been considered previously, ours is the first study in which both types of bath are treated on equal footing. Two types of QPT are shown to take place. One is the well-known freezing of the charge fluctuations on the. A second transition is associated with a special point: for symmetric coupling and on resonance, one obtains perfect conductance through the level in contrast to the zero conductance state in all other cases. Our analysis draws on and is analogous to that for tunneling through a resonant level in a Luttinger liquid. These results deepen the close link between effects produced by dissipation and those caused by electron-electron interactions. Indeed, coupling to dissipation can be used to emulate what happens in a strongly interacting electron system.

In the second extension we focused on the special point of symmetric coupling and on resonance. We show that full transmission does survive large dissipation in the contacts, but extra energy loss in the environment is still possible which then modifies the low-temperature conductance. When the dissipative impedance is close to the quantum value h/e^2, an exact mapping to resonant Majorana levels can be achieved. Losses in the circuit are then embodied in Majorana interaction terms; we show that these are and control the leading behavior of the conductance near the unitary limit. A striking behavior of the inelastic scattering rate (in temperature and voltage) is obtained, which is a hallmark of interacting Majorana quantum criticality that was uncovered in recent experiments.

Future Plans

Multi-Polaronic Approach to Time-Dependent Non-Equilibrium Phenomena

We are extending our multi-polaronic variational approach to time-dependent phenomena. For sufficiently adiabatic and small deviations from the ground state, we are investigating equations of motion for our variational parameters (the oscillator shifts and the weights of the antipoloran contribution). The goal is to address two situations: either a

quantum quench (sudden turning on of interactions, for instance) or scattering of an incoming photonic wavepacket. This work is proceeding in collaboration with researchers in Grenoble, where in addition experiments are starting using for the system a superconducting qubit coupled to a microwave transmission line.

Dissipative Resonant Tunneling

We are extending our study of dissipative resonant tunneling to more complicated situations involving multiple quantum dots and environments. We expect to uncover rich phenomena when spin is included, double quantum dots are considered, or an environment has a sub-ohmic rather than simply ohmic spectrum. Currently we have obtained the weak-coupling RG equations for a number of these situations, and are generalizing them to non-equilibrium situations through the frequency dependent RG techniques.

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4. "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* 488, 61 (2012).
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11. "Transport Signatures of Majorana Quantum Criticality Realized By Dissipative Resonant Tunneling," H. Zheng, S. Florens, and H. U. Baranger, Phys. Rev. B 89, 235135 (2014).
12. "Generalized Multi-Polaron Expansion for the Spin-Boson Model: Environmental Entanglement and the Biased Two-State System," S. Bera, A. Nazir, A. W. Chin, H. U. Baranger, and S. Florens, Phys. Rev. B (in press).

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 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 predicted the existence of a new structural polar phase in epitaxially strained thin films made of $BiFeO_3$ (BFO) and other ferroelectrics/multiferroics. Such phase was further found to exhibit a novel magneto-electric effect. In collaboration with experimentalists, we also discovered that varying the magnitude and sign of the epitaxial strain dramatically affects the magnetic arrangement of BFO films, which may be put in use to craft magnonic and

spintronic responses. *Ab-initio* calculations we performed also demonstrated the occurrence of a whole family of complex nanoscale twinned phases in $EuTiO_3$ (ETO) systems that were found to be degenerate in energy with simpler phases. Such degeneracy provides a successful explanation of recently observed anomalous phenomena. These calculations also lead to revisiting the phased diagram of ETO films.

Thanks to DOE support, a method allowing the computation for the first time of *dynamical* properties of multiferroics from first principles was also developed. Such development allowed us to reveal, and understand at a microscopic level, the ultrafast nature of the electric-field-induced switching of both the electrical polarization and magnetic chirality of BFO systems. Materials being multiferroic near room temperature, and having tunable ferromagnetic and electrical properties were also discovered, which is promising for the design of novel devices.

Future plans:

We now envision developing 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 compounds and effects will be modeled and studied. Examples include the investigation of electromagnons and of the (frequency-dependent) dynamical magneto-electric effect, and the possibility of finding a material having a negative index of refraction. Other examples are the determination of the atomic ordering and/or composition yielding various optimized properties (e.g., piezoelectric and dielectric responses, magnetoelectric coefficients, etc.) in $(Bi_{1-x}R_x)FeO_3$ alloys, where R is a rare-earth ion, and the search for low-dimensional materials having both a large magnetization and a large electrical polarization, with these two quantities being coupled to each other.

Publications (since August 2012):

- 1)``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 109, 057602 (2012).
- 2) ``Magnetic cycloid of $BiFeO_3$ from atomistic simulations," D. Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, Physical Review Letters 09, 037207 (2012).
- 3) ``Atomistic Molecular Dynamic Simulations of Multiferroics," Dawei Wang, Jeevaka Weerasinghe and L. Bellaiche, Physical Review Letters 109, 067203 (2012).
- 4) ``Novel complex phenomena in ferroelectric nanocomposites," Lydie Louis, Igor Kornev, Gregory Geneste, Brahim Dkhil and L. Bellaiche, Journal of Physics Condensed Matter, Fast Track Communication 24, 402201(2012).
- 5) ``Study of strain effect on in-plane polarization in epitaxial $BiFeO_3$ thin films using planar electrodes," Zuhuang Chen, Xi Zou, Wei Ren, Lu You, Chuanwei Huang, Yurong

Yang, Ping Yang, Junling Wang, Thirumany Sritharan, L. Bellaiche, and Lang Chen, Physical Review B 86, 235125 (2012).
- 6) ``Emergence of central mode in the paraelectric phase of ferroelectric perovskites," J. Weerasinghe, L. Bellaiche, T. Ostapchuk, P. Kuzel, C. Kadlec, S. Lisenkov, I. Ponomareva, and J. Hlinka, MRS communications 3, 41 (2013).
- 7) ``Novel Nanoscale Twinned Phases in Perovskite Oxides," S. Prosandeev, Dawei Wang, Wei Ren, Jorge Iniguez and Laurent Bellaiche, Advanced Functional Materials 23, 234 (2013).
- 8) ``Thickness-dependent polarization of strained $BiFeO_3$ films with constant tetragonality," J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthelemy, L. Bellaiche, and N. Barrett, Physical Review Letters 109, 267601 (2012).
- 9) ``Epitaxial short-period $PbTiO_3$/$BiFeO_3$ superlattices studied by first-principles calculations," Yurong Yang, Massimiliano Stengel, Wei Ren, X. H. Yan and L. Bellaiche, Physical Review B 86, 144114 (2012).
- 10) ``Effect of the central mode on the dielectric tunability of ferroelectrics near room temperature: A first-principle-based study," Jeevaka Weerasinghe, Dawei Wang and L. Bellaiche, Journal of Physics Condensed Matter, Fast Track Communication 25, 252202 (2013).
- 11) ``Understanding and Revisiting Properties of $EuTiO_3$ Bulk Material and Films from First Principles," Yurong Yang, Wei Ren, Dawei Wang and L. Bellaiche, Physical Review Letters 109, 267602 (2012).
- 12) ``Ferroelectric domains in multiferroic $BiFeO_3$ films under epitaxial strains," Wei Ren, Yurong Yang, Oswaldo Dieguez, Jorge Iniguez, Narayani Choudhury, and L. Bellaiche, Physical Review Letters 110, 187601 (2013).
- 13) ``Full field electron spectromicroscopy applied to ferroelectric materials," N. Barrett, J. E. Rault, J. L. Wang, C. Mathieu, A. Locatelli, T. O. Mentes, M. A. Nino, S. Fusil, M. Bibes, A. Barthelemy, D. Sando, W. Ren, S. Prosandeev, L. Bellaiche, B. Vilquin, A. Petraru, I. P. Krug, and C. M. Schneider, Review Article, Journal of Applied Physics 113, 187217 (2013).
- 14) ``Elastic excitations in $BaTiO_3$ single crystals and ceramics: mobile domain boundaries and Polar nanoregions observed by resonant ultrasonic spectroscopy," Ekhard K.H. Salje, Michael A. Carpenter, Guillaume Nataf, Gunnar Picht, Kyle Webber, Jeevaka Weerasinghe, S. Lisenkov, and L. Bellaiche, Physical Review B 87, 014106 (2013).
- 15) ``Crafting the magnonic and spintronic response of $BiFeO_3$ films by epitaxial strain," D. Sando, A. Agbelele, D. Rahmedov, J. Liu, P. Rovillain, C. Toulouse, I.C. Infante, A.P. Pyatakov, S. Fusil, E. Jacquet, C. Carretero, C. Deranlot, S. Lisenkov, D. Wang, J.-M. Le Breton, M. Cazayous, A. Sacuto, J. Juraszek, A.K. Zvezdin, L. Bellaiche, B. Dkhil, A. Barthelemy and M. Bibes, Nature Materials 12, 641 (2013)
- 16) ``Field-induced Percolation of Polar Nanoregions in Relaxor Ferroelectrics," S. Prosandeev, Dawei Wang, A. R. Akbarzadeh, B. Dkhil and L. Bellaiche, Physical Review Letters 110, 207601 (2013).
- 17) ``Spin switching and magnetization reversal in single-crystal $NdFeO_3$," Shujuan Yuan, Wei Ren, Fang Hong, Yabin Wang, Jincang Zhang, L. Bellaiche, Shixun Cao, and G. Cao, Physical Review B 87, 184405 (2013).

- 18) ``Predicted Coupling of the Electromagnetic Angular Momentum Density with Magnetic Moments," Aldo Raeliarijaona, Surendra Singh, Huaxiang Fu, and L. Bellaiche, Physical Review Letters 110, 137205 (2013).
- 19) ``Multidomains made of different structural phases in multiferroic $BiFeO_3$: a first-principles-based study," Dawei Wang, Ekhard K.H. Salje, Shao-Bo Mi, Chun-Lin Jia and L. Bellaiche, Physical Review B 88, 134107 (2013).
- 20) ``Effect of chemical and hydrostatic pressures on structural and magnetic properties of rare-earth orthoferrites: a first-principles study," Hong Jian Zhao, Wei Ren, Yurong Yang, Xiang Ming Chen and L. Bellaiche, Journal of Physics: Condensed Matter 25, 466002 (2013).
- 21) ``Universal collaborative couplings between oxygen-octahedral rotations and anti-ferroelectric distortions in perovskites," L. Bellaiche and Jorge Iniguez, Physical Review B 88, 014104 (2013).
- 22) ``Coupling of the angular-momentum density with magnetic moments explains the intrinsic anomalous Hall effect," L. Bellaiche, Wei Ren and Surendra Singh, Physical Review B, Rapid Communications 88, 161102(R) (2013).
- 23) ``Prediction of a novel magnetoelectric switching mechanism in multiferroics," Yurong Yang, Jorge Iniguez, Ai-Jie Mao and L. Bellaiche, Physical Review Letters 112, 057202 (2014).
- 24) ``Novel magnetic arrangement and structural phase transition induced by spin-lattice coupling in multiferroics," Satadeep Bhattacharjee, Dovran Rahmedov, Laurent Bellaiche and Dawei Wang, MRS Communications 3, 213 (2013).
- 25) ``Effects of a rotating electric field on the properties of epitaxial (001) $Pb(Zr,Ti)O_3$ ultrathin film: a first-principles-based study," David Sichuga and L. Bellaiche, Journal of Physics: Condensed Matter 26, 025302 (2014).
- 26) ``Effect of chemical pressure, misfit strain and hydrostatic pressure on structural and magnetic behaviors of rare-earth orthochromates," Hong Jian Zhao, Wei Ren, Xiang Ming Chen, and L. Bellaiche, Journal of Physics: Condensed Matter 25, 385604 (2013).
- 27) ``Terahertz dielectric response and coupled dynamics of ferroelectrics and multiferroics from effective Hamiltonian simulations," Dawei Wang, Jeevaka Weerasinghe, Abdullah Albarakati and L. Bellaiche, International Journal of Modern Physics B 27, 1330016 (2013).
- 28) ``Properties of Epitaxial Films Made of Relaxor Ferroelectrics," S. Prosandeev, Dawei Wang and L. Bellaiche, Physical Review Letters 111, 247602 (2013).
- 29) ``Ultrafast switching of the electric polarization and magnetic chirality in $BiFeO_3$ by an electric field," Satadeep Bhattacharjee, Dovran Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, Physical Review Letters 112, 147601(2014).
- 30) ``Prediction of novel interface-driven spintronic effects," S. Bhattacharjee, S. Singh, D. Wang, M. Viret and L. Bellaiche, Journal of Physics: Condensed Matter, in press.
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- 32) ``Near room-temperature multiferroic materials with tunable ferromagnetic and electrical properties," Hong Jian Zhao, Wei Ren, Yurong Yang, Jorge Iniguez, Xiang Ming Chen and L. Bellaiche, Nature Communications 5, 4021 (2014).

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 devices with desired, novel characteristics. The research projects focus on several broad areas, including carbon nanotube-based molecular sensors, 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 electron transport in nanostructures, evaluation of free-energy barriers, and calculations of quantum interference effects in multi-terminal devices. Our real-space multigrid method is capable of simulating electron transport and dynamics of systems containing thousands of atoms on DOE's leadership-class massively parallel supercomputers.

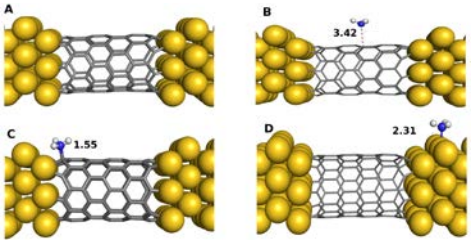

Fig. 1: Optimized structures of the semiconducting (8, 0) CNT-based devices: (a) Pristine CNT attached to Au electrodes, (b) one ammonia molecule physisorbed on the CNT surface, (c) one ammonia chemisorbed near the CNT/Au contact, (d) one ammonia chemisorbed on the Au electrode. The distances between NH_3 and the substrate are also shown.

Recent Progress

Detection Mechanism of Carbon-Nanotube-Based Ammonia Sensor

Electrical detection of trace compounds, contaminants, and biomolecular fragments is an exciting field of research that has potential to deliver dramatic improvements over currently used techniques based on "labels" -- molecules that attach to the target system and fluoresce under illumination. The labeling process is time-consuming, costly and the results cannot be read in real-time. Label-free sensing, on the other hand, has the potential to realize advanced low-cost real-time detectors with direct electronic readouts. Single-walled carbon nanotubes (SWNTs) are among the leading candidates for such sensors. While they have been investigated for over a decade, understanding of sensing mechanisms is often lacking even for detection of simple small molecules, which hampers the development of rationally-devised sensors.

Since the pioneering discovery of ammonia detection in a carbon-nanotube-based device, the origin of the sensing mechanism has been hotly debated. Some researchers postulated that ammonia interacts mainly with the CNT, while others suggested that the signal mainly originates in the contact region. Selective passivation of nanotube and contact regions did not resolve these issues fully, with some workers concluding that both regions are involved in sensing, while others found ammonia sensitivity only in the contact region.

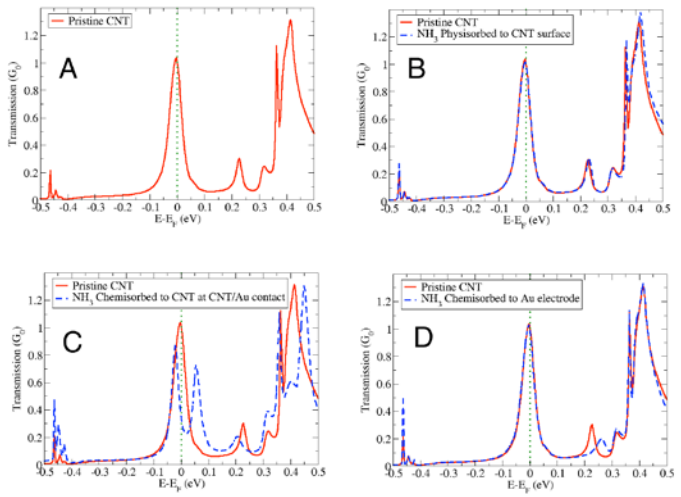

Fig. 2. Transmission spectra of the sensing configurations displayed in Fig. 1 for: (a) pristine CNT as the reference system, (b) after physisorption of ammonia on CNT, (c) after chemisorption of ammonia on CNT at the CNT/Au contact, (d) after chemisorption of ammonia on an Au electrode.

Our simulations employ a CNT/Au geometry that is widely used in experiments, see Fig. 1(a). We use an (8,0) semiconducting SWCNT as the model system. The electrodes are Au nanowires in the (110) direction. The electrode-CNT distance and the structures of the CNT and ammonia molecules are fully optimized using the PBE functional. The quantum calculations are carried out using a non-equilibrium Green's function method expanded in the basis of variationally optimized localized orbitals. The current is calculated self-consistently at a voltage of 100 mV. The detection of several ammonia adsorption configurations is investigated: (i) Direct adsoption of NH_3 molecule on a CNT surface. In this case, the long NH_3-CNT distance corresponds to physisorption, as was also found in earlier work. (ii) NH_3 chemisorbed at CNT near the CNT/metal contact, and (iii) NH_3 chemisorbed on the metal electrode. Fig. 1 shows the optimized geometries for the device regions, together with the distances between the ammonia and the adsorption site. For physisorbed NH_3 on CNT, this distance is 3.42 Å and the binding energy is 0.043 eV. However, when NH_3 is adsorbed on CNT at the CNT/metal contact, chemisorption occurs with a bond distance of 1.55 Å and a binding energy of 0.097 eV. When NH_3 chemisorbs on an Au electrode, the N-Au bond length is 2.31 Å and the binding energy is 0.646 eV.

We show the NEGF calculations of the conductance in Fig. 2. The small-bias transmission near the Fermi level is measured in most experiments. The difference between the conductivities of a pristine CNT and that with physisorbed ammonia is negligible. An increase to six physisorbed molecules does not significantly affect the current either. However, chemisorption near the CNT/Au contact results in a substantial change, see Fig. 2(c). Interestingly, chemisorption on the Au contact does not affect the conductance, because it does not significantly alter the number of conducting channels of the lead. At the experimentally measured bias of 100 mV, ammonia chemisorption on CNT near the CNT/Au interface decreases the current by 62% in our configuration (from 4.48 to 3.41 μA), while other adsorption configurations leave it largely unaffected. Clearly, the interaction between the ammonia and CNT at the CNT/metal contacts dominates the sensing performance, leading to high sensitivity in conductance and current.

Charge Transport in B-DNA Nanowires

Our inherent ability to almost perfectly control the sequence and thus the structure of DNA strands makes them promising candidates for use in nanoelectronics as nanowires and potentially also as chemical sensors and active logic elements. Recent experiments by Barton and co-workers have demonstrated charge transport over a 34 nm DNA nanowire, which received much attention in the scientific community. However, conductive properties of DNA remain poorly understood. Existing experiments report a wide range of behaviors: insulating, semiconducting, metallic and even superconducting. This is because many factors influence DNA conductivity, such as length, sequence, environment (solvent, counterions), contacts, and temperature. Understanding how these factors modulate DNA conductivity is key for evaluating its suitability for use in, e.g., neural nets and other logic structures.

Our calculations consider a 10 base-pair (BP) poly(G)poly(C) B-DNA connected to a (5,5) carbon nanotube leads via alkane linkers, which mimics Barton's group setup, see Fig. 3. We use density functional theory (DFT) and the non-equilibrium Green's function (NEGF) method to calculate the

current passed across the DNA. This methodology evaluates single-step coherent charge transfer, which should dominate charge transport over short distances. Leveraging our highly efficient NEGF code and high-performance computing resources allows for much more extensive studies of DNA conductivity than in prior works. Our quantum transport calculations explicitly include the first solvent shell along with counter ions. We examine 20 room temperature DNA conformations, as extracted from long-time molecular dynamics simulations of the entire system, to account for high flexibility of DNA. This is an improvement over existing *ab initio* charge transport studies, which have only considered a single conformation. The largest configurations include over 1500 atoms in the quantum transport part.

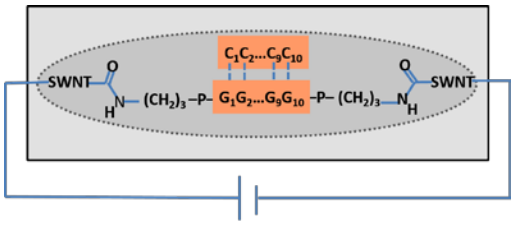

Fig. 3: Setup of DNA transport calculation.

Our results show that the current carried by the DNA nanowire changes dramatically between different room-temperature conformations, varying by up to 12 orders of magnitude. This striking disparity is due to different levels of delocalization of conductive HOMO states between the sampled DNA conformations. Highly conductive states have HOMO states extending through most of the guanine bases, while the low-conductive ones exhibit much lower degree of delocalization. This is demonstrated in Fig. 4, where HOMO states of high- and low-conductivity conformations are shown.

These differences can be due to several factors such as solvent structure, ionic positions or DNA conformation. Our analysis reveals that while each of these factors plays a role, the DNA structure is the most important. This confirms the previously proposed concept of conformational gating, in which only certain conformations contribute to charge transport. Our finding also shows that a single DNA conformation does not represent well the complexity of DNA change transport.

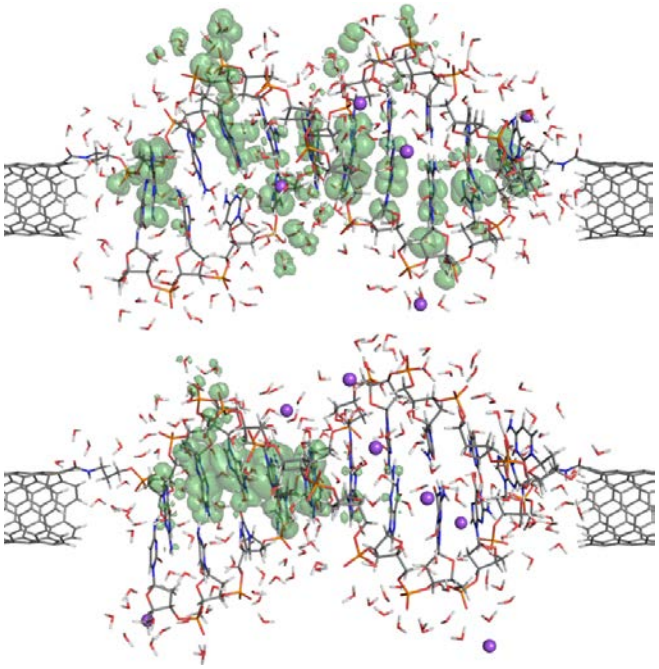
Fig. 4. Isosurfaces of the most conducting HOMO states for a highly conductive (top) and a low conductive (bottom) conformations.

Our further analysis identified the *minimum overlap area* between successive guanines as the best structural parameter determining the conductivity of DNA. The close correlation between the two quantities is displayed in Fig. 5. The fact that the minimum overlap rather than the average overlap is the most relevant parameter shows that charge transport in DNA is highly sensitive to the local geometry. Because the highest values of the overlap are realized for an ideal DNA structure, this result indicates that the low temperature structures are preferred over the room temperature ones. Our calculations also show that the environment surrounding the DNA decreases its conductivity by about an order of magnitude. Water molecules and positively charged ions decrease the current by preventing conductive states from being localized on nearby phosphate groups and purines, respectively.

Our findings have practical implications, because they suggest that a DNA nanowire should be manufactured at low temperatures and be immobilized on a substrate, so that a consistent conductance can be achieved. Furthermore, DNA should be partially dried (full drying would destroy the DNA duplex) to increase its conductive properties.

In addition to poly(G)poly(C) DNA, we have also performed exploratory calculations for other sequences. For poly(A)poly(T) DNA, adenine takes on guanine's role as the main location for conductive HOMO states. Adenine's ionization energy is higher than guanine's and as a result the poly(A)poly(T) DNA in its ideal conformation conducts current seven times worse than poly(G)poly(C). Another important difference is that some of the dynamic room temperature configurations are preferred over the ideal conformation and that the conductivity does not correlate with the minimum overlap area. These differences indicate that the sequence is an important parameter for DNA nanowires. It may provide a way to tune their electric properties.

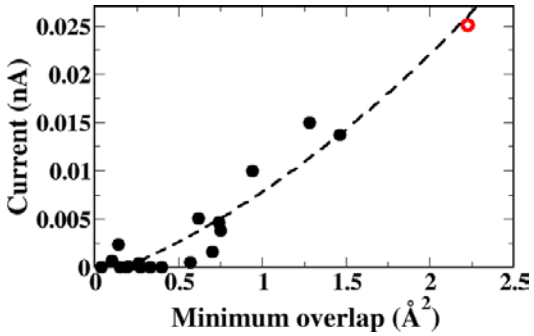

Fig. 5: Dependence of the conductivity of a 10BP poly(G)-poly(C) DNA snapshot on the minimum overlap area between successive guanine bases. The empty circle represents the ideal canonical B-DNA conformation.

Finally, an investigation into mismatches in DNA shows that they affect the conductivity of the ideal DNA conformation, i.e., at low temperatures. However, averaging over multiple room temperature conformations yields results very similar to that of a homogeneous DNA, suggesting that mismatches do not significantly affect the conductivities of dynamic DNA conformations.

Future Plans

We are continuing investigations of carbon-nanotube sensing mechanisms. We consider configurations based both on direct attachment (physisorption and chemisorption), and indirect functionalization via covalent and non-covalent linkers. In functionalized configurations we focus on specificity, i.e., detection of molecules that preferentially attach to the functional group, which should enable tracking of small amounts of specific molecules in the ambient. We will also investigate conductance changes induced by reorganization of large molecules attached to nanotubes, as they undergo reactive changes. Characterization of their conductivity changes may enable electrical detection of various steps in chemical reactions, or of enzyme function.

Turning to methodology, we will implement advanced meta-GGA functionals and approximate GW treatments into our quantum transport NEGF codes in order to improve the band gap and band offset descriptions along all parts of the device.

Publications

1. "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).
2. "Theory of Nitrogen Doping of Carbon Nanoribbons: Edge Effects," J. Jiang, J. Turnbull, W. Lu, P. Boguslawski, and J. Bernholc, .J. Chem. Phys. 136, 014702 (2012).
3. "Scaling the RMG Quantum Mechanics Code," S. Moore, E. Briggs, M. Hodak, W. Lu, J. Bernholc, C. W. Lee, Proc. Extreme Scaling Workshop (BW-XSEDE '12). University of Illinois at Urbana-Champaign, Champaign, IL, USA.
4. "Electronic Control over Attachment and Self-Assembly of Alkyne Groups on Gold," Q. Li, C. Han, M. Fuentes-Cabrera, H. Terrones, B. Sumpter, W. Lu, J. Bernholc, J. Yi, Z. Gai, A. P. Baddorf, P. Maksymovych, M. Pan, ACS Nano 6, 9267 (2012).
5. "Self-Organized and Cu-Coordinated Surface Linear Polymerization," Q. Li, J. R. Owens, C. Han, B. G. Sumpter, W. Lu, J. Bernholc, V. Meunier, P. Maksymovych, M. Fuentes-Cabrera, M. Pan, Nature Scientific Reports 3, 2102 (2013), doi:10.1038/srep02102.
6. "Enzymatic Mechanism of Copper-Containing Nitrite Reductase," Y. Li, M. Hodak, and J. Bernholc, submitted.

7. “Detection Mechanism of Carbon-Nanotube-Based Ammonia Sensor,” Y. Li, M. Hodak and J. Bernholc, in preparation.
8. “Charge Transport in B-DNA Nanowires,” B. Tan, M. Hodak, W. Lu and J. Bernholc, in preparation.

Internal Geometry, Stability and Design of Quantum Hall States

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Project Scope

Research in this program is carried out synergistically at three institutions, and is aimed at understanding the phase diagram of two-dimensional electrons in the fractional quantum Hall (FQH) regime, 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, either currently available, or possible in principle. We use a variety of numerical techniques 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 two years include – (i) further tests and generalization of the effects of geometry and anisotropy in the FQH regime; (ii) a near quantitative understanding of the FQH phase diagram in the anomalous central Landau level of Graphene and (iii) using quantum entanglement to understand FQH states as well as other many-body phenomena, such as many-body localization.

Recent Progress

FQH fluids and Nature of Quasiparticles

Nature of the 5/2 state: A thorough numerical study of the $\nu = 5/2$ state [1] showed that the anti-Pfaffian is preferred over the Pfaffian as a result of Landau level mixing; further, quantum phase transitions from this state are found to be in agreement with experiment in wide quantum wells. This work required using a hexagonal unit cell on the torus with an odd number of electrons with a novel quartered Brillouin zone scheme, which makes the Pfaffian and anti-Pfaffian states orthogonal, and the results unambiguous.

We extended our studies from the nature of FQH states, to the nature of quasiparticle excitations. Using model wavefunctions, a new interpretation of the quasielectron in the $\nu = 1/3$ Laughlin state was found: a composite of $2e/3$ and $-e/3$ objects [21]. Further, exact diagonalization and DMRG studies of quasiholes in the lowest and first excited Landau levels [22] showed a considerable difference in their size, which could influence interferometry and quasiparticle tunneling experiments. Prior to that, we demonstrated the convergence of the DMRG method in different geometries [3].

Geometry and Anisotropy in the FQH regime

Following Haldane's pioneering identification of the geometric degree of freedom in FQH states, we extended the idea to the compressible composite Fermi liquid state at $\nu = ½$. Excellent agreement was found between the theoretical results [15] and experiments by the Shayegan group. In a second, numerical study [12], we investigated the effect of tilting the magnetic field, as is done in experiments by Eisenstein and Shayegan. Effects seen are closely related to the effect of band anisotropy studied previously, and lead for large tilt to broken symmetry phases such as stripes. A study [25] of the geometric "Hall viscosity" of incompressible FQH liquids was related to edge-dipole moments, showing a way to determine thermal quantum Hall anomaly from the orbital entanglement spectrum.

Chiral Edge States in FQH Fluids

An outstanding puzzle has been the apparent lack of universality of the low energy properties of chiral edge states in the QH regime. Our earlier work had implicated edge reconstruction at QH states when the spin splitting is not too large. A comprehensive numerical study [8, 14] for both integer ($\nu = 1, 2$) and fractional ($\nu = 1/3, 2/5, 2/3$ and $5/2$) QH states shows edge spin wave softening in the absence of Zeeman splitting, but reconstruction in the charge channel once Zeeman splitting is introduced, for both integer and fractional states. The exception is the 5/2 state, for which reconstruction is always due to softening of the magnetoplasmon, and spin plays no role.

Graphene: QH and tunneling

We had shown previously (through numerical calculations) the versatility of graphene as a new FQH system. The significant capacity of tuning the Hamiltonian - both the one-electron part (using multilayers), and the electron-electron interaction (through dielectric or metallic screening), we showed, could stabilize different FQH states. Since then, a number of FQH states have been seen in the central Landau level of graphene, which are in good agreement with our more recent numerical calculations [23]. We showed that Landau level mixing could be neglected in graphene for weak interaction strengths [4], despite the fact that both e-e interaction and cyclotron gap scale as $B^{1/2}$ for materials with Dirac dispersion. We also studied the effect of strain on the FQH phase diagram in graphene [9]. Finally, interest in graphene led us to study the effect of non-parabolic bands on Zener tunneling [18]; interestingly, interference effects and nodes were found within the (normally exponential) Zener tunneling region.

Quantum Entanglement in FQH and other many-body systems

The concept of quantum entanglement has proved to be useful in studying topological phases. We have used real space cuts to study quantitatively the edge/bulk connections using conformal field theories [2]. We also calculated [26] the entanglement entropy of the Composite Fermion non-Fermi liquid state at $\nu = ½$ using Monte Carlo methods. Our results show an increase of a factor of two over that for free fermions; this needs further investigation. The concept of quantum entanglement was also found to be very useful in the study of many-body localization in strongly interacting disordered systems [19,20].

Miscellaneous Results

Several other projects on QH states were undertaken, such as non-Abelian states from long range interactions [17], tunable band topologies in 2D lattices [16], categorization of type-I and type-II FQH liquids [5], effect of Landau level mixing in the QH regime [10], Matrix Product States [11] and QH-Nematic transition [13]. Other work included studies on many-body [27, 29] and single particle localization [6, 7, 28] and interacting spin systems [24].

Future Plans

In the near term, we plan to use our recently developed code using matrix product states on finite systems to compare it with DMRG and exact diagonalization for various situations in the FQH regime as well as for fractional Chern insulators. A second area of investigation is the study of quantum Hall states that can be realized in fermionic as well as bosonic cold atom systems. We also plan to study FQH states in more complex band structures, e.g. holes in GaAs, currently being investigated experimentally at Princeton. We hope to study bilayer fractional Chern insulators, and use quantum entanglement methods to study a number of issues such as entanglement entropy of FQH states in spherical geometry and of non-Abelian states on the torus geometry, as well as in the context of disordered many-body systems.

List of Publications

[1] *Quantum Phase Transitions and the v = 5/2 Fractional Hall State in Wide Quantum Wells*, Z. Papic, F. D. M. Haldane, and E. H. Rezayi, Phys. Rev. Lett. 109, 266806 (2012).

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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 (quasi-1D) carbon nanomaterials. Ultra-fast quantum processes in pristine and atomically doped carbon nanotubes (CNs) are being explored in the near-field to learn how to control and manipulate by surface atomic, photonic and excitonic states in these systems. 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 near-field optics and plasmonics with CNs, 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, communication, energy conversion and storage technologies.

Recent Progress

Exciton Bose-Einstein condensation (BEC) in carbon nanotubes

We demonstrate theoretically the possibility of the exciton BEC in individual small-diameter (∼1−2 nm) semiconducting CNs. The effect occurs under the exciton-interband-plasmon coupling (see Fig.1) controlled by an external electrostatic field applied perpendicular to the CN axis. The field mixes excitons and inter-band plasmons of the same band to result in the formation of strongly coupled hybridized excitations (Fig.2) – exciton-plasmons in one individual nanotube [I.V.Bondarev, PRB85,035448(2012)]. Such hybridized excitations are strongly correlated collective Bose-type quasi-particles and could likely be condensed under appropriately created external conditions, in spite of the well-known statements of the BEC impossibility in ideal 1D/2D systems [see, e.g., R.P.Feynman, Statistical Mechanics]. Possibilities for achieving BEC in 1D/2D systems are theoretically demonstrated under extra confinement potential [V.Bagnato & D.Kleppner, PRA44,7439(1991)]. We show that the strongly correlated exciton-plasmon system in a semiconducting CN presents such a special case. We find the critical BEC temperature, the condensate fraction and its exciton contribution (Fig.2) as functions of temperature and electrostatic field applied. The effect requires fields ∼1 V/nm and temperatures below 100 K that are experimentally accessible. The exciton BEC effect will manifest itself as highly coherent, longitudinally polarized, far-field exciton emission appearing at temperatures below 100 K as one smoothly increases the perpendicular electrostatic field strength. The narrow BEC emission peak is blue shifted by the Rabi-splitting energy from the first exciton excitation energy which the CN should be pumped at by an external laser source. The effect offers a testing ground for fundamentals of condensed matter physics in one dimension and opens up perspectives to develop tunable coherent polarized light source with carbon nanotubes. [Figures 1&2; I.V.Bondarev and A.V.Meliksetyan, Physical Review B 89, 045414 (2014)]

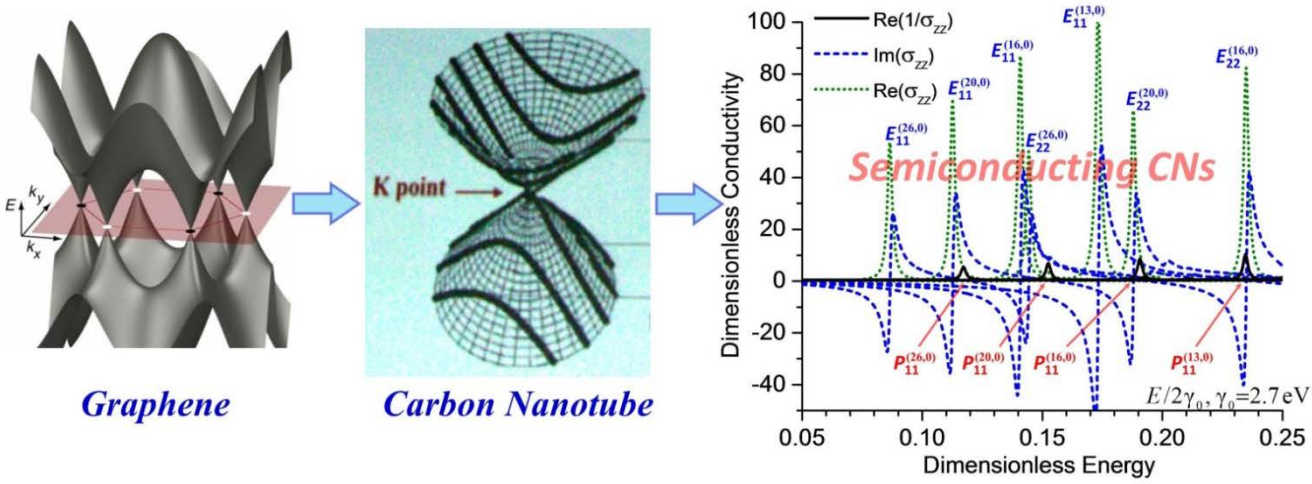

Fig. 1 Physical properties of single wall carbon nanotubes originate from graphene (Brillouin zone structure shown left) and circumferential quantization of electron motion due to rolling it up in a tubule (middle, black quantization lines to represent allowed longitudinal momentum states). As a result of this quantization, real axial optical conductivities of semiconducting nanotubes (calculations shown right) consist of series of peaks (E_{11},E_{22},...) representing the 1st, 2nd, etc. excitons, respectively. Imaginary conductivities are linked with the real ones by the Kramers-Kronig relation, which is why real *inverse* conductivities show the resonances P_{11},P_{22},... right next to E_{11},E_{22},... These are interband plasmon resonances. On the right are shown the calculations of the relevant dimensionless (normalized by $e^2/2\pi$) conductivity functions for the four zigzag nanotubes, (13,0), (16,0), (20,0) and (26,0), of increasing diameter.

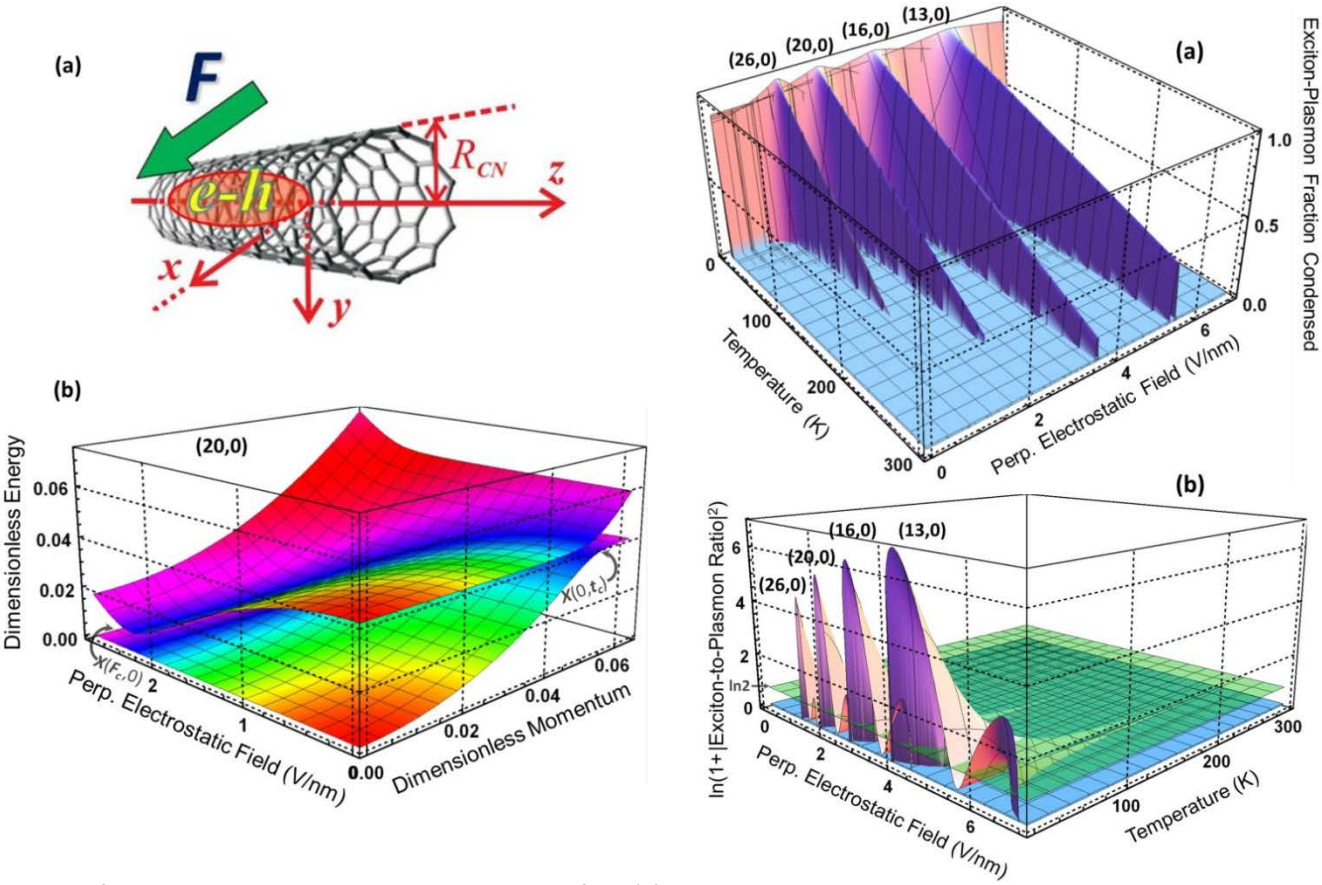

Fig. 2 *Left*: By applying a perpendicular electrostatic field (a), one mixes excitons and interband plasmons to create the hybrid exciton-plasmon excitation with the dispersion shown in (b) for the lowest bright exciton coupled to the nearest interband plasmon in the (20,0) CN [$E_{11}^{(20,0)}$ and $P_{11}^{(20,0)}$ in Fig.1, right]. *Right*: Mean exciton-plasmon BEC population (a) and the exciton contribution (b) to the exciton-plasmon BEC population calculated for the four CNs in Fig.1, right.

Excitonic complexes in quasi-1D semiconductors

A configuration space approach is developed to obtain universal asymptotic relationships between the lowest energy trion, biexciton and exciton binding energies in quasi-1D semiconductors, including small-diameter semiconducting CNs. The model operates in terms of the under-barrier tunneling current between the equivalent configurations of the system in the configuration space, and so it allows one to interpret theoretically and thus to better understand some stability peculiarities of neutral and charged exciton complexes in quasi-1D systems, such as why in semiconducting quantum wires the trion binding energy is less than the biexciton binding energy, whereas in semiconducting CNs the binding energy of the trion is greater than that of the biexciton. For CNs with diameters ~1 nm, the model predicts the trion binding energy greater than that of the biexciton by a factor ~1.4 decreasing with the CN diameter, in agreement with the latest non-linear spectroscopy measurements. [I.V.Bondarev, arXiv1405.0777, *submitted to PRL*]

Bipartite entanglement in hybrid CN systems

Hybrid CN systems, nanotubes containing extrinsic atomic type species (dopants), such as extrinsic atoms, or ions, or semiconductor quantum dots, 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 and solid-state quantum information science. We study theoretically a pair of spatially separated two-level dipole emitters, two-level systems (TLSs) to model atomic type dopants mentioned above, which are coupled both indirectly through the virtual surface plasmon exchange of a metallic CN and directly via the inter-TLS dipole-dipole interactions. We show that the CN-assisted bipartite TLS entanglement can be identified unambiguously through the presence of the cross-peaks in the 2D photon-echo spectra. We also show that the direct dipole-dipole interactions generally quench the bipartite entanglement; however, this effect can be reduced by means of a proper initial optical preparation of the TLSs. We analyze various experimental conditions and formulate practical recommendations for creating the robust bipartite TLS entanglement in hybrid CN systems by using strong shape-optimized laser pulses, to allow for reliable experimental observation of this unique quantum phenomenon of relevance to solid-state quantum information science. Work done in collaboration with the Munich Advanced Photonics Center (MAP), Technical University of Munich, Germany. [M.F.Gelin, I.V.Bondarev, and A.Meliksetyan, Chemical Physics 413, 123 (2013); J. Chem. Phys. 140, 064301 (2014)]

Plasmon enhanced Raman scattering near a carbon nanotube

Quantum electrodynamics theory of the resonance Raman scattering is developed for an atom in a close proximity to a carbon nanotube. The theory describes both weak and strong atomic coupling to nanotube's plasmon near-fields, and predicts a dramatic enhancement of the Raman intensity in the strong coupling regime. This resonance scattering is a manifestation of the surface enhanced Raman scattering (SERS) effect, and can be used in designing highly efficient nanotube based SERS substrates for single atom detection, precision spontaneous emission control and manipulation. [I.V.Bondarev, *submitted to APL*]

Future Plans

In the future, we plan to continue our studies of near-field effects in complex CN structures, focusing on pristine double wall carbon nanotubes and hybrid quantum systems of molecular-array/metal-atomic-wire encapsulating nanotubes as follows:

- Exciton-plasmons in double wall CNs with matching exciton/plasmon resonances, that is the exciton resonance of one tubule overlaps in energy with a plasmon resonance of another tubule: derivation of the dispersion relation, theory for the Bose-Einstein condensation, revealing the connection between the BEC and superfluidity for exciton-plasmons and excitons;
- Theory of molecular absorption/emission/SERS in the presence of interband plasmon resonances in complex hybrid molecular-array encapsulating CN systems;
- Theory of the plasmon-assisted transport through metal-atomic-wire encapsulating semiconducting CNs, to investigate the inter-play between the intrinsic 1D conductance of a metal atomic wire and CN-mediated near-field plasmonic effects.

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Correlated Electrons in Reduced Dimensions

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Project Scope

The combination of strong correlations and reduced dimensionality can lead to the formation of exotic states of matter for which conventional "textbook" methods of condensed matter physics break down. An example of such states are those with so-called topological order, a type of quantum order not characterized by any local order parameter but rather by global properties, (e.g., ground state degeneracies on topologically nontrivial surfaces, fractionalized quasiparticle excitations with exotic quantum statistics, etc.). One goal of this project is to better understand topological order, and, in particular, the intimate connection it has with the theory of fault-tolerant quantum computation. This widely appreciated connection has motivated much of the recent work which attempts to physically realize topologically ordered states with non-Abelian anyon excitations (e.g., the Majorana zero modes predicted to appear in certain fractional quantum Hall states, topological insulators and superconductors), as well as ideas for how one could essentially simulate topological order on a "conventional" quantum computer and thus have the computer inherit the built in protection of these states from decoherence, (the so-called "surface code" approach --- currently the leading candidate for realizing fault-tolerant quantum computation). The project is also focused on understanding the properties of metals with sharp Fermi surfaces but without well-defined Landau quasiparticles (and thus, again, a class of states which lies outside of standard condensed matter physics). The question of how the breakdown of Fermi liquid theory affects the quantum phase transitions which can occur in these systems, (e.g., BCS pairing, excitonic condensation), is actively being studied, with work focusing on the composite fermion "metal" description of the compressible $\nu=1/2$ quantum Hall state, for which the Halperin-Lee-Read theory provides a powerful theoretical framework for studying at least one flavor of non-Fermi liquid behavior.

Recent Progress

Non-abelian topological order and surface codes

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 ~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 computation using "non-Abelian" surface codes. These codes are the topologically ordered 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 their worldlines, (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. Such measurements will be required in order to detect errors in the quantum error-correcting code defined by the ground states of this model, and our quantum circuits provide, for the first time, a measure of the resources that will be needed to do this.

Pulse sequences for exchange-only quantum computation

We have obtained pulse sequences which can be used to carry out entangling two-qubit gates for exchange-only quantum computation in which the spin states of electrons in quantum dots are manipulated by turning on and off, (i.e. "pulsing"), the exchange interaction between neighboring spins. Previous work finding such sequences has always required numerical methods due to the large search space of unitary operators acting on the space of the encoded qubits, each of which consists of three physical spins. By contrast, our constructions can be understood entirely in terms of three-dimensional rotations of effective spin-1/2 pseudospins which allows us to use geometric intuition to determine the required sequence of operations analytically. The price we pay for this simplification is that, at 39 pulses, our sequences are significantly longer than the best numerically obtained sequences. The techniques used in our construction are based on those used to describe non-Abelian anyons and thus represent a useful "spin off" application of ideas from topological quantum computation to the experimentally active area of spin-based quantum computation.

Gauge fluctuations and interlayer coherence in bilayer systems

The quantum Hall bilayer with total Landau level filling fraction $\nu = 1$ is a particularly rich system for studying quantum Hall physics. In this system, two parallel two-dimensional electron gases, separated by a distance *d*, have the total electron density of a filled Landau level for a single layer. For the symmetrically doped case, each layer has Landau level filling fraction $\nu = 1/2$, and if interlayer electron tunneling can be ignored, the only coupling between layers is through the Coulomb repulsion. The scale of this coupling, relative to the scale of interactions within each

layer, is then set by the dimensionless ratio d/l_0, (l_0 = magnetic length). In the limit of large d/l_0 (weak interlayer coupling) the system decouples into two separate $\nu = 1/2$ "non-Fermi liquid" composite fermion metals, while in the limit of small d/l_0 (strong interlayer coupling) it enters a remarkable bilayer quantum Hall state in which electrons develop spontaneous interlayer phase coherence. Despite a great deal of experimental and theoretical work, the transition between these two limiting states is still poorly understood.

We studied the effect of the Chern-Simons gauge fields on a transition which might occur at intermediate d/l_0 from two decoupled composite fermion metals to the recently proposed interlayer coherent composite fermion state. In this transition, interlayer Coulomb repulsion leads to excitonic condensation of composite fermions (rather than physical electrons) which are then free to tunnel coherently between layers, even though physical electrons do not. We find that this coherent tunneling is strongly suppressed by the layer-dependent Aharonov-Bohm phases experienced by composite fermions as they propagate through the fluctuating gauge fields in the system (the same gauge fluctuations which lead to a breakdown of Landau Fermi liquid theory). This suppression is analyzed by treating these gauge fluctuations within the random-phase approximation (RPA) (see Fig. 1) and calculating their contribution to the energy cost for forming an exciton condensate of composite fermions. This energy cost leads to (1) an increase in the critical interlayer repulsion needed to drive the transition and (2) a discontinuous jump in the energy gaps to out-of-phase excitations (i.e., excitations involving currents with opposite signs in the two layers) at the transition. The first effect may account for the fact that the interlayer coherent state has not yet been observed experimentally in $\nu=1$ bilayers. The second effect suggests that if such a transition were to be observed, the detection of a discontinuous jump in the out-of-phase energy gaps would provide indirect experimental evidence for the presence of gauge fluctuations in the system.

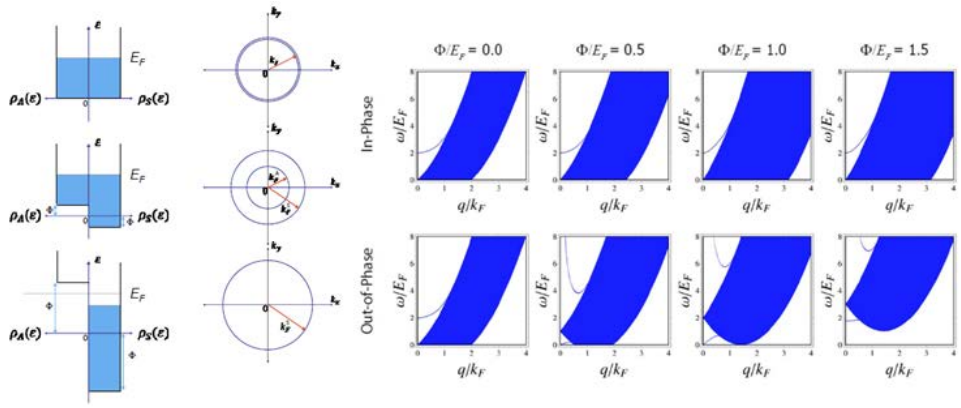

Figure 1 (Left) Densities of states and Fermi surfaces for the symmetric and antisymmetric bands in a bilayer composite fermion metal for different values the interlayer coherent order parameter, Φ (the effective tunneling amplitude between layers). For $\Phi = 0$ the Fermi surfaces for the two bands coincide, for $0 < \Phi < E_F$, (E_F = Fermi energy), the symmetric Fermi surface has grown, while the antisymmetric Fermi surface has shrunk, but is still present, and for $\Phi > E_F$ the antisymmetric Fermi surface has shrunk to 0 and only the antisymmetric Fermi surface is present. (Right) Regions in q and ω space for which the imaginary part of the in-phase and out-of-phase Chern-Simons gauge field propagators are non-zero, again for different values of Φ, computed within the Random-Phase Approximation. The spectrum of particle-hole excitations, which give rise to the broad continua, as well as sharp collective magentoplasmon modes can be seen. These gauge fluctuations both lead to a breakdown of Fermi liquid theory in the composite fermion metal and drive the Stoner instability to the interlayer coherent phase from a continuous transition to a first-order transition.

Future Plans

Future plans for this project include building on our recent bilayer study in order to further investigate the effect of gauge fluctuations and non-Fermi liquid behavior on possible phase transitions in dense Fermi systems. One motivation for this is a recent renormalization group (RG) analysis of BCS pairing in the presence of such gauge fluctuations which suggests that the mean-field analysis described above may miss some of the essential physics of this transition (resulting in a continuous rather than a first-order transition for BCS pairing). To address this discrepancy, a similar RG analysis can be applied to determine the nature of the Stoner instability to the interlayer coherent composite fermion state, and the results compared with our mean-field results. 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, particularly in the context of "surface codes" (both Abelian and non-Abelian). The long term goal of this work is to develop a full suite of quantum circuits which can be used to measure vertex and plaquette operators in the Levin-Wen model, and then "move" any errors (which behave as non-Abelian anyons) through the lattice so they can be "fused" with other errors in order to eliminate them. With these tools in hand, we will then address a question at the heart of this line of research, namely whether or not there is a finite error threshold for quantum computation using non-Abelian surface codes. This question amounts to asking whether topological quantum computation with non-Abelian anyons is, indeed, truly fault tolerant, and thus is a fundamental question about the nature and potentiality of some of the most exotic forms of matter known.

Publications

(2012-2014)

"*Analytic Pulse Sequence Construction for Exchange-Only Quantum Computation,*" D. Zeuch, R. Cipri, and N.E. Bonesteel, Phys. Rev. B **90**, 045306 (2014).

"*Gauge Fluctuations and Interlayer Coherence in Bilayer Composite Fermion Metals,*" R. Cipri and N.E. Bonesteel, Phys. Rev. B **89**, 085109 (2014). [**Editors' Suggestion**]

"*Violation of Entanglement-Area Law in Bosonic Systems with Bose Surfaces: Possible Application to Bose Metals,*" H.-H. Lai, K. Yang, and N.E. Bonesteel, Phys. Rev. Lett. **111**, 210402 (2013).

"*Quantum Circuits for Measuring Levin-Wen Operators,*" N.E. Bonesteel and D.P. DiVincenzo, Phys. Rev. B **86**, 165113 (2012). [**Editors' Suggestion**]

Non-equilibrium steady state design of electronic material properties

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Project scope:

Non-equilibrium quantum systems stand at a natural frontier of physics that is only beginning to be probed by theory and experiment. Particularly exciting is the possibility of attaining material properties that are unreachable at equilibrium. We are investigating fundamental aspects of non-equilibrium condensed matter theory; most notably we want to understand the nature of the steady states reached in systems that are driven by an AC electric field while in contact with a thermal reservoir. The presence of dissipation due to the bath is characteristic of solid state systems, and is to be contrasted with the case of artificial structures built on optical lattices, where the systems are well isolated from their environment.

Fundamental guiding principles and tools for the understanding of driven-dissipative quantum systems still need to be developed. The goal of our work is twofold. First, we are formulating a generic theory of periodically driven systems placed in contact with a thermal reservoir. These studies are guided by a concrete solvable example we have found, namely periodically driven graphene-like lattices, which support Dirac fermions on a time-dependent background. Second, we are investigating a number of possible routes to push the extent to which phases of matter can be observed. Most remarkably, we are investigating photo-induced superconductivity is systems where superconductivity does not occur at equilibrium, for example in simple semiconductors and at room temperature.

Recent progress:

• *Photo-induced superconductivity in semiconductors*

We unveiled a new route to superconductivity that relies on establishing a non-equilibrium population of carriers via optical pumping. Specifically, we showed that optically pumped semiconductors can exhibit superconductivity. We illustrated this phenomenon in the case of a two-band semiconductor tunnel-coupled to broad-band reservoirs and driven by a continuous wave laser. We also showed that superconductivity can be induced in a two-band semiconductor interacting with a broad-spectrum light source. We furthermore discussed the case of a three-band model in which the middle band replaces the broad-band reservoirs as the source of dissipation (depicted in Fig. 1). In all three cases, we derived simple conditions on the band structure, electron-electron interaction, and coupling to the reservoirs that enable superconductivity. We computed the finite superconducting gap and argued that the mechanism can be induced through both attractive and repulsive interactions and is robust to high temperatures.

The essence of the mechanism for such photo-induced superconductivity is to create a non-equilibrium population of the electrons in the valence and conduction bands of the semiconductor. The photo-excited electrons then form Cooper pairs. The non-equilibrium population needed for superconductivity is established by driving with a laser source at frequency ω_0. This driving induces transitions between two semiconducting bands if there are momenta k_0 such that $E_2(k_0) = E_1(k_0) + \omega_0$. In practice this condition is easily met and the corresponding momenta lie on a finite closed surface $S_{\omega 0}$ in the Brillouin zone. This resonant surface plays the role of the Fermi surface, and it hosts the

electron pairs with opposite momenta. The laser acts as a source of energy, and coupling each band to a reservoir, with which it can exchange particles and energy, provides dissipation. The possibility of the electronic bands acquiring non-trivial populations is crucial to the occurrence of superconductivity.

In order to establish that superconductivity can be realized in a driven-dissipative semiconducting system, we first solved for its non-equilibrium steady-state dynamics by means of a master equation approach. Within a self-consistent mean-field approach, we then obtained the criteria for superconducting pairing and estimated the size of the superconducting gap.

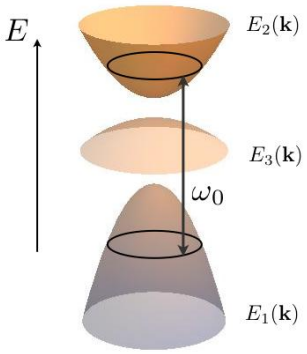

Figure 1: A laser with frequency ω_0 drives transitions between the lower (1) and upper (2) bands. The middle band (3) serves as reservoir. This creates an effective resonant surface S_{ω_0} consisting of the set of momenta k_0 for which the laser resonantly connects the two bands. The electrons in the upper and lower band can form Cooper pairs as long as the sum of the occupations of these two bands (at a given momentum on the resonant surface) deviates from unity. This is only possible in the presence of the reservoir – in this case the middle band.

• *Electronic gap design from non-equilibrium steady states*

We demonstrated the possibility of inducing a tunable gap in monolayer graphene by the excitation of certain optical phonon modes. We showed that the system reaches a steady state whose transport properties are the same as if the system had a static electronic gap, controllable by the driven phonon amplitude. Moreover, the steady state displays topological phenomena: there are chiral edge currents (depicted in Fig. 2), which circulate a fractional charge e/2 per rotation cycle, with frequency set by the optical phonon frequency.

The gap we found is controlled by a time-dependent Kekulé-pattern bond density wave, which appears in the effective field theory as a complex-valued order parameter Δ that rotates with the frequency Ω of the driven phonon mode. The time-dependence in this order parameter is completely removable by an axial (valley) gauge transformation, which can be viewed as a kind of boost to a co-moving reference frame. The gauge transformation has no effect on the coupling of the system to a heat bath, thereby guaranteeing thermal equilibration in the new frame, and leaves the fermion currents invariant. This implies that the electric response of the system is equivalent to that of one with a static gap; all non-equilibrium aspects of the problem are removed and the system can be studied as if it were at equilibrium.

We have studied the same system within the Floquet formalism. These studies are important for expanding the scope of the analysis that we were able to carry out in this exactly solvable model. We considered the steady state reached by a system of Dirac fermions in graphene when coupled to a heat bath of acoustic phonons in the presence of a rotating Kekulé mass term. This problem can be solved exactly both with and without Floquet theory. We showed that the fact that this problem is gauge-equivalent to a time-independent problem implies that the quasi-energies of Floquet theory correspond to a continuous symmetry of the full time-dependent Lagrangian. We used the conserved Noether charge associated with this symmetry to recover notions of equilibrium statistical mechanics.

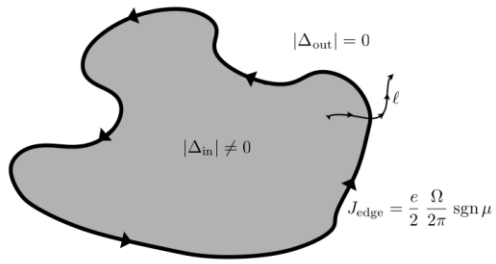

Figure 2: Chiral edge current resulting from the out-of-equilibrium steady-state arising from the excitation of optical phonons at wavevector K_+ in a graphene flake. The direction of the current is inverted for K_- phonons, for which $\Omega \rightarrow -\Omega$.

Planned activities:

The planned effort for the next year will focus on two directions. The first is to fully explore the new route to photo-induced superconductivity that we found possible in semiconductors. Such photo-induced superconductivity is attainable at temperatures smaller than the semiconducting band gap, which itself is a very high temperature. Hence, the mechanism may enable dissipationless current transport for frequencies smaller than that set by the superconducting gap at room temperature. In many ways the ultimate limit of our setup is the temperature dependence of the rate Γ of the non-equilibrium population decay. With the basic theoretical understanding of the mechanism in place and the conditions for superconductivity to occur with both attractive and repulsive interactions understood, we now plan to quantitatively predict the sizes of gaps and the rates Γ for different types of dissipative environments. We shall consider Si and GaAs as specific examples.

Additionally, we would like to investigate the case when superconductivity is induced for short periods of time by laser pulses and is allowed to decay when the laser is off. This opens the door for superconducting switches. Together with a collaborator (Camille Aron) with expertise in Dynamical Mean Field Theory, we plan to perform a numerical study of the effects of strong correlations and strong laser driving on photo-induced superconductivity. Also, we plan to study the time dependence of the conductivity after photo-excitation.

Our second research direction is to devise a general framework to understand the steady states of periodically driven systems. One possible approach is using the Floquet formalism, which can be viewed as a time-domain analog of Bloch's theorem. However, the apparent simplicity of Floquet theory belies certain conceptual difficulties. In particular, because quasi-energies are only well defined modulo the driving frequency, there is no way of defining a lowest quasi-energy. Consequently, there is no notion of the ground state of a driven system in Floquet theory. For systems placed in contact with a heat bath at finite temperature, it is possible to derive master equations for the time evolution of the reduced density matrix, but this approach is only practicable on a case-by-case basis and frequently involves the use of various approximations, so that no general and intuitive notion of the occupation of a Floquet state exists for such systems. The inclusion of dissipation for many-body systems remains quite challenging. We plan to proceed, profiting from our understanding of the exactly solvable models in graphene-like lattices that we have studied thus far.

Publications: DOE support, explicitly referred to as "DOE Grant DEFG02-06ER46316", is acknowledged in every publication listed below.

1. “Magnetic translation algebra with or without magnetic field in the continuum or on arbitrary Bravais lattices in any dimension”
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2. “Enhancing the stability of a fractional Chern insulator against competing phases”
   Adolfo G. Grushin, Titus Neupert, Claudio Chamon, and Christopher Mudry
   Phys. Rev. B 86, 205125 (2012)

3. “Networks of quantum wire junctions: A system with quantized integer Hall resistance without vanishing longitudinal resistivity”
   Jaime Medina, Dmitry Green, and Claudio Chamon
   Phys. Rev. B 87, 045128 (2013)

4. “Cooling through optimal control of quantum evolution”
   Armin Rahmani, Takuya Kitagawa, Eugene Demler, and Claudio Chamon
   Phys. Rev. A 87, 043607 (2013)

5. “Materials Design from Non-equilibrium Steady States: Driven Graphene as a Tunable Semiconductor with Topological Properties”
   Thomas Iadecola, David Campbell, Claudio Chamon, Chang-Yu Hou, Roman Jackiw, So- Young Pi, and Silvia Viola Kusminskiy
   Phys. Rev. Lett. 110, 176603 (2013)
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   http://physics.aps.org/synopsis-for/10.1103/PhysRevLett.110.176603

6. “Measuring the quantum geometry of Bloch bands with current noise”
   Titus Neupert, Claudio Chamon, and Christopher Mudry
   Phys. Rev. B 87, 245103 (2013)

7. “Generalized energy and time-translation invariance in a driven dissipative system”
   Thomas Iadecola, Claudio Chamon, Roman Jackiw, and So-Young Pi
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8. “Fractional Chern insulators with strong interactions far exceeding bandgaps”
   Stefanos Kourtis, Titus Neupert, Claudio Chamon, and Christopher Mudry
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9. “Topological gaps without masses in driven graphene-like systems”
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10. “Wire deconstructionism and classification of topological phases”
    Titus Neupert, Claudio Chamon, Christopher Mudry, and Ronny Thomale
    arXiv:1403.0953

11. “Photo-induced superconductivity in semiconductors”
    Garry Goldstein, Camille Aron, and Claudio Chamon
    arXiv:1406.7299

12. “Effective field theory for the bulk-edge correspondence in a two-dimensional Z_2 topological insulator with Rashba interactions”
    Pedro R. S. Gomes, Po-Hao Huang, Claudio Chamon, and Christopher Mudry
    arXiv:1407.2633

Along the path to an *ab-initio* description of high temperature superconductivity

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An *ab-initio* determination of a cuprate phase diagram remains a significant motivating challenge for modern numerical condensed matter and materials physics. In recent years, impressive contributions have been made through the combination of density functional parameterized models with single- or few-site dynamical mean-field theory. However, moving beyond these approaches to fully converged, material specific, methodology without *any* empirical parameters, will be necessary to nail down the many uncertainties that arise at low-energy scales. I will argue that with the rapid progress being made in three major numerical challenges, namely (i) the treatment of many strongly correlated degrees of freedom with unbiased approaches such as *ab-initio* density matrix renormalization group; (ii) efficient descriptions of screening with local quantum chemistry methods; and (iii) numerically efficacious quantum embedding procedures such as density matrix embedding theory, we now have the tools at hand for a first attempt at a fully *ab-initio* description of high temperature superconductivity.

Numerical challenges of high T_c superconductivity.

The desired goal in a correlated electronic structure description of a cuprate is to go from the material formula to the phase diagram. Naturally, this involves significant challenges. Most obviously, we must tackle the strongly correlated degrees of freedom (i.e. the electrons involved in the relevant Cu and O bands). But beyond this, we must also treat the external orbital degrees of freedom (as involved in screening), impurities, coupling to phonons, the challenge of computing finite temperature and spectral properties, all at the thermodynamic limit. Despite the daunting nature of these challenges, in each of these areas, significant progress is being made.

Strongly correlated electrons. For example, in the area of strongly correlated electrons, the density matrix renormalization group has greatly extended the number of degrees of freedom that can be treated essentially exactly. *Ab-initio* algorithms have become widespread in the last decade and are now widely employed in chemistry. These algorithms have recently been applied to biological systems – metalloenzymes – which contain finite metal clusters, including Cu(II)-oxo systems, Fe-S clusters [1], and Mn-O clusters [2], that are finite analogues of strongly correlated materials such as the cuprates. The success of *ab-initio* DMRG calculations as first trialed in these finite settings – correlating more than 40 strongly correlated orbitals – holds great promise for the condensed phase cuprate setting, where they translate into an *ab-initio* treatment of at least 16 CuO_2 unit cells.

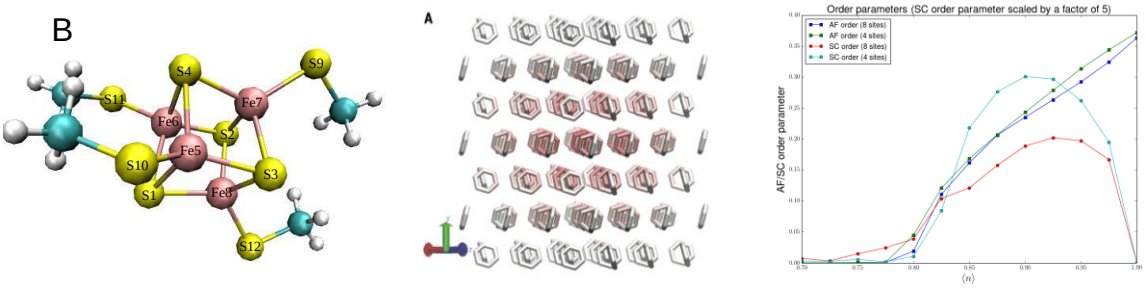

Figure 1 Results along the way to high temperature superconductivity. Left. [4Fe-4S] cluster at the heart of many metalloenzymes. This can be viewed as a finite chunk of a correlated material, which can now be successfully treated with *ab-initio* DMRG. Middle. Benzene molecular crystal. Using local coupled cluster methods, the detailed weak correlations can described to very high accuracy, yielding lattice energies converged beyond experimentally reachable accuracies. Right. Superconducting order parameters. Density matrix embedding theory can be used with very large impurity clusters in a quantum embedding treatment, allowing the study of the competition between charge density ordering and superconductivity in the Hubbard model at the thermodynamic limit.

Perturbative degrees of freedom and screening. In addition to the strongly correlated degrees of freedom, to reach the accuracy associated with low-energy scales (say 10K or below) we must handle the more weakly coupled degrees of freedom that give rise to screening and long-range exchange. These effects require considering correlations from a very large number of virtual orbitals (empty bands). However, new diagrammatic resummation algorithms, including local coupled cluster theory and canonical transformation methods, are extremely efficient and can readily handle several hundred to more than a thousand virtual orbitals. In materials without strong correlation (such as organic molecular crystals) the complete convergence of the correlations obtained through these techniques yields essentially *exact* solutions of the condensed phase Schrödinger equation on the 10K (sub kJ/mole) scale [3]. These methods can be readily combined with *ab-initio* DMRG techniques to converge the description of the perturbative degrees of freedom in more strongly correlated materials.

Thermodynamic limit and phase diagrams. Finally, as a bulk phenomenon, any treatment of a cuprate must be carried out in the thermodynamic limit. Cluster-based dynamical mean-field theory techniques have proved powerful in this regard, however, despite progress in impurity solvers, there remain many difficulties both in obtaining converged results with very large clusters at low temperatures, as well as to handle realistic Hamiltonians with many orbitals and *ab-initio* (i.e. non-local) interactions. Both these challenges are alleviated within a more flexible quantum embedding formalism that we recently introduced, the density matrix embedding theory, based on entanglement theory. The simple structure of DMET has enabled the immediate combination with powerful and unbiased impurity solvers such as the DMRG, as well as the use of large clusters with more than 16 impurity sites at zero temperature and with arbitrary interactions [4]. Using the DMET with DMRG solvers we have recently obtained superconducting phase diagrams in the Hubbard model with large clusters at zero temperature, enabling us to study for the first time the close competition between charge ordering and superconductivity in the pseudogap regime with a quantum embedding method.

With these rapid advances, the natural next step is to combine them for a cuprate material. I will describe each of these advances in more detail and outline the roadmap in the next few years for their combination in an initial *ab-initio* computation of the cuprate phase diagram.

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2. Low energy spectrum of iron-sulfur clusters directly from many-particle quantum mechanics, S. Sharma, K. Sivangulam, F. Neese, G. K.-L. Chan, Nature Chemistry, in press (2014)
3. Ab initio determination of the lattice energy of crystalline benzene to sub-kJ/mole accuracy, Jun Yang, Weifeng Hu, Denis Usvyat, Devin Matthews, Martin Schütz, Garnet Kin-Lic Chan, Science, in press (2014)
4. Density Matrix Embedding: A Simple Alternative to Dynamical Mean-Field Theory G. Knizia, G. K.-L. Chan, Physical Review Letters, 109, 186404 (2012)

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Entangled quantum electronic wavefunctions of the Mn_4CaO_5 cluster in photosystem II, Y. Kurashige, G. K.-L. Chan, T. Yanai, Nature Chemistry, 5, 660 (2013)

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Computational approach to complex interfaces and junctions

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The scope of this project covers 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, Markus theory, classical molecular dynamics, and van der Waals corrections 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) field effects in layered 2D materials such as graphene, *h*-BN, silicence, etc.; and c) electronic and magnetic properties of small particles (e.g. single-molecule nanomagnets and zinc oxide clusters) and implications for transport measurements. A 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 efforts to develop 1) a hybrid quantum-Boltzmann framework for properly treating electron transport across 2D and 3D junctions and 2) new methods 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

Electron and spin transport through nano-junctions

We employed the existence of multiple thermodynamically stable isomer states, which is one of the most fundamental properties of small clusters to illustrate that the conformational dependence of the Coulomb charging energy of a nanocluster leads to a giant electroresistance, where charging induced conformational distortion changes the blockade voltage. We demonstrated the intricate interplay between charging and conformation change in a nanocluster Zn_3O_4 by combining a first-principles calculation with a temperature-dependent transport model. The predicted hysteretic Coulomb blockade staircase in the current-voltage curve adds another dimension to the rich phenomena of tunneling electroresistance. The new mechanism provides a better controlled and repeatable platform to study conformational electroresistance. This paper has been accepted recently and it is available online (pubs.acs.org/doi/full/10.1021/nl5014458).

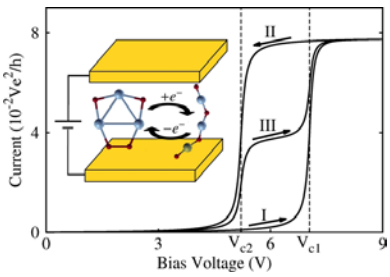

Fig. 1. Ensemble averaged **I–V** characteristic for the two-geometry transport model.

We studied effects of impurity and disorder on $Fe_{1-x}Co_x$/MgO junctions [1]. The question was the optimal Co concentration in $Fe_{1-x}Co_x$/MgO magnetic tunnel junctions (MTJs) to maximize tunneling magnetoresistance (TMR). We performed a transport study on MTJs using variously modeled disordered electrodes. We find that a10-20% Co concentration maximizes TMR, which arises due to a minority *d*-type interfacial resonance state (IRS) that becomes filled with small Co doping, leading to a decrease in antiparallel conductance. Our results explain recent experimental findings and provide insight for the impact of IRS on conductance and TMR in $Fe_{1-x}Co_x$/MgO tunnel junctions.

We carried out theoretical calculations to obtain the interfacial structure of Ag-silicene-Ag junctions and studied the transport characteristics for monolayer and bilayer silicone [2]. Stand-alone silicene has electronic structure similar to that of graphene. By projecting the unfolded band structure from a super cell to a primitive cell, we find that the Dirac cone at the Fermi surface is completely destroyed, and thus clarified a confusion in the community. Our transport study suggests that an experiment can be done to study current-perpendicular-to-plane transport properties of silicene. Our results show these junctions have relatively small resistances, comparable to those of grain boundaries in metals. The results indicate strong interaction between silicene and Ag, in agreement with our band-structure study of silicene on Ag surfaces [3].

Nano-particles, arrays, and supported nano-particles

We examined a number of systems involving nano-particles to study self-capacitance, charge hopping, doping, and surface diffusion. First, through investigating the spin-dependent charging energy of nanoparticles, we introduce a new concept of intrinsic molecular magnetocapacitance (MC) [4]. In molecules and nano-size quantum dots that undergo a spin state transition, the MC can be as high as 12%. In a number of nanoscale systems, the quantum capacitance is highly sensitive to the system spin and charge states. In single molecule junctions, one can exploit molecular MC through the Coulomb blockade effect by modulating the bias voltage and applying an external magnetic field, which turns electron conductance on or off. We can enhance MC by placing the molecule on dielectric surfaces.

We investigated the charge transport in a semiconductor quantum dot (QD) (of 10^3 atoms) supercrystal connected by small molecules, Sn_2S_6 and ABM [5, 6]. We examined the likelihood of four different possible transport mechanisms: mini-band bulk Bloch state transport, direct tunneling, over-the-barrier thermal transport, and phonon-assisted hopping. The left panel in Fig. 3 depicts the system. We found that phonon-assisted hopping is responsible for the charge transport in our systems. We discovered that different atomic attachment plays an important role in the charge transport, as does the quantum dot size. In systems with an ABM, the *cis* isomer provides significantly greater coupling between the two QDs, and hence the electron hopping rate is greater than for the *trans* isomer. As a result, the carrier mobility of the QD array in the low carrier density, weak external electric-field regime is several orders of magnitude higher in the *cis* compared to the *trans* configuration. Finally, from a theoretical point of

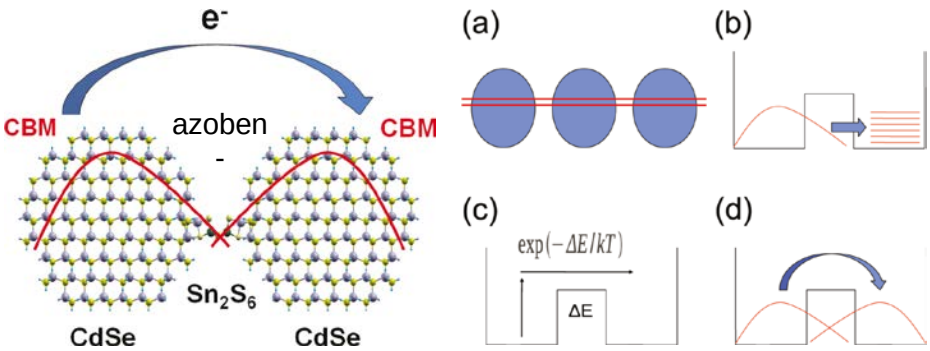

Fig. 2 Different possible mechanisms for the electron transport in a QD supercrystal: (a) bulk crystal-like Bloch state electron transport; (b) direct tunneling mechanism without the help of phonon; (c) over-the-barrier activation mechanism; and (d) phonon-assisted hopping.

view, we have examined the validity of the classical Marcus theory using the quantum mechanical treatment for the phonon. We found that Marcus theory is remarkably accurate in this regard. The phonon-assisted charge hopping is mostly caused by a handful of acoustic phonon modes with the largest Huang_Rhys factors.

Graphitic materials and other interesting problems

In addition to the above mentioned spin-transport in graphene nano-ribbons, we studied several other problems in carbon-based systems (1-3D forms) that have attracted intense experimental attention over many decades. We studied electron relaxation dynamics in molecule-adsorbed carbon nanotubes [7] using a combined DFT-density matrix approach [8]. The functional group that can be firmly attached to the tube using a pyrene-anchoring fragment contributes additional states in the band gap of the CNT. We find that an excited state of the functionalized CNT undergoes electronic dynamics coupled to thermal lattice vibrations, and electronic energy dissipates into lattice vibrations. Our studies of the dynamics of intraband relaxations indicate that upon initial photoexcitation an electron from the CNT ends up being transferred to the adsorbate, while a hole stays in the CNT. We predict that electron relaxation in the conduction band is faster than hole relaxation in the valence band in such CNT systems, with and without the adsorbed dinitromethane molecules, due to the stronger electron−phonon interaction in the conduction band than the hole−phonon interaction in the valence band. Our results provide an important step toward developing solar energy harvesting materials. We also studied small metal clusters Au_n and Fe_n (n=1-5) on single layer 2D graphene sheets, both perfect sheet and graphene with a point defect. Interesting findings include an odd-even oscillation in the doping level of perfect graphene with Au clusters, and an induced magnetic moment in graphene with Fe clusters. Magnetization of the defected graphene becomes more delocalized as the cluster size increases. An odd-even oscillation in the magnetic moment of Au clusters on both perfect and defected graphene is observed. Perfect graphene with Fe clusters is magnetic in all cases, while defected graphene is magnetic for clusters with $n > 1$.

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 [9] and pseudopotentials in conjunction with a planewave expansion, we finished 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 2012, we have finished coding and testing the module of scattering due to the local part of the pseudopotential. This development is one significant step beyond our effort [10] 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. [10]

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Disorder, Dynamics, and Transport in Quantum Magnets

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Project Scope

Within the current project we perform a set of interrelated theoretical studies with the goal of deepening our understanding of the dynamical and transport phenomena in quantum magnets, in particular those induced or influenced by disorder. Fundamentally, in the field of spin dynamics and magneto-thermal transport, the problems of mutual interactions of spin and phonon excitations, role of the dimensionality of spin system, and effects of disorder are largely unexplored. Experimental discoveries of a variety of unusually strong field-dependent phenomena and of the signatures of quasi-ballistic transport in a number of materials require an insight into the role of intrinsic and extrinsic disorder and of the interactions among spin excitations in their dynamics. We expect our study to advance basic understanding of fundamental properties of a large class of quantum materials and yield predictions of new phenomena in them.

Recent progress

Lifetime of gapped excitations in antiferromagnets

Highly precise measurements of the spin-excitation lifetimes by the resonant neutron-spin-echo experiments are becoming available due to the efforts of several groups in Europe and the US. We have conducted a theoretical study of a class of materials with the goal of analyzing the leading source of the temperature-dependence of the relaxation rate of spin excitations in them [1]. We have found that the traditional view on such source is completely inadequate, and that a different, generic mechanism completely dominates the low-temperature relaxation rate of gapped excitations in a wide class of antiferromagnets. This has resulted in a joint theoretical-experimental work, with the data on $BaNi_2(PO4)_2$ giving an unequivocal confirmation of our theory.
In this work, we have demonstrated that scattering on the local distortions of magnetic couplings should completely dominate the low-temperature relaxation rate of gapped excitations in a wide class of antiferromagnets. In particular, we show that in 2D, in addition to a temperature-independent scattering rate associated with the impurity scattering, there exist an impurity-assisted temperature-dependent scattering of the gapped excitation on the thermally-excited gapless magnons. At low temperatures, this mechanism should overwhelm the conventional magnon-magnon scattering, which carries much higher power of temperature. We find these results in a close agreement with the recent resonant neutron spin-echo experiment in the 2D planar XY antiferromagnet $BaNi_2(PO4)_2$ and propose to further verify our predictions in the other systems. We predict even larger dominance of the impurity-assisted over the magnon-magnon scattering in for the non-collinear antiferromagnets. Needless to say, identifying leading scattering

mechanisms is essential for the prospective thermal conductivity experiments in these systems.

Roton energy in ^{4}He.

The high-resolution neutron scattering neutron-resonance spin-echo method shows that the roton linewidth and energy shift in superfluid ^{4}He have different temperature dependencies, in particular at low temperatures. Specifically, the roton energy initially increases with temperature. This is in contrast with the theory by Landau-Khalatnikov and others which predict the *same* temperature dependence for the roton lifetime and2 energy shift, both simply proportional to the thermal roton population.
We demonstrated theoretically [2], that the resolution of this long-standing problem is due to previously ignored three-particle processes in superfluid ^{4}He. Such particle-nonconserving interactions is a hallmark of Bose-Einstein condensation. Given a variety of parallels between spin and bosonic systems, together with the number of explicit realizations of analogs of Bose-Einstein condensation of magnons in quantum magnets, this work is of general importance for them. We also expect that this study will have a wide-ranging impact for Bose-condensed systems in general, covering areas such as excitons in semiconductors, magnon decay, non-linear effects in spintronics, and strongly interacting ultracold Bose gases.

Anomalous defect scattering in noncollinear magnets.

Defects in non-collinear and frustrated quantum magnets have come into focus only recently, displaying rich physics, and — in particular — spin textures. Adding a defect spin locally perturbs the balance of exchange fields and requires the surrounding spins of the non-collinear host to readjust, resulting in a spin texture. In our recent work [3], we have advanced the field by investigation of the magnon impurity-scattering in non-collinear magnets. We have discoveredthat the scattering amplitude displays a strongly dispersive feature, clearly tracing the magnon dispersion shifted by the magnetic ordering vector. We have shown that this effect is an unequivocal consequence of the spin texture. Intuitively, an effective staggering of the magnetic field is generated by the texture. This serves as a potential for umklapp scattering of magnons, which, in turn, leads to the new feature in the *T*-matrix — the momentum-dependent resonance. This result should be valid for a wide class of frustrated non-collinear magnets and is of a direct relevance to their excitation spectra. One may expect to observe anomalous **k**-dependent broadening of the spectrum and an equally unusual field-dependence of such a broadening. These features should be observable by inelastic neutron scattering.

Spin dynamics in complex antiferromagnets

The Heisenberg triangular-lattice antiferromagnets are prominent in low-dimensional and frustrated magnetism and are the subject of significant experimental and theoretical interest. Their non-collinear magnetic order has profound consequences for their spin dynamics: elementary excitations (magnons) become unstable with respect to sponta-

neous decay into pairs of other magnons. To describe their excitation spectrum within the spin-wave theory, the inclusion of magnon interaction is, therefore, crucial.

We have elucidated [4] the role of magnon interaction and spontaneous decays in the spin dynamics of the triangular-lattice Heisenberg antiferromagnet by calculating its dynamical structure factor, $S(q,\omega)$, within the spin-wave theory. The dynamical structure factor was shown to exhibit unconventional features such as quasiparticle peaks broadened by decays, non-Lorentzian lineshapes, and significant spectral weight redistribution to the two-magnon continuum. This rich spectrum illustrates the complexity of the triangular-lattice antiferromagnet and provides distinct qualitative and quantitative fingerprints for experimental observation of the decay-induced magnon dynamics.

Our detailed calculations provide a guide for experimental observation of the effects of magnon interaction and decays as well as a direct analytical scheme to predict the spin dynamics for realistic single-crystalline materials. This study is of a direct relevance to the neutron-scattering experiments conducted at ORNL and NIST as well as international user facilities and institutions in Europe.

Disorder in 1D chains

We have addressed the problem of the influence of strong disorder on the spectral properties of 1D spin-1/2 chains [5], a cornerstone example of quantum criticality with scale-free antiferromagnetic correlations. The collaboration has involved neutron-scattering groups from Brookhaven, ORNL, ISIS, ILL, ETH and Dresden, and with the PI of this Project responsible for the theoretical model presented in the paper. Both NMR and neutron-scattering experiments on one of the best known spin-chain materials $SrCuO_2$ showed a depletion of low-energy magnetic states in samples disordered by low-level doping, referred to as the “spin-pseudogap”. This is opposite to the strong-disorder Renormalization Group (RG) theory, which predicts *divergent* low-energy density of states and spin structure factor.

The main message of our work is that the spin dynamics of S=1/2 antiferromagnetic chains can be fully explained by the effective fragmentation of the spin chains by the screened defects, regardless of the nature of the latter. We also argue that such a pseudogap is a *generic* spectral feature of S=1/2 antiferromagnetic chains with defects, a situation which is far from the strong-disorder RG fixed point. Finally, we have demonstrated that defects do not wipe out the universal scaling properties of the correlation functions. The latter are only “masked” by a universal envelope function described by our theory, and can be recovered. A model based on the idea of the effective fragmentation of the spin chains, has *no adjustable parameters,* yet it quantitatively accounts for the experimental data in the entire experimental temperature range and allows to represent the momentum-integrated dynamic structure factor in a universal scaling form.

The extreme depletion of spectral weight at low energies [pseudogap] is shown to be due to the exponentially low probability of having very long uninterrupted chain segments in the diluted system. The most convincing argument in favor of our interpretation, is that the same envelope function that follows from fragmentation theory can simultaneously reproduce the measurements at all available temperatures. Our approach is argued to be generic and can be applied to describing the spin dynamics in chains with other types of defects, such as vacancies or broken bonds.

We have shown that doping of antiferromagnetic 1D spin-1/2 chains opens a pseudogap in the spin excitation spectrum. It can be generically explained in terms of site defects in the one-dimensional Heisenberg model, yielding a universal scaling behavior and without the involvement any structural phase transitions. Our work will have consequences for the studies of many real disordered spin chain materials and may also account for the unexplained behavior of S=1/2 chains with weak-bond defects.

Future plans

For the next year, we plan to continue our studies of the dynamical properties of frustrated spin systems and of heat transport in layered antiferromagnets. Specifically:
• we will advance the theory of thermal conductivity in layered 2D antiferromagnets to address an excellent set of new experimental data in cuprate La_2CuO_4.
• we will study effects of impurity doping on thermal conductivity in La_2CuO_4 and in related 1D systems, for which a high-quality experimental data has been accumulated.
• study of the scattering effect of impurities in noncollinear antiferromagnets will provide new understanding of the scattering mechanisms to our studies of thermal conductivity.
• we plan to continue our studies of the dynamical properties of frustrated spin systems, including real kagome-lattice antiferromagnetic materials.

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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 (QMC) methods for systems with considerable electron correlation, density-functional perturbation theory (DFPT) 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, metal thin films, and semiconductor nanowires.

Recent Progress

Electronic properties of Si nanowires: Surface passivation and orientation dependence

Various surface passivations for silicon nanowires (SiNWs) have previously been investigated to extend their stability and utility. However, the fundamental mechanisms by which such passivations alter the electronic properties of silicon nanowires have not been clearly understood thus far. In this work, we address this issue through first-principles calculations on fluorine, methyl and hydrogen passivated [110] and [111] silicon nanowires.

In [110] SiNWs, both F and CH_3 passivation lower the band gaps of SiNWs but by different mechanisms. The high electronegativity of F strongly alters the electron potential thereby changing the confinement of electronic states. On the other hand, the dominant effect in CH_3-passivated SiNWs is strain which causes charge redistribution. The larger size of CH_3 groups can only be accommodated with longer lattice constants that induce axial strain. Depending on the local bond geometry, CH_3 groups also put more strain on certain facets than others. The effect of strain induced by CH_3 passivation is far more effective than quantum confinement at reducing the [110] SiNW band gap. In contrast, [111] SiNWs are only minimally affected by surface passivation. Canted and well-aligned Si-passivant bonds on the {100} facets of [110] SiNWs allow greater penetration of the surface potential which affects their electronic states. This is not so in [111] SiNWs as passivants are evenly spread over the surface. Unlike [111] SiNWs, [110]

SiNWs also have shorter lattice constants and lack Si-Si bonds that are parallel to the wire axis. Therefore, for a set strain, Si-Si bonds in [110] SiNWs will have to stretch more than Si-Si bonds in [111] SiNWs, giving rise to a larger change of the band gap.

Anomalous phase relations of quantum size effects in ultrathin Pb films on Si(111)

Quantum oscillations of work function and film stability as a function of the film thickness in Pb thin films on Si(111) are studied in a combined experimental and theoretical investigation. The comparison of the phase relationship in quantum oscillations (surface energy versus work function) reveals a complete surprise: In contrast to a previously predicted quarter wavelength phase shift in the phase relationship, we found that their quantum oscillations have identical phase for this particular system. We further proposed a conjecture to resolve this apparent inconsistency by arguing that this phenomenon is related to the critical roles that the substrate band edges play in the quantum size effect of the surface energy. We also argue that the anomalous lateral mass enhancement for quantum well states near the Fermi energy, reported earlier, is due to a similar manifestation of the band edge on the quantum confinements of electronic states in ultrathin Pb films.

Electron-phonon coupling in two-dimensional silicene and germanene

Following the previous work in graphene, we have performed a first-principles study of electron-phonon coupling (EPC) in low-buckled monolayer silicene and germanene. Despite the similar honeycomb atomic arrangement and linear-band dispersion, the EPC matrix-element squares of the Γ-E_g and K-A_1 modes in silicene are only about 50% of those in graphene. However, the smaller Fermi velocity in silicene compensates for this reduction by providing a larger joint electronic density of states near the Dirac point, giving rise to comparable phonon linewidths. We predicted that Kohn anomalies associated with these two optical modes are significant in silicene. In addition, the EPC-induced frequency shift and linewidth of the Raman-active Γ-E_g mode in silicene are calculated as a function of doping. The results are comparable to those in graphene, indicating a similar nonadiabatic dynamical origin. In contrast, the EPC in germanene is found to be much reduced.

Coupled Dirac fermions and neutrino-like oscillations in twisted bilayer graphene

The low-energy quasiparticles in graphene can be described by a Dirac-Weyl Hamiltonian for massless fermions, hence graphene has been proposed to be an effective medium to study exotic phenomena originally predicted for relativistic particle physics, such as Klein tunneling and Zitterbewegung. In this work, we show that another important particle-physics phenomenon, the neutrino oscillation, can be studied and observed in a particular graphene system, namely, twisted bilayer graphene. It has been found that graphene layers grown epitaxially on SiC or by the chemical vapor deposition method on metal substrates display a stacking pattern with adjacent layers rotated by an angle with respect to each other. The quasiparticle states in two distinct graphene layers act as neutrinos with two flavors, and the interlayer interaction between them induces an appreciable coupling between these two "flavors" of massless fermions, leading to neutrino-like oscillations. In addition, our calculation shows that anisotropic transport properties manifest in a specific energy window, which is

accessible experimentally in twisted bilayer graphene. Combining two graphene layers enables us to probe the rich physics involving multiple interacting Dirac fermions.

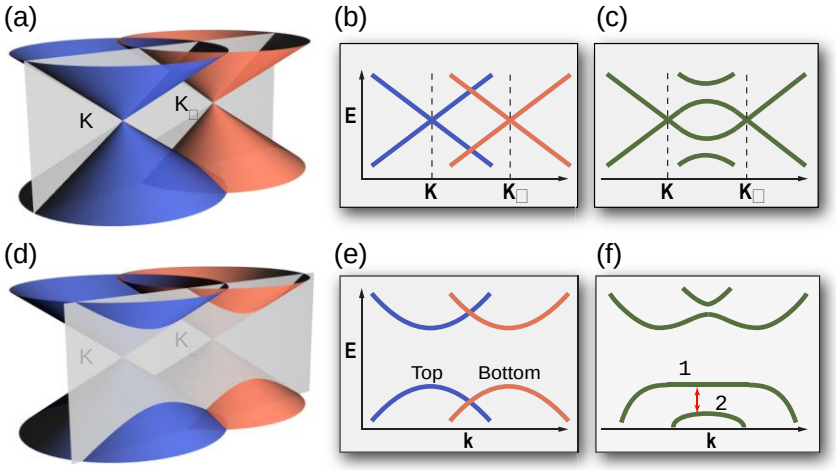

Figure 1. Schematic illustration of interlayer interaction in twisted bilayer graphene. (a) A plane cutting through the Dirac points of the two Dirac cones associated with the two twisted layers. The energy bands on the cross section shown in (a) are drawn in (b) and (c) for cases without and with interlayer interaction, respectively. (d) A plane cutting through the two Dirac cones without including the two Dirac points. The energy bands on the cross section shown in (d) are drawn in (e) and (f) for cases without and with interlayer interaction, respectively.

Future Plans

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 learned how the two Dirac cones associated with two graphene layers interact to give rise to interesting features in the electronic structure of twisted bilayer graphene. Since a lot of experiments produce multilayer graphene, we plan to extend the study of the interlayer coupling to trilayers graphene. With various combinations of the stacking order, we expect to see both the monolayer-like energy bands as well as bilayer features. It is also expected to see multiple van Hove singularities in the density of states, which presents a unique feature for possible applications of these two-dimensional layers.

In addition, we plan to reexamine the magnetism in graphene flakes. Lieb's theorem for a bipartite system is a starting point and has been applied successfully to count the ground-state magnetic moment of graphene vacancy defects. However, it is physically unclear why the number of midgap states is connected with the imbalance of atomic A and B sites. Furthermore, Lieb's theorem underestimates the midgap states of some graphene fragments with a complex geometry. Work is underway to develop a counting scheme based on the number of dangling π bonds in order to determine the midgap states and ground-state magnetic moments.

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INTERPLAY BETWEEN SUPERCONDUCTIVITY AND MAGNETISM IN IRON-BASED SUPERCONDUCTORS

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Project scope

My research on Fe-pnictides was focused on several issues issues: a search for non-trivial superconductivity, chiefly the one which breaks time-reversal symmetry, on the understanding of superconductivity and magnetic properties in systems with only hole or only electron pockets, on the evolution of the superconducting gap structure with doping, and on possible novel s-wave superconductivity in LeFeAs. The key goal of these studies was to understand whether multi-orbital/multi-band structure of Fe-pnictides leads to qualitatively new physics, which is not present in other unconventional superconductors, like cuprates and heavy-fermion materials. I am mostly interested in the possibility to obtain superconductivity which breaks time-reversal symmetry. Such superconductivity exhibits a wealth of fascinating properties which are highly sought after for nano-science applications.

Recent progress

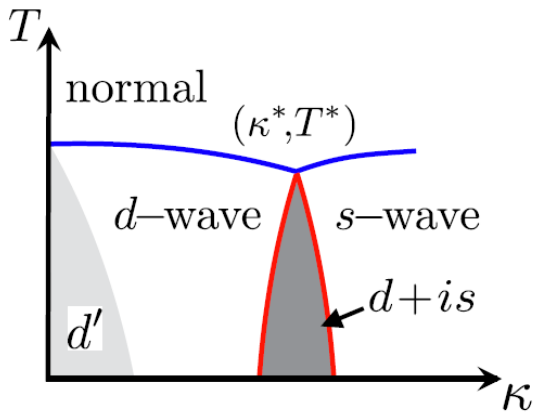
Superconductivity which breaks time-reversal symmetry

With my student S. Maiti, we analyzed the evolution of the superconducting gap structure in strongly hole doped $Ba_{1-x}K_xFe_2As_2$ between x=1 and x=0.4 (optimal doping). In the latter case, the pairing state is most likely s+-, with different gap signs on hole and electron pockets, but with the same signs of the gap on the two Γ-centered hole pockets (a ++ state on hole pockets). In a pure KFe_2As_2 (x=1), which has only hole pockets, laser ARPES data suggested another s+- state, in which the gap changes sign between hole pockets (a +- state). We analyzed how ++ gap transforms into a +- gap as x tends 1. We found that this transformation occurs via an intermediate s+is state in which the gaps on the two hole pockets differ in phase by a non-zero ϕ which gradually involves from $\phi=\pi$ (the +-state) to $\phi=0$ (the ++ state). This state breaks time-reversal symmetry and has huge potential for applications. We computed the dispersion of collective excitations and showed that two different Leggett-type phase modes soften at the two end points of TRSB state.

With my other student A. Hinojosa, we analyzed superconductivity in the coexistence region with spin-density-wave (SDW) order in weakly doped Fe-pnictides and argued that it differs qualitatively from the ordinary s+- state outside the coexistence region, as it develops an additional gap component, which is a mixture of intra-pocket singlet (s^{++}) and inter-pocket spin-triplet pairings (the t-state). The coupling constant for the t-channel is proportional to the SDW order and involves interactions that do not contribute to superconductivity outside of the SDW region.

Superconductivity in systems with only electron pockets.

With M. Khodas from U. of Iowa we analyzed the pairing symmetry in Fe-based superconductors AF_2Se_2 (A = K, Rb, Cs) which contain only electron pockets. We argued that the pairing condensate in such systems contains not only intra-pocket component, but also inter-pocket component, made of fermions belonging to different electron pockets. We analyzed the interplay between intra-pocket and inter-pocket pairing depending on the ellipticity of electron pockets and the strength of their hybridization. We showed that with increasing hybridization the system undergoes a transition from a d-wave state to a novel s+- state, in which the gap changes sign between hybridized pockets. This s+- state has the full gap and at the same time supports spin resonance, in agreement with the data. Near the boundary between d and s+- states we found a long-sought s+id state which breaks time-reversal symmetry. We show phase diagram in the Figure. In subsequent papers we analyzed the excitation spectrum and neutron and Raman intensities in such novel s-wave state.



The phase diagram in (κ,T)--plane for superconductors with only electron pockets (κ is the ratio of the hybridization and the degree of ellipticity of the electron pockets).

Nematic order in Fe-based superconductors.

With R. Fernandes and J. Schmalian, we analyzed in detail the origin of nematic order in Fe-pnictides. The existence of nematic order in iron-based superconductors is now a well-established experimental fact, yet its origin remains controversial. Nematic order breaks the discrete lattice rotational symmetry by making the x- and y-directions in the iron plane non-equivalent. This can happen because of a regular structural transition or due to a electronically-driven instability -- an orbital order or a spin-driven Ising-nematic order. The latter is a magnetic state that breaks rotational symmetry but preserves time-reversal symmetry. Symmetry dictates that the development of one of these orders immediately induces the other two, making the origin of nematicity a physics realizationof the “chicken and egg problem”. We reviewed different scenarios and argued that the evidence strongly points to an electronic mechanism of nematicity, placing nematic order in the class of correlation-driven electronic instabilities, like superconductivity and density-wave transitions. We discussed different microscopic models for nematicity and linked them to the properties of the magnetic and superconducting states, what allowed us to provide a unified perspective on the phase diagram of the iron pnictides.

Highly unconventional superconductivity in LiFeAs

With F. Ahn and others we analyzed the structure of the pairing interaction and superconducting gap in LiFeAs by decomposing the pairing interaction for various k_z cuts into s- and d-wave components and by studying the leading superconducting instabilities. We used the ten orbital tight-binding model, derived from ab-initio LDA calculations with hopping parameters extracted from the fit to ARPES experiments. We found that the pairing interaction almost decouples between two subsets, one consists of the outer hole pocket and two electron pockets, which are quasi-2D and are made largely out of dxy orbital, and the other consists of the two inner hole pockets, which are quasi-3D and are made mostly out of dxz and dyz orbitals. The bare inter-pocket and intra-pocket interactions within each subset are nearly equal, and small changes in the intra-pocket and inter-pocket interactions due to renormalizations by high-energy fermions give rise to a variety of different gap structures. We focus on s-wave pairing which, as experiments show, is the most likely pairing symmetry in LiFeAs. We found four different configurations of the s-wave gap immediately below Tc: the one in which superconducting gap changes sign between two inner hole pockets and between the outer hole pocket and two electron pockets, the one in which the gap changes sign between two electron pockets and three hole pockets, the one in which the gap on the outer hole pocket differs in sign from the gaps on the other four pockets, and the one in which the gaps on two inner hole pockets have one sign, and the gaps on the outer hole pockets and on electron pockets have different sign. Different s-wave gap configurations emerge depending on whether the renormalized interactions increase attraction within each subset or increase the coupling between particular components of the two subsets. We discuss the phase diagram and experimental probes to determine the structure of the superconducting gap in LiFeAs. We argued that the state with opposite sign of the gaps on the two inner hole pockets has the best overlap with ARPES data

Other projects in Fe-based superconductors

I also studied the behavior of the London penetration depth near a magnetic quantum-critical point, the effect of fluctuations in the Cooper channel on the spin resonance in s+- superconductors, the interplay between nematicity and superconductivity, and on the development of a novel magnetic order near a critical doping where magnetism ends (the last work was done in collaboration with experimentalists from Argonne Natl. Lab)

I wrote three review articles on Fe-pnictides and related materials. One is on electronic itinerant mechanism of superconductivity and magnetism in Fe-pnictides. This is the summary of my research on pnictides over the two years of DOE grant period. The two other reviews are on general theoretical consideration of superconductivity in itinerant systems with repulsive interaction.

Future plans

My plan for the next year is to continue work on unconventional superconductivity which breaks time-reversal symmetry. I plan to do full-scale analysis of experimental consequences of s-wave superconductivity which breaks time-reversal symmetry. I also plan to move beyond BCS-like analysis and consider seriously fermionic self-energy and lifetime of quasiparticles in the normal state. I will use

this information to construct Eliashberg-type theory of multi-orbital superconductivity, which we allow me to not only compute Tc with the prefactor but also settle the issue what sets the overall scale of Tc – the dynamics of the interaction or the RG scale at which the system develops a static attraction in the s+- pairing channel. I also plan to analyze in detail recently discovered superconductivity in FeSe, where the Fermi energy is very low, of order of superconducting gap. I plan to verify whether in this situation Tc is universally related to Fermi energy. I also plan to address an issue whether spin-nematic order can develop at T=0 at larger dopings than SDW order.

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DYNAMICS OF THE MAGNETIC FLUX IN SUPERCONDUCTORS

DOE/BES Grant No. DE-FG02-93ER45487

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SELECTED TOPIC: RANDOM FIELDS AND TOPOLOGY

I. PROJECT SCOPE

The ongoing work on the DOE/BES grant and research planned for the nearest future include analytical and large scale numerical studies of the effects of static random fields on correlations in superconductors and random magnets, stability of skyrmions in the presence of random fields and lattice deformations, and coupled quantum dynamics of nanomagnets and Josephson junctions. This abstract focuses on the random-field work. Pinning in type-II superconductors affects translational correlations in the flux-line lattice and determines the size of the vortex bundle that becomes depinned by the transport current. This in turn determines the critical current. Pinning of the vortex lattice by the quenched disorder described by the Hamiltonian for the displacement field ***u(r)***,

$$\mathrm{H}=\frac{1}{2}\int d^3r\left[(C_{11}-C_{66})(\partial_\alpha u_\alpha)^2+C_{66}(\partial_\alpha u_\beta)^2+C_{44}(\partial_z u_\alpha)^2\right]+U_{pin}(\vec{u})$$

has been studied in the past. The problem is conceptually similar to the problem of ferromagnetically interacting spins disturbed by the static random field h_i at each lattice cite i, that can also be treated as a field-theory problem for the spin field ***S(r)***,

$$\mathrm{H}=-\frac{1}{2}\sum_{ij}J_{ij}\vec{s}_i\cdot\vec{s}_j-\sum_i\vec{h}_i\cdot\vec{s}_i=\int d^dr\left[\frac{1}{2}\alpha\left(\frac{d\vec{S}}{dr_i}\right)^2-\vec{h}\cdot\vec{S}\right]$$

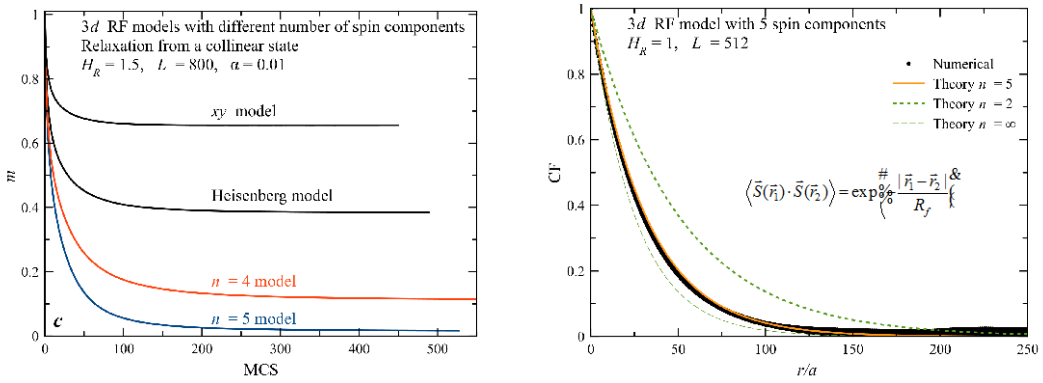
Early arguments of Larkin, and of Imry and Ma, suggested that the scaling of the exchange and random field energies shown below, generates a finite length, $R_{LIM,}$

$$E_{ex}\propto\alpha/R^2,\quad E_{RF}\propto -h/R^{d/2},\quad R_{LIM}\propto 1/h^{2/(4-d)}$$

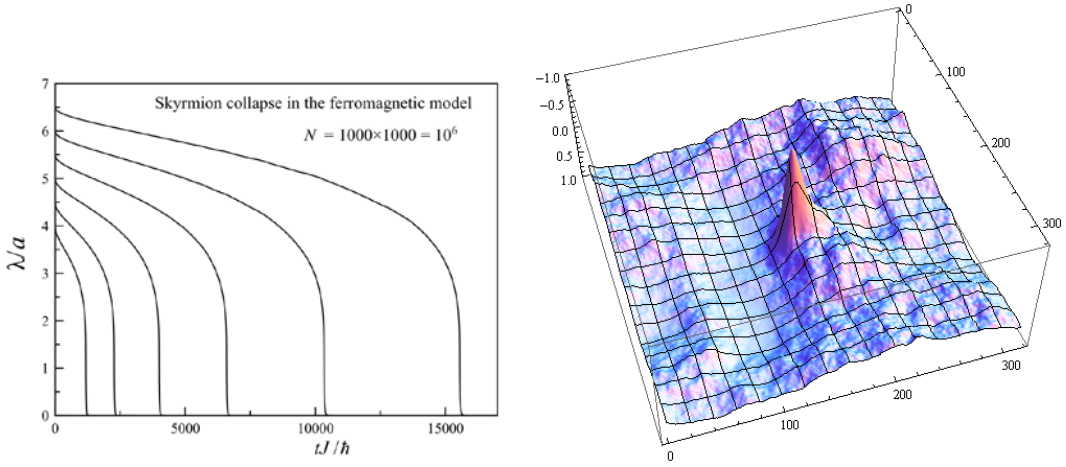
that provides the spatial scale of the destruction of the long-range order. It occurs in less than four dimensions regardless of the strength of the random field. The subsequent work of Nattermann, and of Giamarchi and Le Doussal, based upon renormalization group and replica symmetry breaking arguments, suggested power-law decay of correlations. Experiments have been inconclusive and the question of long-range correlations has been left open. Recently we have readdressed this fundamental problem using modern computer capabilities. Our research is integrated with education through involvement of doctoral and undergraduate students in analytical and computational work.

II. RECENT PROGRESS

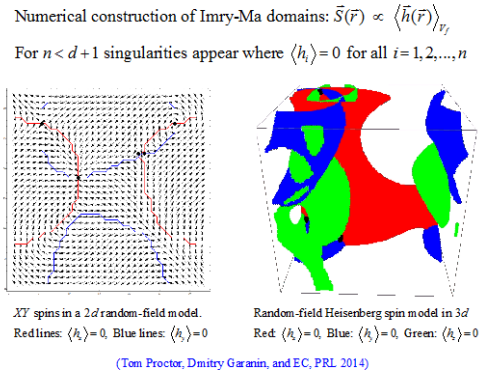
Our main achievement so far is demonstration of the fact that the behavior of the random-field system is controlled by topology. Three types of behavior have been found depending on whether the symmetry of the order parameter and the dimensionality of space permit topological defects and whether the defects are singular or not. The random-field system with a fixed-length n-component continuous-symmetry order parameter in d dimensions possesses topological defects with singularities at $n < d + 1$, e.g., vortices, vortex loops, and hedgehogs. At $n = d + 1$ the defects are non-singular, e.g., skyrmions. At $n > d + 1$ topologically stable defects are absent. The xy model in $3d$ has vortex loops, the Heisenberg model has hedgehogs, the $n = 4$ model has defects similar to skyrmions, and the $n = 5$ model has no topological defects at all. This is reflected in the relaxation from the initially ordered state shown in the figure (left) below. The $n = 2$ and $n = 3$ systems relax to the state with a finite magnetization. It is rather small for $n = 4$ and is zero for $n = 5$. Only the latter case exhibits exponential decay of correlations with $R_f = 8\pi(1 - 1/n)^{-1}(Js/h)^2$ in a quantitative agreement with the Larkin-Imry-Ma argument,

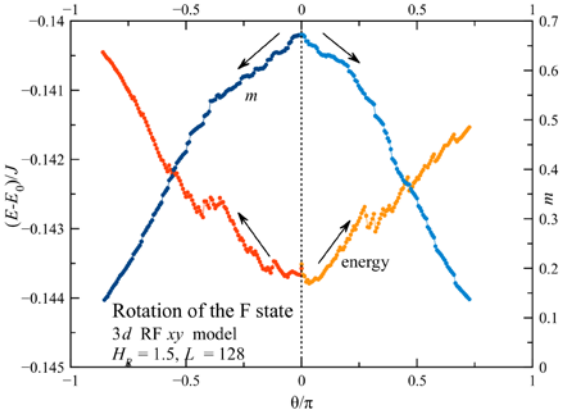


see figure above (right). Pinning of the topological defects plays a crucial role in determining the glassy properties of the random-field system. For instance, as we demonstrated earlier (PRB-2012), in the absence of the random field, the skyrmions in a $2d$ square lattice collapse due to the violation of the scale invariance by the lattice, see figure below (left). Pinning by the random field stabilizes skyrmions, see figure below (right), leading to the irreversible glassy behavior, with the final state depending on the initial condition.



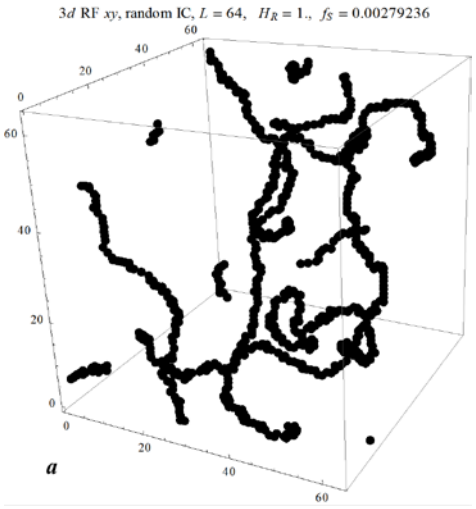
The presence of singularities in the Larkin-Imry-Ma state for *n* less than *d + 1* is mandated by topology, see figure below (left). The resulting states exhibit memory effects as is demonstrated in the figure below (right): The F-state obtained by the relaxation from the initially ordered state remembers the initial direction of the ordering.

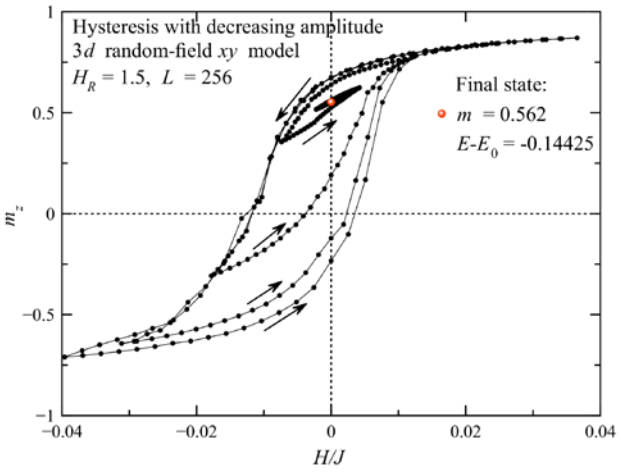


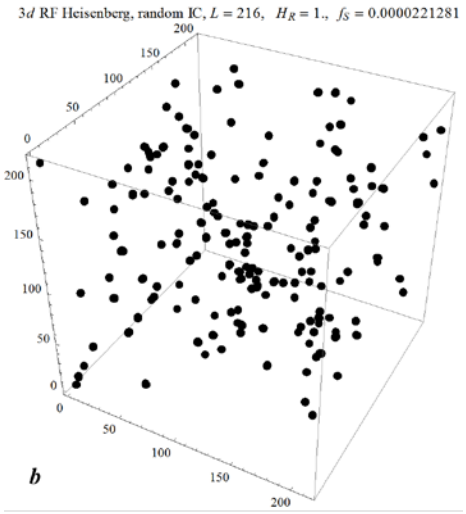


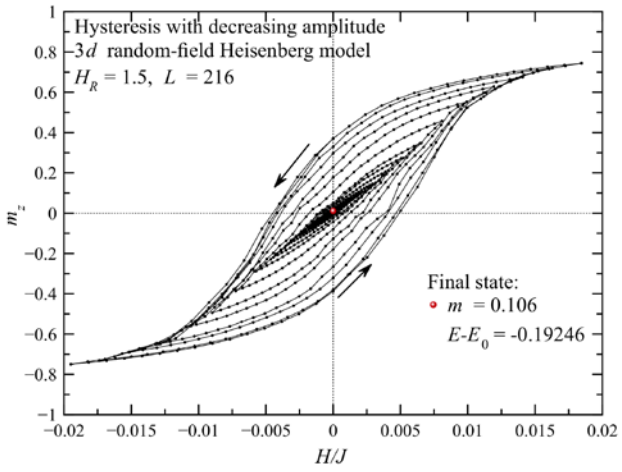
III. FUTURE PLANS

Our future plans on the random field subject include studies of the glassy behavior due to topological defects pinned by a weak quenched disorder. Besides relevance to the physics of superconductors and random magnets, these studies can provide potentially new models of a glassy state. Some limited numerical effort will be devoted to the ground state that may or may not be possible to obtain in a random-field glass. So far we found a profound difference in the behavior of random-field systems of different symmetry when trying to obtain the absolute energy minimum. For instance, application of a sequence of hysteresis cycles of decreasing amplitude, while helping to lower energy, leads in *3d* to the ordered state with a finite magnetization for the *xy* model (*n = 2*) but to the disordered state with near-zero magnetization for the Heisenberg model (*n = 3*), see the figures below. This is clearly related to the large energy of the vortex loops in the *xy* model as compared to the relatively small energy of hedgehogs in the Heisenberg model.









We plan to investigate in more detail the correspondence between the *3d* random-field *xy* spin model and the *3d* random-field flux-lattice model. While the two models appear conceptually similar, the symmetry of the underlying order parameters is somewhat different and this, in principle, may lead to a different long-range behavior. Therefore the problem of the elastic lattice of vortices in a static random background, that permits dislocations and disclinations analogous to the topological defects of the spin model, requires a separate numerical effort. Heisenberg spins with random-anisotropy in two and three dimensions is another problem that is conceptually similar to the one we have investigated for the random field. The random-anisotropy problem has significant applied value because it is related to properties of amorphous and sintered magnets. We will look into how the area of the hysteresis loop scales with the strength of the random anisotropy.

IV. RECENT PUBLICATIONS ON RANDOM FIELDS (DOE/BES support acknowledged)

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2. D. A. Garanin, E. M. Chudnovsky, and T. C. Proctor, Random-Field XY Model in Three Dimensions, Physical Review B **88**, 224418 (2013).

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4. D. A. Garanin and E. M. Chudnovsky, Ordered vs Disordered States of the Random-Field Model in Three Dimensions, arXiv:1406.1165 [cond-mat.stat-mech] (2014).

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

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Project Scope

The goal of this program is to understand the consequences of lattice frustration in quasi-two dimensional strongly-correlated superconductors. The systems of particular interest are the carbon-based superconductors including organic charge-transfer solids (CTS) and the very recently discovered superconducting doped polycyclic aromatic hydrocarbons (PAHs). The latter exhibit many novel features that are shared by the doped fullerides, although this last family is three-dimensional in structure. One goal of our project is to demonstrate that the normal states of these three different families of carbon-based molecular superconductors can be understood within a common theoretical model. A second goal is to arrive at a unified theory of superconductivity (SC).

Recent Progress: Summary

A. We developed a correlated-electron minimal model for the normal state of metal-intercalated PAHs [1]. Exact finite cluster calculations showed that while the systems with molecular charges of -1 and -2 are one- and two-band Mott-Hubbard semiconductors, respectively, molecular charge -3 gives two nearly 3/4-filled bands. The carrier density per molecular orbital is thus nearly the same in the normal states of the superconducting PAHs and CTS, and may be the key to understanding unconventional SC in the family of doped PAH.

B. We performed the first correlated-electron calculation of the conducting layer of the organic superconductor family $\boldsymbol{\kappa}$-(BEDT-TTF)$_2$X, without assuming an effective 1/2-filled band description. We find that within the single-band Hubbard model the system remains a correlated metal even for very strong onsite Coulomb interaction U, with no signs of charge or spin ordering. This may explain why long-range antiferromagnetic order is found experimentally in only few members of the $\boldsymbol{\kappa}$-(BEDT-TTF)$_2$X family.

C. We have developed a new tensor-network Monte Carlo method for strongly-correlated systems and benchmarked our technique against the Density Matrix Renormalization Group (DMRG) method for the interacting spinless fermion model [2].

D. We revisited the theory of the spin-Peierls (SP) state in the organic salt (TMTTF)$_2$X [3]. We showed that claims of two distinct SP states exist [4] as a result of poor parameter choices in the two-dimensional model.

E. We have shown that there exist an unusually large number of unconventional superconductors that share two peculiar features: (i) carrier density of exactly 1/2 per molecule or unit cell, and (ii) lattice frustration. While this "data collection" is still in its early stages, it reinforces the idea we have pursued that the proximity of SC to antiferromagnetism is not the only signature of correlated-electron SC.

Highlight: Theory of superconducting phenacenes: Why is valence −3 special?

The discovery of SC in metal-intercalated polycyclic aromatic hydrocarbons (PAHs) like phenacenes (phenanthrene [5] and picene [6]), coronene [7], and dibenzopentacene [8] are exciting recent developments. Experimental studies have suggested that electron-electron (e-e) rather than electron-phonon interactions are responsible for SC. Furthermore, it has also been shown that the metal ions act only as electron donors and have no contribution in SC. Three intriguing questions have perplexed researchers: (i) In spite of their similarities, why is SC present only in the phenacenes and not in the acenes anthracene and pentacene? (ii) Why do only the trinegative ions of these hydrocarbons show SC and not the mono and di anions? (iii) What, if any, is the relevance of these observations to SC in A_3C_{60}?

We have proposed a theory of the normal state of superconducting PAHs [1] which is able to answer all the above questions. Our initial theoretical work is for phenanthrene and anthracene ions of all three molecular charges (−1, −2, and −3). The difference between the phenacenes and acenes arise from the very small LUMO-LUMO+1 (L-L+1) energy gap $\Delta_{L,L+1}$ in the former, and large $\Delta_{L,L+1}$ in the latter, as shown in Fig. 1 (a). Thus both L and L+1 MOs are relevant in the theoretical description of the normal states of phenacene ions.

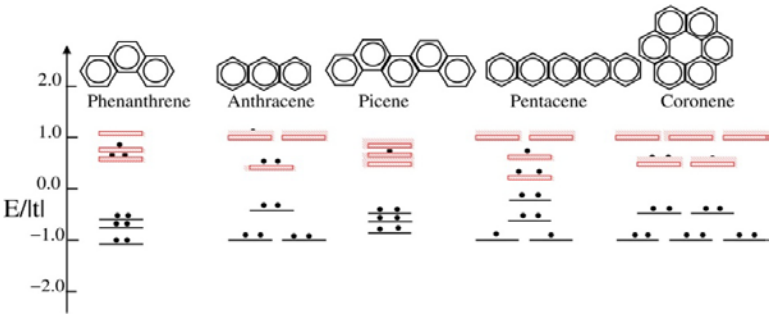

Fig. 1(a): Bonding (black line) and antibonding (red box) molecular orbitals within nearest-neighbor tight-binding theory near the chemical potential of triply charged negative ions of phenacenes and acenes. Energies are in units of the hopping integral |t|. The LUMO(L) and LUMO+1(L+1) orbitals are unusually close in phenanthrene and picene compared to anthracene and pentacene. In coronene the LUMOs are doubly degenerate.

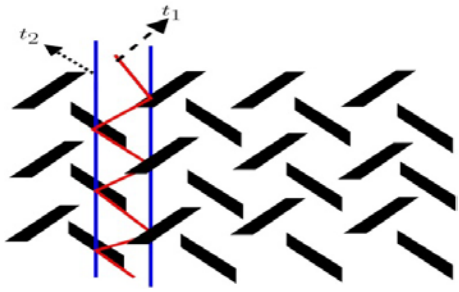

Fig. 1(b): Schematic representation of the 2D Herringbone lattice of phenanthrene ions with the 1D lattice superposed. t_1 and t_2 are the first and second nearest-neighbor hoppings.

We derived an effective Hamiltonian $H_{L,L+1}$ in the reduced space of the L and L+1 MOs, using the localized MO basis, for phenanthrene and anthracene MOs. $H_{L,L+1}$ contains all intermolecular hoppings and the intramolecular e-e interactions derived from the atomic Hubbard U. We have solved $H_{L,L+1}$ for phenanthrene and anthracene ions with the Herringbone crystal structure of Fig. 1(b). For each ionic valence we calculate the ratio n_{L+1}/n_L, where n_L and n_{L+1} are the average charges on the L and L+1 MOs, respectively. In Fig. 2(a) we show the numerically calculated exact n_{L+1}/n_L for zero e-e interaction but realistic intermolecular electron hops, for a lattice of 20 x 20 molecules (800 orbitals). Our calculations show that while n_{L+1} remains zero for the monoanion crystal, the L+1 occupancies are substantially larger in the dianion and trianion crystals than in the respective isolated molecules.

When U ≠0, $H_{L,L+1}$ can be solved exactly for finite clusters only. The 1D clusters used in this study are derived from the 2D Herringbone crystal structures of pristine and doped phenacenes and acenes [Fig. 1(b)]. Clusters of 6, 8 and 10 (largest possible within current computational resources) molecules are considered. For the dianion the largest cluster possible is 8 molecules. From exact U ≠ 0 computations [see Fig. 2(b)] of occupancies of the L (n_L) and the L+1 (n_{L+1}) for phenanthrene we find:

A. $n_L \sim 0$ and $n_{L+1} \sim 1$, respectively, independent of U and $\Delta_{L,L+1}$, in the monoanion. The monoanion is a metal for U = 0 and is a one-band Mott-Hubbard semiconductor with antiferromagnetic spin-spin correlations for U ≠ 0.

B. The dianions have U-dependent orbital occupancies and with increase in U, become a two-band Mott-Hubbard semiconductor, with ferromagnetic intramolecule and antiferromagnetic intermolecule correlations.

C. For realistic $\Delta_{L,L+1}$ U drives the trianion towards a nearly 3/4-filled two-band system with no spin ordering. We then see why molecular valence -3 is special: the system is not a Mott-Hubbard semiconductor; rather, the carrier density per active MO is the same as in the superconducting CTS.

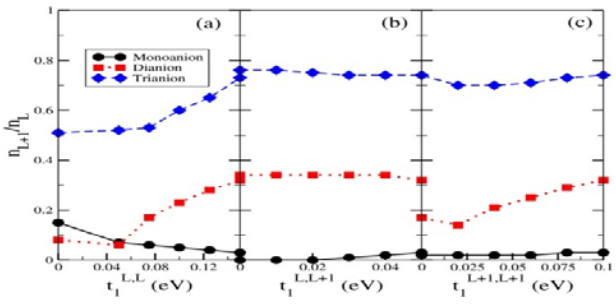

Fig. 2(a): Ratio of electronic populations in L+1 and L versus different hopping integrals for a periodic 2D 20× 20 lattice of phenanthrene ions at U(atomic) =0 and $\Delta_{L,L+1}$ = 0.4 eV.

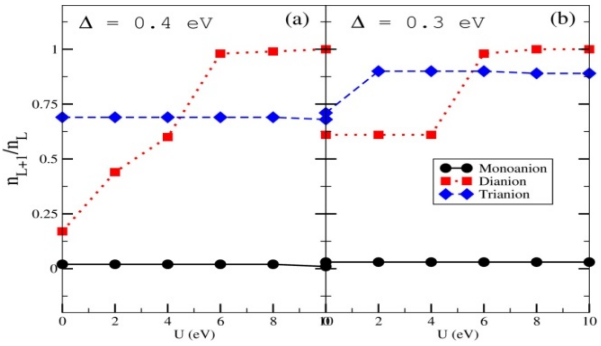

Fig. 2(b): $\frac{n_{L+1}}{n_L}$ vs atomic U for finite clusters of phenanthrene mono and trianions (10 molecules) and dianions (8 molecules) for hopping parameters corresponding to the terminal points in Fig. 2(a). $\Delta_{L,L+1}$ = 0.4 eV (a) and 0.3 eV (b).

Future Plans

1. *Metal-intercalated hydrocarbons*: This will be a major activity in the coming year. Our detailed investigation of why the trianions of phenacenes are special is currently based on calculations that are for finite 1D clusters. We intend to pursue Path Integral Renormalization Group (PIRG) calculations for realistic two-dimensional clusters. Our long term goal is to extend these calculations to bcc Cs_3C_{60}, to understand the antiferromagnetic-superconducting transition there. We believe that the orbital occupancy of the superconductor is different from the antiferromagnet, and is closer to that in the trianions of phenacenes.

2. *Superconductivity in 1/4-filled bands*: We have begun calculations of superconducting pair-pair correlations on 6×6 and 10×10 frustrated lattices using the PIRG method. Initial results are extremely promising: we find enhancement of the long-range superconducting pair-pair correlations for $d_{x^2-y^2}$ pairing over the non-interacting (U=0) system. This enhancement is large *only* at 1/4 filling. Should the current results - enhanced long range superconducting pair-pair correlations only at or near 1/4-filling - continue to prevail they will constitute a remarkable step forward in the search for a correct theory of correlated-electron superconductivity.

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SPIN DRIVEN PHENOMENA IN HIGHLY CORRELATED MATERIALS

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Post Doctoral Fellow: T. Tzen Ong

Project Scope

My current research covers three separate areas.

1) Topological Kondo Insulators (TKI's), particularly SmB_6.
2) Iron Based Superconductivity.
3) Frustrated Magnetism, and emergent Kosterlitz Thouless phases in 2D Heisenberg Antiferromagnets.

Here, I will focus on our most recent work on iron based superconductors which suggests a possible non-trivial orbital entanglement in the superconductor, reminiscent of He-3B.

Orbital Triplet Entanglement in Iron Based Superconductivity

A key question in high temperature iron-based superconductivity is the mechanism by which the paired electrons minimize their strong mutual Coulomb repulsion. While electronically paired superconductors generally avoid the Coulomb interaction through the formation of nodal, higher angular momentum pairs, iron based superconductors appear to form singlet s-wave ($s^{\pm}$) pairs. We have been exploring the role of orbital physics in the pair condensate of the iron-based superconductors. Current theories of these materials assume the pairing is orbitally diagonal. We have shown that there is a much larger class of possibilities and have proposed that the $s^{\pm}$ pairing state should be considered as a d-wave orbital triplet or "tao" (triplet and orbital) state[1]. One of the interesting aspects of this idea, is that it allows us to understand how these materials can undergo abrupt phase transitions from fully gapped to nodal superconductivity[2,3].

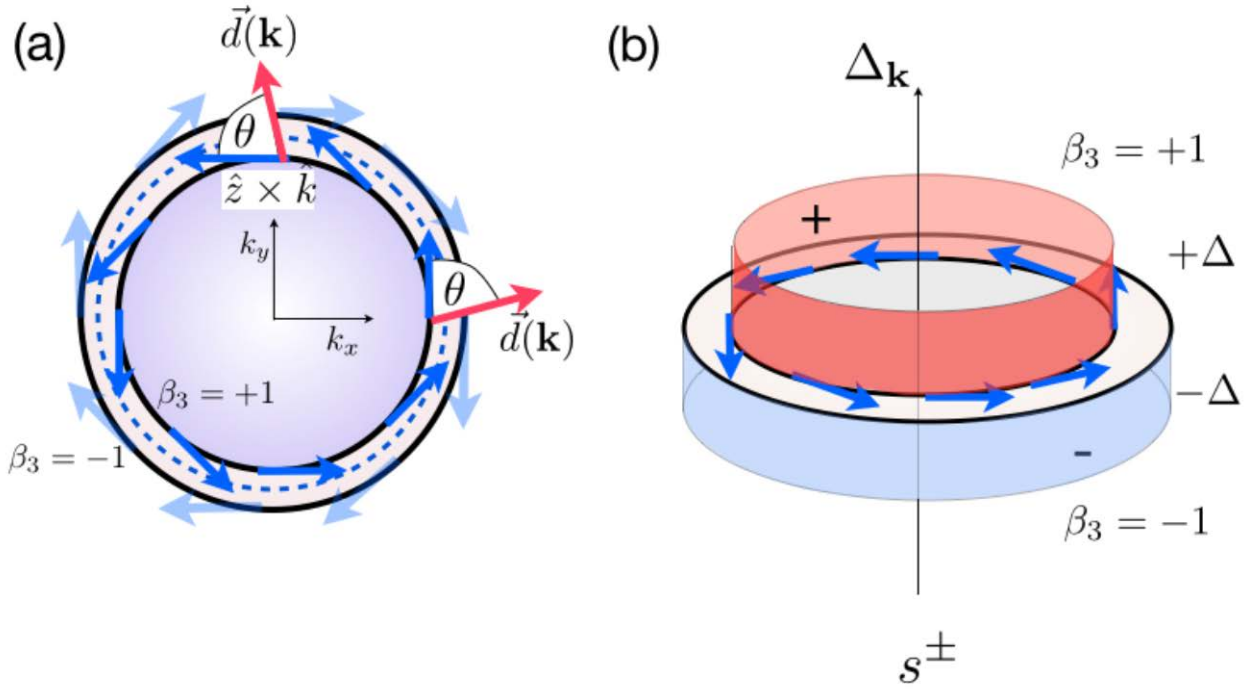

FIG. 1. (a) Pedagogical example illustrating the idea of orbital triplet pairing, considering the effect of Rashba coupling on the superfluid ground-state of He-3B.With Rashba coupling, the 2D Fermi surface issplit into two with opposing helicities $\beta_3 = \pm 1$. The relative orientation of the helicity vector $\hat{z} \times \hat{k}$ and the triplet pairing d(k) vector is θ. (b) In the superfluid He-R condensate, the gap is maximized when the helicity and d(k) vectors align (θ = 0), developing an $s^{\pm}$ gap function with opposite signs on the two Fermi surfaces.

As a pedagogical example of this phenomenon, we have also studied a simplified model of 2D He-3 coupled to a strong spin-orbit Rashba term[2]. This model shows that with spin orbit coupling, the L=1 S=1 spin triplet state can become a low spin L+S=0 splus-minus or a high spin L+S=2 d-wave state, and can undergo a sudden first order transition between the two. Extending this phenomenon to the iron-based superconductors, we have shown that the chirality of the underlying d-bands in the iron based superconductors plays the role of an orbital Rashba term, mixing the orbital angular momentum f the pairs with the internal atomic orbitals. The atomic orbitals can be regarded as S=2 spins, coupled to the L=2 motion of the Cooper pairs. This allows the possibility of a low spin splus-minus J = 2-2=0 state and a high-spin J= 2+2=4 state. With this simple picture, we are able to account for the unusual properties of KFe_2Se_2, which undergoes a transition

from a high spin nodal superconducting state at low pressures to a low spin fully gapped state at high pressure.

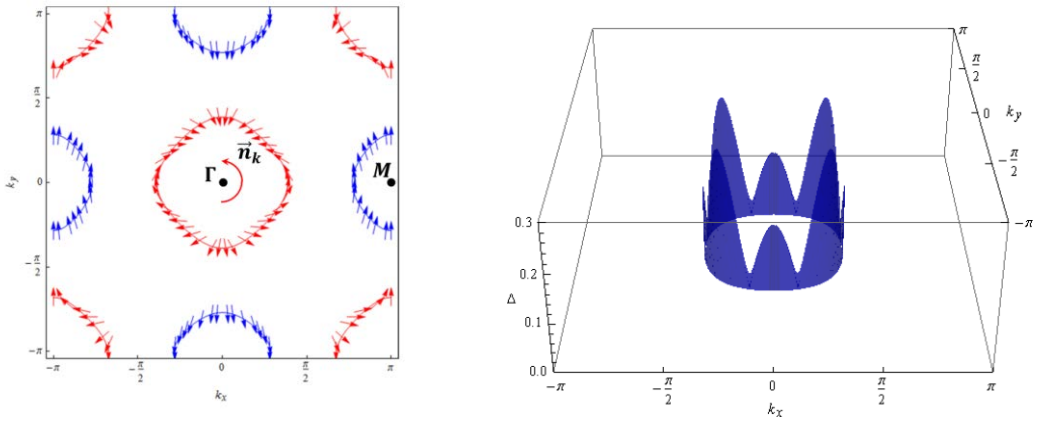

Figure 2: (a) Simplified Fermi surface model for the iron-based superconductors in an extended zone scheme, showing the orbital Rashba vector, n_k. The orbital Rashba vector winds twice in an anti- clockwise direction as one proceeds anticlockwise around the Γ point. Electron pockets (blue) have a positive helicity. (b) Octahedral structure of superconducting gap on the hole pocket around Γ, when n_k and d_k have opposite helicities.

By taking the orbital degrees of freedom of the iron atoms into account, we argue that the $s^{\pm}$ state in these materials possesses internal d-wave structure, in which a relative d-wave (L = 2) motion of the pairs entangles with the (I = 2) internal angular momenta of the d-orbitals to form an "s-wave" or "low spin" J = L + I = 0 singlet. This theory provides a simple explanation of the observation of a nodal gap with octahedral structure in KFe_2As_2[3,4] as a high spin (J = L + I = 4) configuration of the orbital and isospin angular momenta; the observed pressure-induced phase transition into a fully gapped state[2] can then interpreted as a high-to-low spin phase transition of the Cooper pairs (S-L = 2-2 = 0)[5] (Fig. 2). This theory predicts the presence of topologically protected edge states between epitaxially grown interfaces of "high spin" and "low spin" paired states (Fig. 3).

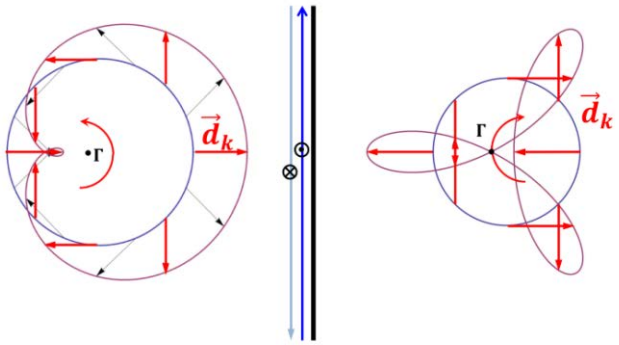

Fig. 3. Helical gapless Andreev edge states are predicted to develop at a domain wall between a low-spin and high-spin orbital triplet superconductor, with opposite chirality.

Future Directions

The recent discovery of a Majorana-like zero bias peak [6] that does not split in a field excites us greatly and makes us suspect there is an underlying topological character to the iron based superconductors. We shall be exploring this possibility in detail as part of our future work.

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2. **^{3}He-R: A Topological $s^{\pm}$ Superfluid with Triplet Pairing**, T.Tzen Ong, Piers Coleman arXiv:1402.7372 submitted to Phys. Rev. B.

3. **On the internal** d**-wave structure of $s^{\pm}$ pairs in Iron-based Superconductors**, T. Tzen Ong [1], P. Coleman and J. Schmalian, submitted for publication.

4. **Octet Line Node Structure of Superconducting Order Parameter in KFe_2As_2.** Okazaki,K.et al. Science 337, 1314–1317 (2012).

5. **Sudden reversal in the pressure dependence of T_c in the iron-based superconductor KFe_2As_2**, Tafti, F. F. et al., NATURE PHYSICS 9, 349–352 (2013).

6. **Observation of a Robust Zero-energy Bound State in Iron-based Superconductor Fe(Te,Se)**, J. X. Yin et al, arXiv 1403.1027.

First Principles Predictions of Phase Stability in Complex Oxides

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Project Scope

The goal of this project is to use first principles methods to predict materials with enhanced properties that can be synthesized and remain active under device relevant conditions. This project aims to develop and implement robust, high-throughput computational approaches for exploring phase stability. The ultimate goal is to facilitate the prediction-to-synthesis process through a synergistic effort involving (i) electronic structure calculations for properties predictions, (ii) phenomenological/empirical models for examining phase stability and (iii) experimental validation. The abundance of possible cation chemical identities and arrangements makes complex oxides (such as perovskites) an ideal playground for first principles studies. This variability gives rise to an array of physical, chemical, electrical and magnetic properties as well as possible competing structures. In this vein, this project is focused on the identification of solid solutions of complex oxides with enhanced physical and chemical properties. Initial efforts have emphasized ferroelectric/piezoelectric oxides and oxide interfaces and surfaces. It is anticipated that the framework implemented in this project will be applicable to a wide range of materials; thus having a broader impact for accelerating the design and experimental realization of novel materials.

Recent Progress

Ferroelectrics and Piezoelectrics

Piezoelectrics have numerous applications, including use as actuators in fuel injector technology which enable clean burning and efficient diesel engines. Improvements in the responses of these materials may afford even more advances. For example, in the past decade, due to the discovery of new piezoelectric ceramics, we have seen ultrasound images progress from the traditional 2D images to 3D images. Studies have demonstrated that solid solutions (or alloys) of complex, perovskite ferroelectrics have tremendous promise for the discovery of piezoelectrics. Depending on the ferroelectric properties of the component perovskites, an extremely high-response region which is dependent upon temperature, pressure, composition and/or strain, can emerge. This is the underlying principle behind the favorable electro-mechanical properties of the ABO_3 $Pb(Zr_{1/2}Ti_{12})O_3$ (PZT). Challenges to the first-principles modeling and discovery of new high performance, lead-free ferroelectrics/piezoelectrics therefore include the ability to simulate disorder in relatively small unit cells and to find morphotropic phase boundaries; i.e. regions of phase space between different phases which facilitate the transformation between these phases. Our research focuses on the development of methods to mimic disorder in relatively small unit cells as well as examining the electromechanical response in oxide structures with phase inhomogeneities.

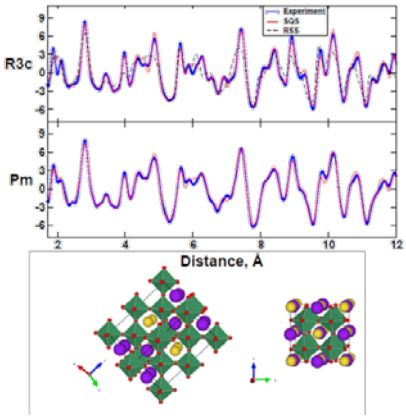

Figure 1 Comparison of the experimentally determined reduced PDF and the theoretical PDF. The top frame shows results for the rhombohedral phase and the middle frame depicts the monoclinic phase. The bottom panel shows a comparison of the SQS structure versus a standard rock-salt ordered structure.

To mimic disorder in relatively ordered supercells we employ the special quasirandom structure (SQS) method. In the SQS approach, a supercell is designed by selectively populating a site (in the case of a perovskite either the *A* or *B* cation site) such that the short-ranged, geometric correlations approximate that of the random alloy. It should be noted that, although this approach has been extensively applied to the study of metals and semiconductors has only received minimal attention by the oxide community. Using the SQS method we have explored the high temperature *Pm* and low temperature *R3c* phases of the $(K_{1/2}Na_{1/2})NbO_3$ (KNN) solid solution; a promising candidate for a lead free piezoelectric. Our results indicate that the SQS approach is capable of accurately capturing the local structure patterns derived from the random distribution of K and Na on the perovskite *A*-site (**Figure 1**). Furthermore, these results allow for insights into the local structure interactions that give rise to the macroscopic phases in this material. These results highlight the effectiveness of a SQS for predicting the structures and properties of oxide solid solutions directly from first principles calculations using relatively small supercells. Such an approach has clear consequences for the first principles discovery of novel materials with properties such as ferroelectricity, piezoelectricity, ferromagnetism and thermoelectricity.

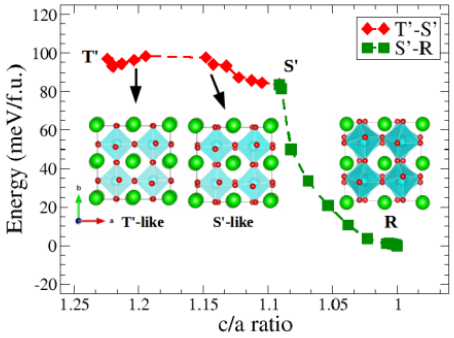

Figure 2 Computed potential energy landscape for the transition between the T', S' and R phases.

The search for composition-dependent morphotropic phase boundaries has been fundamental to the discovery of new materials with high electromechanical responses. Recently, it has been observed that a morphotropic phase boundary could be induced through strain in $BiFeO_3$ (BFO) thin films grown on $LaAlO_3$. Interestingly enough it has been found that these films are not structurally uniform and the interplay between the two phases (a pseudo-tetragonal T' phase and a second triclinic phase, refered to as S') results in a large electromechanical response. Through a joint theoretical and experimental effort, we characterize these distinct phases (specifically the S' phase). We find that the structure and polarization of ths S' phase are intermediate to the *R3c* rhombohedral (R) groundstate phase and the pseudotetragonal T' phase. Using first-principles calculations we find that although the S' phase, is energetically very close to the T' phase it exhibits similar FeO_6 octahedral rotations as the R phase. By mapping out the energy landscape that characterizes the phase transitions between the T', S' and R phases (**Figure 2**) we are able to understand the co-existence of the T' and S' phases observed in experiment while gaining insights into the large electromechanical response found in this co-existing phase material. This knowledge offers new routes to strain engineering electromechanical responses in oxide thin films.

Oxide Surfaces and Interfaces

It has been demonstrated that a two-dimensional electron gas (2DEG) could be created either through interfacial electronic reconstruction in an oxide heterostructure or the introduction of oxygen vacancies at an oxide surface. These 2DEGs have been shown to be hosts to a variety of electronic phenomena, including superconductivity, magnetism, and Rashba spin-orbit coupling. Despite tremendous progress in understanding their origins, very little is known about how to control the conduction pathways and the distribution of charge carriers. Through a combined theory and experimental study we demonstrate that it is possible to manipulate the density and distribution of a 2DEG through the modulation of the $SrTiO_3$ spacer layers in La δ-doped $SrTiO_3$ superlattices; transitioning

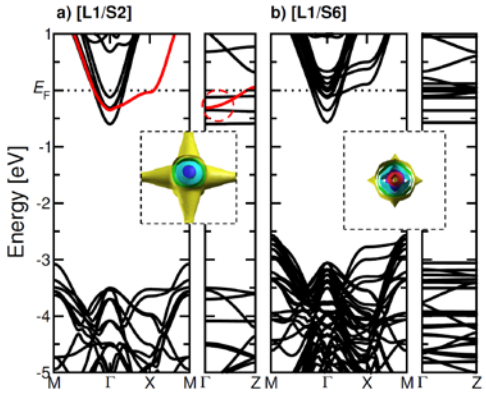

Figure 3 Electronic band structure for the La δ-doped 1 $LaTiO_3$/2 $SrTiO_3$ and 1 $LaTiO_3$/6 $SrTiO_3$ superlattices emphasizing the respective 3D and 2D Fermi surfaces.

from 2D to 3D conductivity as the spacer layer thickness decreases. From first principles calculations, we predict that the three-dimensional conduction arises due to an appreciable overlap of quantum mechanical wavefunctions between neighboring δ-doped layers. Furthermore, these superlattices remain transparent at all STO spacer layer thicknesses. As such, these results highlight the potential for using oxide heterostructures in optoelectronic devices by providing a unique route for creating novel transparent conducting oxides.

While initial studies of 2DEGs focused on the (001) superlattice interface, more recent efforts have sought to explore the emergence of 2DEGs at (111) and (110) interfaces. In these cases, even SrTiO3 has alternating charged planes, which may lead to a divergent potential at the surface. This results in the transfer of charge to the surface to compensate for this potential (the so-called polar catastrophe); even in the absence of $LaAlO_3$ overlayers. Using density functional theory, we investigate the surface electronic structure of $SrTiO_3$ (111) slabs. We find that for stoichiometric slabs, the surface carrier density (2DEG) displays a strong thickness dependence due to the competition between the electronic reconstruction and polar distortions (this is similar to the thickness dependence of the $LaAlO_3$ overlayers). Our results thus emphasize the importance of both electronic reconstruction and polar distortions when analyzing the 2DEG behavior of (111) and (110) interfaces.

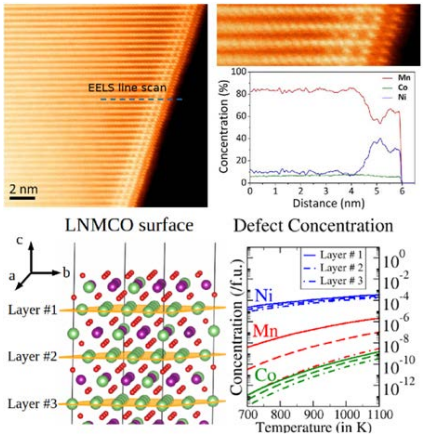

Figure 4 (Top) Z-contrast STEM images and EELS spectra highlighting the presence of antisite defects and segregation of defects to the surface. (Bottom) Model of LMNCO surface and predicted defect concentration as a function of layer from the surface.

High-voltage lithium-manganese-rich oxide cathodes have almost twice the energy density of standard cathode materials like lithium cobalt oxide. Defects and surface reconstructions have been observed in these stoichiometric compositions even in their pristine state. This preexisting disorder is thought to play a role in driving the structural transitions responsible for voltage fade during electrochemical cycling. Using a synergistic combination of atomic scale experiments and theoretical calculations, our results indicate that, due to low interlayer migration barriers and favorable defect formation energies, Ni antisite defect pairs are the most prevalent defects observed in imaging studies of surfaces and nanoparticles of pristine (uncycled) Lithium-Manganese rich composite cathode materials. This suggests that the stabilization of Ni^{2+} cations in the transition metal layers may be useful for minimizing surface segregation; thereby providing a possible remedy for long standing issues such as capacity fading and voltage instabilities.

Future Plans

In the upcoming year, we plan to continue our efforts towards understanding the prediction-to-synthesis cycle. Focus will remain on (i) the discovery of high performance piezoelectrics, (ii) exploring the physics at oxide interfaces and (iii) tailoring the properties of oxide composite materials. In this regard, the second specific aim of this research project will be emphasized: the development and application of phenomenological/empirical models for examining phase stability. Specific areas of research will include extending the SQS method to explore more complex compounds; e.g. materials with disorder on both the *A*- and *B*-site. Knowledge gained from density functional theory calculations will be used to parameterize phenomenological models to explore the temperature and pressure dependent phase transitions in these materials. Further studies will seek to use these models to further understand the origin of the electromechanical response in structurally inhomogenous materials, like $BiFeO_3$ under strain. A large part of the upcoming effort will therefore be centered on the development of the framework for the exploration

of the possible chemical space using density functional theory and the aforementioned phenomenological models.

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N. Sivadas, H. Dixit, V. R. Cooper and D. Xiao “Thickness dependent carrier density at the surface of $SrTiO_3$ (111) slabs” *Phy. Rev. B* **89**, 075303 (2014)

B. K. Voas, T.-M. Usher, X. Liu, J. L. Jones, X. Tan, V. R. Cooper and S. P. Beckman “Special quasirandom structures to study the $(K_{0.5}Na_{0.5})NbO_3$ random alloy” (accepted; *Phys. Rev. B*)

V. R. Cooper, S. S. A. Seo, S. Lee, J. S. Kim, S. Okamoto and H. N. Lee “Transparent conducting oxides: A δ-doped superlattice approach” (under review; *Sci. Rep.*)

H. Dixit, W. Zhou, J.-C. Idrobo, J. Nanda and V. R. Cooper “Unraveling the nature of disorder in the pristine high voltage Lithium-Manganese-rich composite cathode” (under review; *Phys. Rev. Lett.*)

H. Dixit, C. Beekman, W. Siemons, M. Chi, H. M. Christen and V. R. Cooper “Characterization of distinct co-existing polymorhs observed in strained $BiFeO_3$ thin films” (in preparation)

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 specific materials that are investigated include iron- and copper-based high temperature superconductors, cobaltites, molecule-based magnets, multiferroics, manganites, 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; (2) the study of competing interactions in frustrated magnets and associated multiferroic tendencies; (3) the study of the iron-based superconductors via spin fermion models and Monte Carlo simulations, with focus on the nematic state. 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. Below, our recent progress is illustrated via three specific publications.

RECENT PROGRESS

(1) Nematic State of Pnictides Stabilized by Interplay between Spin, Orbital, and Lattice Degrees of Freedom [S. Liang, A. Moreo, and E. Dagotto, Phys. Rev. Lett. **111**, 047004 (2013)]. The discovery of high temperature superconductivity in the iron-based pnictides and selenides has provided a novel playground where several simultaneously active degrees of freedom (DOF) determine the complex properties of these materials. The purpose of this paper was to revisit the influence of the lattice DOF in the pnictides via its introduction into the spin-fermion model for these materials, studied via Monte Carlo (MC) simulations. This is the first time that all these ingredients are simultaneously analyzed, and the complexity of the problem requires a computational framework. Our numerical approach allows us to study temperatures above the magnetic order but below the structural transition, i.e. the nematic regime, as well as higher temperatures where all DOF develop short-range fluctuations, a range difficult to reach by standard mean-field procedures. Our main result is that a complete description of the phenomenology of the undoped Fe-based superconductors requires

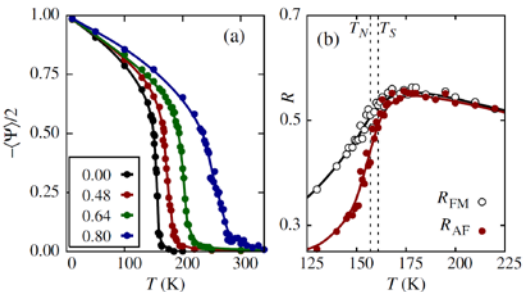

Fig. 1: (a) Spin-nematic order parameter vs temperatures at the e-ph couplings shown. (b) MC resistance along the AFM and FM directions varying T. For details, the reader should consult the original reference.

the simultaneous presence of both the spin- and orbital-lattice couplings, suggesting a degree of complexity in these materials that was not previously anticipated.

(2) Spin state and spectroscopic modes of multiferroic BiFeO3. [R. Fishman *et al.*, Phys. Rev. B **87**, 134416 (2013)]. As the only known room-temperature multiferroic, BiFeO3 continues to attract considerable attention. Multiferroic materials offer the tantalizing prospect of controlling magnetic properties with electric fields or electric polarizations with magnetic fields. Although the ferroelectric transition temperature Tc ≈ 1100 K of BiFeO3 is far higher than its Neel temperature TN ≈ 640 K, the electric polarization P is enhanced by its coupling to a long wavelength cycloid state below TN. Before BiFeO3 can be used in technological applications, however, it is essential to understand the microscopic mechanisms and interactions responsible for its magnetic behavior. Based on a model that includes two types of Dzyaloshinskii-Moriya interactions as well as easy axis anisotropy, we have evaluated the spin state and spectroscopic modes of BiFeO3. The figure shows an example of the good agreement between theory and experiments that we have reached.

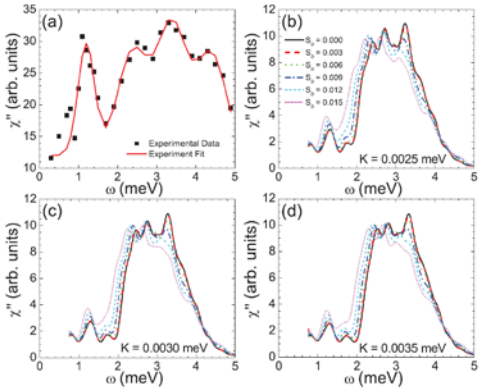

Fig. 2: The measured inelastic neutron scattering spectrum and the predicted spectrum. The reader should consult the original reference for more details.

(3) Correlation effects in (111) bilayers of perovskite transition-metal oxides. [S. Okamoto *et al.*, Phys. Rev. B **89**, 195121 (2014)]. Topological insulators (TIs) are novel quantum states of matter characterized by a nontrivial band topology induced by the spin-orbit coupling (SOC). In addition, bilayers of perovskite transition-metal oxides (TMOs) ABO3 grown along the (111) crystallographic axis, i.e., (111) bilayers, were recently proposed as possible candidates for two-dimensional TIs. In such (111) bilayers, a buckled honeycomb lattice is formed by B-site transition-metal ions (see figure). In this publication, we provide concrete examples of the interplay between SOC and orbital degrees of freedom. In particular, SrIrO3 (SIO) and LaAuO3 (LAO) are investigated by means of the dynamical-mean-field theory. It is shown that the LAO bilayer is far from the Mott insulating regime, and a TI state is robust. However, the correlation effect is significant for the SIO bilayer, and an AFM standard insulating state is realized. The interplay between the SOC and correlations shows a strong material dependence.

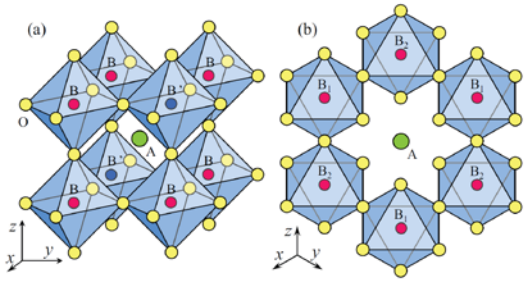

Fig. 3: Buckled honeycomb lattice formed in (111) bilayer of perovskite TMO ABO3. (a) (111) bilayer of ABO3 sandwiched by insulating AB'O3. (b) ABO3 forms buckled honeycomb lattice with two sublattices B1 and B2.

FUTURE PLANS

(1) We plan to continue the study of iron superconductors via the spin fermion model and Monte Carlo simulations, extending our previous work in the undoped case to the finite doping regime.
(2) We plan to continue our interaction with ORNL neutron scattering experimentalists to address the magnetic properties of many interesting multiferroic materials.

(3) We plan to continue our search for exotic states in oxide heterostructures, including the presence of spin orbit coupling.

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New Formalism and Method of Calculating Vibrational Mode Lifetimes

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PROGRAM SCOPE

We are implementing a practical formalism for calculating vibrational mode lifetimes in complex materials based on first-principles electronic structure calculations. The first stage of the project includes analytic studies of simple systems as well as implementation for semi-empirical potentials and application to corresponding materials. The second stage of the project focuses on implementation with first-principles electronic structure codes.

This proposal is aimed at a significant advancement in the calculation of lifetimes of vibrational modes. The approach is to implement a recently developed scheme for calculating mode lifetimes. (See Dickel & Daw, *Comp Mat Sci*, v47 p698 and v49 p445, 2010). The formalism is based on ensemble-averaged moments of the Liouvillian. The result is an expression for the lifetime of a normal mode that is obtained directly from Monte Carlo averages of products involving displacements and forces. This technique represents a substantial improvement over existing techniques.

The first milestone was the testing on simple, low-dimensional models of anharmonic behavior. Second, was the testing on three-dimensional lattice models of non-linear vibrations. Third, we extended the Sandia LAMMPS atomistic simulation package to carry out the calculations for all of the semi-empirical potentials available in that package. Tests with that package have been conducted on several cases, including disorder in generic (that is, Lennard-Jones) FCC binary alloys, and Si/C/Ge-based clathrates (using Tersoff potentials).

RECENT PROGRESS

Simple models

In developing the formalism and in building up our understanding, we have relied on analysis of simple models of increasing robustness: (i) one dimensional oscillator with fourth-order anharmonicity; (ii) two harmonic oscillators coupled by a fourth-order interaction; (iii) two anharmonic oscillators coupled by a third-order interaction; (iv) 1D chain of nearest-neighbor, anharmonically coupled masses; (v) 3D SC lattice of nearest-neighbor, anharmonically coupled masses; (vi) FCC lattice of masses interacting with Lennard-Jones potential (cutoff beyond fourth nearest neighbors). As a result of this methodical consideration of simple models, we have determined the conditions under which the basic premise of this proposal can be realized: namely, that the *mode-resolved* density of states (DOS) is dominated by a single, moderately broadened peak. Under that condition, which is quite broadly realized, we can use the lowest two moments of the Liouvillian to obtain a reliable estimate of the mode lifetimes of the system.

It is now possible to obtain the mode lifetimes from moments of the Liouvillian. For the mode indexed k, with amplitude u_k and associated acceleration a_k, the second moment is $\mu_{2,k} = -\langle u_k a_k \rangle / \langle (u_k)^2 \rangle$, which can be identified as the square of the quasi-harmonic frequency (ω_k) for that mode. The fourth moment $\mu_{4,k} = -\langle (a_k)^2 \rangle / \langle (u_k)^2 \rangle$, combined with the second moment, gives a good approximation to the lifetime τ_k of the normal mode. In the usual case of a system with third-order anharmonic couplings,

$$\tau_k = \frac{c}{\omega_k(\gamma_{4,k} - 1)}$$

where c (of order 3-4) is a constant determined in the analysis above, and $\gamma_4 = \mu_4 / (\mu_2)^2$. The combination $(\gamma_4 - 1)$ is a measure of the anharmonicity of the mode beyond what can be taken to be quasi-harmonic. This relation for the lifetime is born out in our testing over all of the modes and over a wide range of temperatures for the systems listed above.

Jazz for LAMMPS

To facilitate the moments calculation for a variety of empirical potentials, we have built a python wrapper for LAMMPS (a massively parallel, classical molecular dynamics program, freely distributed by Sandia National Labs). The wrapper (called Jazz) performs the ensemble averages (via Metropolis Monte Carlo) of the moments of the normal modes for any system that can be treated in LAMMPS. No assumption is made with regards to the structure of the empirical potential; in that sense, Jazz treats LAMMPS as a black box. This makes immediately available a wide range of applications based on the extensive set of empirical potentials implemented in LAMMPS. We plan to release this Fall the Jazz package through the LAMMPS distribution for use by the general community.

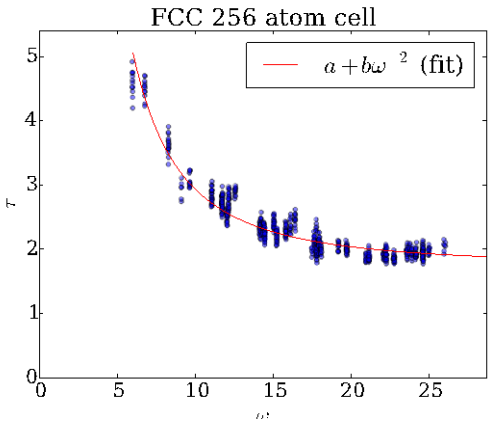

Figure 1: Lifetime-frequency relation for normal modes of an FCC cell with 256 atoms (with Lennard-Jones interactions). The expected inverse square relation holds, but with an additional minimum lifetime that is attributed to the finite cell size.

As a first example of application of Jazz, we have studied the normal modes of an FCC crystal interacting with Lennard-Jones potential. The LJ potential is well-studied and so we will be able to make comparison to many calculations available in the literature. One result of the present studies shows an expected aspect of the lifetime of the normal modes. For a 256 atom cell, we show in Fig. 1 a scatterplot of the lifetimes (τ) vs. quasiharmonic frequency (ω) at a moderately low temperature. The relation between τ and ω corresponds to the expected ω^{-2} dependence, except for the present calculations there is an additional constant (a minimum lifetime) which is attributed to finite-cell effects.

In Fig. 2, we also show the distribution $n(Q)$ of oscillator quality factors $Q = \omega\tau$ of the normal modes. An understanding of the distribution of quality factors among the normal modes can aid in an understanding of aggregate properties such as lattice thermal conductivity: the LTC is a combination of both harmonic aspects (through the group velocities) and anharmonic aspects (through the lifetimes or quality factors).

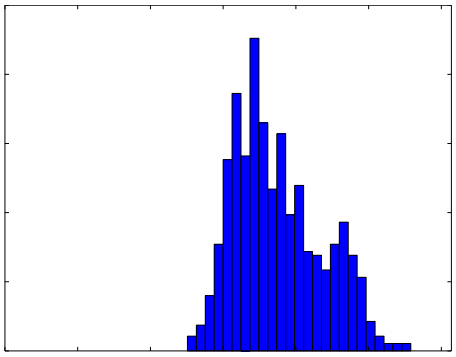

Figure 2: Distribution of quality factors in a perfect cell of 256 atoms (Lennard-Jones interactions).

Disorder and mode lifetimes

Disorder involving mass differences or bond strength differences has been studied analytically in the literature using perturbation treatment of harmonic systems (see, for example, Klemens). It is well known that such disorder in a lattice alters the harmonic properties, such as frequency and group velocities of the normal modes. However, we can find no comparable work identifying the possible effect of disorder on the *anharmonicity* of the normal modes. We have begun such a generic study, by constructing binary LJ alloys with differences in mass, bond length, and bond strength (the three parameters available in the LJ potential). For example, we constructed a binary alloy involving uniform masses and bond strengths but with different bond lengths, mimicking as it were an alloy of elements differing *only in* size. Two cells were generated --- one with perfect ordering among the two types, and the other disordered. We find the expected alteration of the normal DOS (and consequently in group velocities). However, we also find something not considered in previous treatments, that the strain caused by bond-length disorder can also cause a significant alteration of the *anharmonicity* of the normal modes, as seen in Fig. 3. In fact, in this case, the distribution of Q-factors shows that bond length disorder actually *increases* the average oscillator quality.

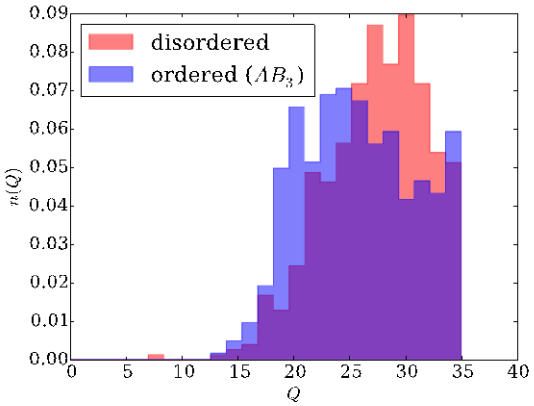

Figure 3: Effect of disorder of bond length (magnitude 10%) on the quality factors of normal modes in a binary alloy. Disorder actually *increases* the average oscillator quality.

Nanowires

We have begun a study of the lifetimes of normal modes in nanowires (at this stage, using LJ). We find (see Fig. 4) that for very thin nanowires, the lifetime follows an inverse-square-root dependence on the mode frequency, in contrast to the inverse-square dependence in bulk. We also observe several modes with significantly shorter lifetimes. In particular, the *radial breathing mode* of the nanowire is observed to have very much shorter lifetime, as a direct result of its ready anharmonic coupling to a large number

of the other modes in the wire. The effect of this mode on the LTC of the nanowire is anticipated to be significant, but that work has yet to be completed.

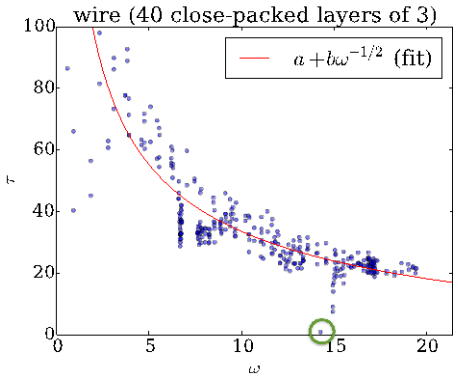

Figure 4: Mode lifetime vs. frequency for a thin nanowire constructed of Lennard-Jonesium. An inverse square root relation holds for most modes, except some particular modes with anomalously short lifetimes (radial breathing mode is indicated by the circle).

FUTURE PLANS

Our next goals will be to learn about anharmonic effects in systems for which semi-empirical potentials exist, and from that experience to implement the method in an existing first-principles electronic structure code.

- Complete study of effect of disorder on anharmonicity
- Publish Jazz for LAMMPS (in journal and on LAMMPS website)
- Incorporate calculation of group velocities, along with lifetimes, into Peierls expression for lattice thermal conductivity tensor
- Study anharmonicity of normal modes in nanostructures (beginning with nanowires) [initially based on Lennard-Jones]
- Study anharmonicity in diamond and clathrates (Tersoff potential)
- Collaboration with John Purton (Daresbury) on incorporating method into DL-Monte (similar to LAMMPS, but with significantly improved MC efficiency for local potentials)
- Collaboration with Alan Wright (Sandia) on incorporating method into Socorro (first-principles electronic code)

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Competing Orders in Correlated Materials: Impact of Disorder and Non-Equilibrium Perturbations

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Program Scope

The goal of this new program is to explore, understand, and ultimately control the competing electronic ordered states ubiquitously present in correlated materials, with particular emphasis in unconventional superconductors, such as iron-based and copper-based materials. While on the one hand the competition with different types of magnetic, orbital, and charge order limits the transition temperatures of these unconventional superconductors, on the other hand the enlarged ground-state degeneracy associated with these multiple many-body instabilities can give rise to unusual inhomogeneous correlated normal states, such as electronic smectic and nematic phases. To achieve the aforementioned goals, the PI will employ a multi-faceted theoretical approach consisting of: (i) The investigation of relatively unexplored regimes with the potential to unveil novel behaviors – in particular, the PI will explore the behavior of competing phases taken out of equilibrium, determining under which conditions the transition temperatures of iron-based and copper-based materials can be enhanced by optical pulses. (ii) The embracement of realistic features of correlated materials in their microscopic descriptions – in particular, the PI will investigate the impact that disorder, in its various forms, has on emergent inhomogeneous states present in the phase diagrams of unconventional superconductors. (iii) The promotion of synergy with established and novel experimental probes (with particular emphasis on scanning tunneling microscopy and ultrafast spectroscopy) not only by using data as input of theoretical models, but also by providing concrete guidance for experiments.

Future Plans

For the upcoming first two years of the program, within the general scope presented above, the PI will focus on the following specific research projects:

- The role of disorder on the nematic properties of iron-based superconductors. Different types of disorder present in these materials will be considered, namely, impurity scattering introduced by vacancies and defects, random dilution promoted by chemical substitution or doping, and random strain fields introduced during the crystal growth process. The goal is to explore not only the stability of the nematic state, but also potentially new physics promoted by disorder, such as Griffiths phases, impurity-driven quantum criticality, smeared phase transitions, and enhanced fluctuations in the symmetry-unbroken state.
- The impact of non-equilibrium perturbations on the competition between unconventional superconductivity and density-wave states present in the phase diagram of iron-based and copper-based superconductors. In particular, the PI will study how changes in the quasi-particle spectrum promoted by different types of

optical pulses affect the competition and coexistence between these different phases, focusing on whether higher values of Tc can be achieved. The relaxation of intertwined order parameters taken out of equilibrium by ultrafast laser pulses will also be investigated.

- Direct extraction of the pair-breaking impurity potential from scanning tunneling microscopy data on conventional and unconventional superconductors, revisiting the issue of why many high-temperature superconductors seem much more robust against disorder than expected by current theories.

Previous Publications

The list below contains select publications by the PI from previously funded research that are relevant for the PI's new DOE-funded research program.

- "*What drives nematic order in iron-based superconductors?*" R. M. Fernandes, A. V. Chubukov, and J. Schmalian. Nature Phys. **10**, 97 (2014).

- "*Ultrafast observation of critical nematic fluctuations and giant magnetoelastic coupling in iron pnictides.*" A. Patz, T. Li, S. Ran, R. M. Fernandes, J. Schmalian, S. L. Bud'ko, P. C. Canfield, I. E. Perakis, and J. Wang. Nature Comm. **5**, 3229 (2014).

- "*How many quantum phase transitions exist inside the superconducting dome of the iron pnictides?*" R. M. Fernandes, S. Maiti, P. Wölfle, and A. V. Chubukov. Phys. Rev. Lett. **111**, 057001 (2013).

- "*Suppression of superconductivity by Neel-type magnetic fluctuations in the iron pnictides.*" R. M. Fernandes and A. J. Millis. Phys. Rev. Lett. **110**, 117004 (2013).

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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 how electrons and phonons interact when the electrons are driven by a large pulsed field. 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 also part of a CMCSN team on pump/probe spectroscopies (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

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. 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 appeared in Physical Review Letters.

In addition to the photoemission work, we also completed publications on Bloch oscillations and dielectric breakdown in the CDW system (published in Physical Review B), on the quantum excitation between bands (currently under review), and on the high harmonic generation of light at odd multiples of the Bloch frequency due to attosecond Bloch oscillations (currently under review).

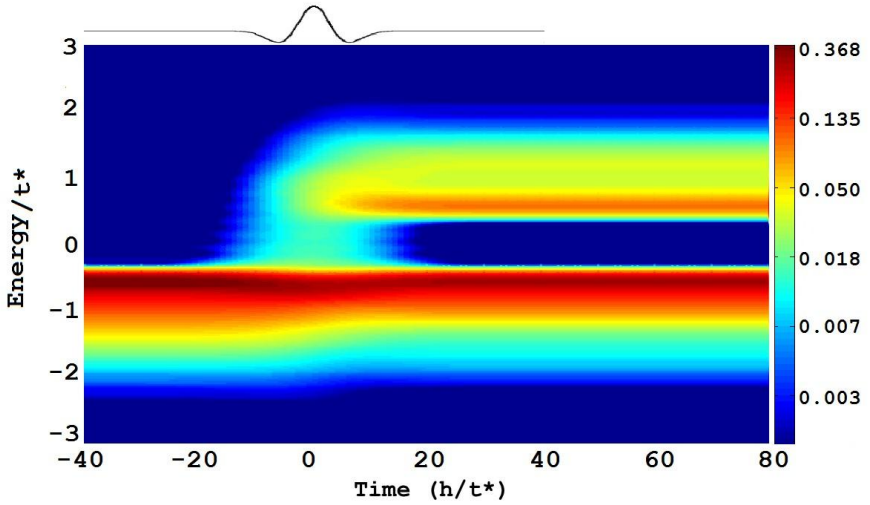

Figure 1: *False-color image of the transient closing of a charge-density-wave gap (light green and cyan for times between −15 and 30) when pumped by an electric field (shown schematically above the image). The gap closes and reforms while the order parameter (not shown) remains large. One time step 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.*

Thermalization of a Mott insulator

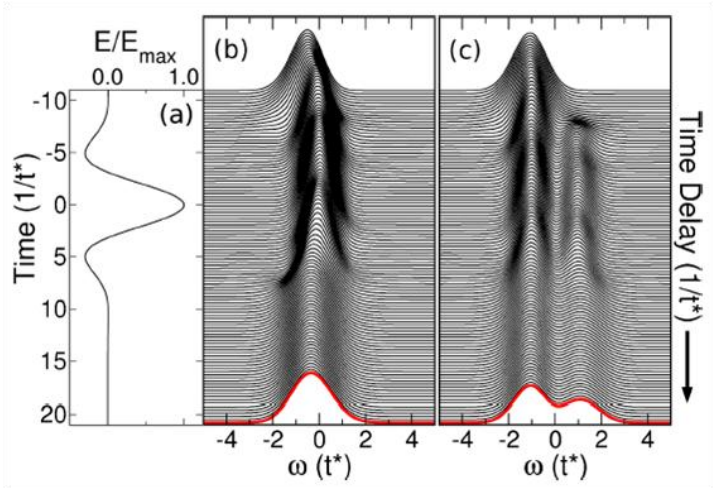

Figure 2: *Transient photoemission spectroscopy of a metal (left) and a Mott insulator (right) when pumped by a large ultrafast electric field. While the final plots appear to be thermal, a detailed analysis shows the metal is very nearly thermal, while the insulator is markedly nonthermal.*

One might expect metals and insulators to act differently when they are driven by large electric field pulses. In both cases, we expect the systems to absorb energy as the field generates current, but after the pulse dies off, the system may or may not thermalize at long times. Our work on the Falicov-Kimball model shows that the metal thermalizes rapidly after the pulse disappears, but the Mott insulator remains nonthermal for long times afterwards, and likely becomes stuck in a nonthermal distribution. This work appeared in Physical Review Letters.

Time-resolved Compton scattering

We have analyzed a new class of pump/probe experiments that directly measure the momentum distribution of the electrons as a function of the time delay after a large pump pulse has been applied. Such experiments can be conducted with X-rays via Compton scattering, or, for cases when a single isolated band lies at the Fermi energy, via an integration of angle-resolved photoemission spectra. We find that by studying the oscillations of the momentum distribution function for momenta near the Fermi surface, one can map out the electron dispersion for the unoccupied states that lie above the Fermi energy. This work was published in Physical Review B.

Time-resolved ARPES in electron-phonon coupled systems

We also examined the behavior of time and angle resolved photoemission from an electron-phonon system in the normal phase. The relaxation of excited electrons falls into two regimes. Electrons excited far above the Fermi energy relax quickly as they emit phonons that carry away their excess energy. But electrons within the Debye energy of the Fermi surface relax more slowly and show long-lived oscillations, just as seen in experiments. When the pump pulse is weak, the relaxation towards equilibrium is governed by the equilibrium self-energy relaxation times, and a full analysis of the spectra allows one to reconstruct the self-energy and in turn, the electron-boson coupling. This technique provides an alternative method for extracting information on electron-boson couplings from other techniques such as analyzing line-widths in conventional ARPES sepctra. This work was published in Physical Review X.

When the pump pulse becomes stronger, the nonequilibrium nature of the electron distribution modifies the electronic self-energy in a fashion that is consistent with nonequilibrium sum rules for the Green's functions and the self-energy. Namely, the total spectral weight is conserved in the imaginary part of the local self-energy, but it is redistributed, with weight moving from high energies to low energies. In this regime, one can examine the transient relaxation of nonequilibrium reconstructions of the density of states and of the self-energy via a similar analysis of the time-resolved ARPES data. This work has been submitted to Physical Review Letters, and the sum rules work has been subnmitted as a conference proceeding.

X-ray photoemission spectroscopy and X-ray absorption spectroscopy

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 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. We are currently working on the nonequilibrium case which can eventually have applications to a wide range of new probes including time-resolved X-ray dichroism studies for magnetic systems.

Future work for 2014-2015

The main work planned for the next year is to examine time-resolved pump-probe experiments in ordered phases, starting with simplified charge density wave systems and with electron-phonon mediated superconductors. We will examine TR-ARPES along with other related experiments of interest. At the same time, we will extend our sum-rule work to higher order in the moments and to include the possibility for superconducting or CDW order.

We also plan to spend some time applying these techniques to more real materials systems like graphene and transition metal dichalchogenides.

Publications supported by DOE 2013-2014

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THEORY OF FLUCTUATIONS IN SUPERCONDUCTORS

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1. Project Scope

The scope of this research project is to develop a general theory of fluctuations in superconductors and apply its results and methods to a broad variety of distinct strongly-correlated electron systems. The main underlying idea of this research is that while the classical theory of symmetry broken phases relies on the assumption that an order parameter is a classical field with no internal dynamics, this picture is incomplete and there are important corrections to it, associated with fluctuations relative to this classical mean-field. The observable manifestations of these fluctuation physics are manifold and this DOE project aims at studying both fundamental aspects and potentially useful features of these fluctuation phenomena. Of particular current interest in this project is a new class of material – topological Kondo insulator – that has been predicted theoretically by the PI and collaborators and recently discovered experimentally in Samarium hexaboride by a number of experimental groups. One of the key general goals of PI's research here is to explore the role of strong interactions in this class of material and identify effects qualitatively different from more conventional weakly-correlated topological compounds (e.g., possible phase transitions in the topological surface states of SmB6). At the technical level, this research involves an analysis of Kondo fluctuations in the Kondo insulator phase. Another example of recent work involves studies of the Casimir effect – a force acting between macroscopic bodies mediated by quantum fluctuations of the electromagnetic field between them – with an eye on singular contributions to Casimir that may occur across a phase transition in one of the interacting plates due to strong fluctuations in the latter. An ambitious goal here is to develop a theory of Casimir effect involving strongly-interacting condensed matter systems (including low-dimensional structures) that would enable its use a measurement tool to probe and characterize their electronic properties.

2. Recent Progress

2.1 Anderson insulator of bosons: application to the problem of superconductor-to-insulator transition in thin films

In a recent Letter **[1]**, we presented a theoretical solution (involving both analytical and numerical methods) to the difficult problem of magneto-resistance in the Anderson-insulating phase of bosons. A motivation for this work came from a variety of experiments in disordered superconducting films (e.g., Indium oxide) that exhibit a magnetic-field-tuned superconductor-to-insulator transition and a giant magneto-resistance peak. The nature of this peak currently remains a mystery, but it is widely believed that transport in this regime involves electronic pairs "left over" from the superconducting phase that occurs in lower fields. In other words, it is likely that superconductivity may disappear before the electronic pairs do, and they instead get

localized by disorder in an insulating state. One of the key results of our work is *that the effect of the magnetic field on the resistance in a bosonic Anderson insulator is opposite to that in a fermionic insulator*. This is fully consistent with the exotic scenario of the giant magneto-resistance peak, where an increase in resistance with magnetic field could be explained with the primarily bosonic nature of charged excitations, while a drop in resistance on the high-field side is consistent with fermionic, single-electron carriers. Furthermore, our theory derives (by mapping the problem on the seemingly-unrelated problem of directed polymers in a random potential) a non-trivial scaling behavior of the resistance as a function of temperature and the magnetic field, thereby providing a verifiable prediction to be probed in experiment.

2.2 Strong correlations and fluctuations in topological Kondo insulators

Topological Kondo insulators are qualitatively different from the conventional Bismuth-based topological materials in that the former are intrinsically strongly-correlated systems. However, no theory so far has adequately addressed the interaction effects beyond a mean-field description. In recent **Ref. [9]**, we put forward such a theoretical study and show that importantly the topological *surface states in SmB6 form an intrinsically strongly-interacting Dirac liquid*. These results also suggest that a magnetic instability may occur on the topological Kondo insulator's surface. This exotic scenario is consistent with the recent experimental work of the Paglione group (http://arxiv.org/abs/1312.6132) who observed a hysteresis in select SmB6 compounds.

One of the experimental puzzles in the recent studies of Samarium hexaboride – the first discovered topological Kondo insulator – is a very light "effective mass" inferred from quantum oscillation measurements by the Lu Li group (http://arxiv.org/abs/1306.5221). SmB6 is a heavy fermion compound and consequently the Fermi velocity of surface electrons is expected to be very low and a naïve mean-field theory predicts so. In **Ref. [8]**, we put together a microscopic theory of topological surface states in the hexaboride family of TKIs and *resolve the "light electron puzzle" in SmB6*, by pointing out that the band bending on the surface results in dragging down of the Dirac points into the valence band, and it strongly enhances the effective velocity on the surface. The basic idea is that energy scales involved in band bending and are unrelated to and generally much larger than the Kondo gap and consequently the Dirac points are expected to be hidden in all topological hexaborides.

2.3 Magnetic phases in topological insulators

In a recent experimental paper Science **340**, 167 (2013), Cheng et al. claim to have observed anomalous quantum Hall effect on TI's surface, which results from a ferromagnetic ordering of magnetic impurities due to RKKY interactions mediated by topological surface states. The RKKY interactions induce ferromagnetic interactions, ferromagnetic interactions lead to long-range order, which in turns leads to a gap in the spectrum and quantized Hall response. In **Ref. [6]**, we put together a self-consistent theory, where we take into account the renormalization of ferromagnetic interactions by long-range ferromagnetic order. The main result of Ref. [6] is that the temperature dependence of the topological gap on TI's surface *would be highly unusual, which can be used to verify or rule out the intrinsic ferromagnetism scenario*.

2.4 Interplay between odd-frequency pairing and topological superconductivity in superconducting proximity systems

Ref. [7] brings together two areas of research in condensed matter physics: studies of Majorana fermions in topological superconductors and odd-frequency pairing in superconducting proximity systems. We showed in Ref. [7] that the by now standard experimental setups used to proximity-induce Majorana fermions inevitably lead to the appearance of a delocalized odd-frequency component in the semiconductor host. Most importantly, we prove within a general model that *it is impossible to create a localized Majorana mode in the currently used setups*, because in the absence of superconducting interactions in the semiconductor, there is no actual superconducting order parameter and superconducting correlations are delocalized. In some sense, we have proven a no-go statement that should have important general implications for Majorana experiments, and it also indicates that in order to induce localized Majorana fermions one has to put a semiconductor in full contact with (e.g. coat it with) a superconductor.

2.5 Fluctuation-induced Singular Casimir effect

In **Ref. [5]**, we attempt to propose essentially a new line of research where the well-known Casimir effect (interaction between macroscopic bodies mediated by quantum fluctuations of the electromagnetic field) could be used to probe the internal structure and transitions in materials experiencing the Casimir forces. As a proof of principle of this general concept, we show in a particular model of a spin-orbit-coupled semiconductor that the Casimir force acting on it shows a singular behavior across a topological Lifshitz transition that can be tuned by simply changing the magnetic field. An experimental group of Jing Xia at UC Irvine got interested in this our proposed experiment and we are collaborating with them to implement the proposed setup and demonstrate experimentally *our new idea that Casimir effect can be used to probe transitions in low-dimensional materials*.

3. Future plans

- A natural follow question, following up on our Ref. [9] that established strong interactions in topological Kondo insulators, is what kinds of phase transitions can be driven by them. We are currently exploring this issue, taking advantage of a seemingly unrelated similarity between the band structure of SmB6 and that of the pnictides, where various density wave and nematic instabilities have been discussed.

- We are currently finalizing a paper with an exact solution to non-linear Eilenberger equations with disorder for p-wave proximity effect, where we show that, contrary to common a belief, disorder does NOT suppress unconventional proximity effect any differently than s-wave proximity effect. I.e., there is no Anderson theorem for proximity superconductivity.

- To follow up on Ref. [7], the PI will develop a theory of topological odd-frequency pairing. The main idea is that the "usual" topological superconductivity occurs due to a twisted structure of order parameter in momentum space, while odd-frequency pairing (a well-known experimentally observed phenomenon) may give rise to topological structure in the time domain.

- The PI will further develop his idea (Ref. [5]) of using Casimir effect to probe transitions in low-dimensional systems. In particular, the PI will calculate the effect of fluctuations on and jump in the Casimir force across the superconducting transition.

- The PI will continue the work on developing the non-perturbative theory of superconducting fluctuations and its connections with quantum dynamics.

- Motivated by the recent experimental results by the Andrea Cavaleri group on time-dependent stimulation of superconducting correlations in the cuprates, the PI will look into the theory of non-equilibrium melting of competing orders in fluctuating cuprate superconductors.

- The PI currently collaborates with Prof. Nuh Gedik's group at MIT (see, e.g., Ref. [3]) and Prof. Zahid Hasan's group at Princeton, which both are involved in experimental studies of photo-excited topological insulators. However, they work in different regimes (of low and high pump probe frequencies, correspondingly) and observe qualitatively different phenomena. While the Gedik's results are understood (Floquet reconstruction proposed by the PI earlier), Hasan's results (currently unpublished) indicate the presence of extremely long-lived photo-Voltage in the topological states. The PI will explain this phenomenon, which is likely related to different mechanism of charge relaxation in three dimensions and in topological states in 2D.

4. Publications

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Semiconductor nanostructure by scientific design

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Project Scope

This project aims at the development and use of microscopic simulation techniques to understand and predict opto-electronic and heat transport properties of nanostructured materials, for solar and thermoelectric applications. In particular, we aim at providing a first principles description of integrated systems, inclusive of surfaces and interfaces at the nanoscale, so as to model realistic environments, directly comparable with experimental conditions. The two main objectives are the efficient and accurate description of excited state properties of nanostructured materials within many body perturbation theory, in particular emission and absorption spectra; and the efficient and accurate description of heat transport properties, including predictive calculations of thermal and electrical conductivity and of Seebeck coefficients. The focus of the project is on semiconducting materials, including Si and Ge based systems and II-VI compounds, and includes both isolated nanostructures and embedded nanoparticles.

Recent progress

1. Opto-electronic properties of semiconductor nanoparticles

Methodological advances -- We recently devised an approach to evaluate quasi-particle energies based on the spectral decomposition of the static dielectric matrix [Phys. Rev. B **85** 081101 (2012)]. This method does not require the calculation of unoccupied electronic single particle states nor the direct diagonalization of dielectric matrices, and it avoids the use of plasmon-pole models. The numerical accuracy of the approach is controlled by a single parameter, i.e. the number of eigenvectors used in the spectral decomposition of the dielectric matrix. In the last two years, we completed a comprehensive validation of the method, encompassing calculations of ionization potentials and electron affinities of various molecules and of band gaps for several crystalline and disordered semiconductors. We demonstrated the efficiency of our approach by carrying out *GW* calculations for systems with several hundred valence electrons [1]. We also used the approach to devise a new method to identify and rationalize the contribution of core electron polarization to dielectric screening [2].

The spectral decomposition technique to evaluate the dielectric matrix was also used to efficiently solve the Bethe-Salpeter equation (BSE) and compute the absorption spectra of nanoparticles. We carried out a study of the excited state properties of silicon nanoparticles (NPs) with diameters of 1.2 and 1.6 nm. The absorption spectra were computed by time-dependent density functional theory (TDDFT) using the adiabatic PBE approximation, and by solving the BSE [3]. We found that a scissor operator reliably describes quasiparticle corrections for states in the low energy part of the spectra. Our results also showed good agreement between the positions of the absorption peaks obtained using TDDFT and the BSE in the low part of the spectra, although the peak intensities differed. Finally we carried out a detailed

analysis of the validity of the Tamn Damcoff approximation.

Isolated nanoparticles-- We investigated hydrogen terminated Si and Ge NP with high pressure core structures and we computed Multiple Exciton Generation (MEG) rates [4,5]. In nanoparticle-based solar cells MEG promises to increase the cell-efficiency above the Shockley–Queisser limit. However the utilization of MEG is hampered by a Quantum Confinement Dilemma (QCD): quantum confinement advantageously increases the effective Coulomb interaction, but at the same time disadvantageously increases the electronic gap. Using ab initio calculations we showed that germanium nanoparticles with core structures of high pressure phases of bulk Ge can transcend the QCD, by simultaneously lowering gaps *and* increasing the MEG rates above those of NPs with a cubic diamond core. The effect is even more marked for NPs with the BC8 core structure, which is found in compressed bulk Si (although not in bulk Ge under pressure). We also carried out [4] similar studies for hydrogenated Si nanoparticles. We found that those with a BC8 core structure exhibit significantly lower optical gaps and MEG thresholds, and an order of magnitude higher MEG rates than diamond-like NPs of the same size. We analyzed several mechanisms to further reduce the gap, including surface reconstruction, excitonic effects, and embedding pressure. Experiments reported the formation of BC8 NPs embedded in amorphous Si and in amorphous regions of femtosecond-laser doped "black silicon." For all these reasons, BC8 nanoparticles may be promising candidates for MEG-based solar energy conversion.

Embedded nanoparticles-- We investigated silicon nanoparticles (NP) embedded into amorphous, non-stoichiometric ZnS and we found that these nano-composites are promising materials for solar energy conversion. Using ab initio molecular dynamics simulations we showed that, upon high temperature amorphization of the host chalcogenide, sulfur atoms are drawn to the NP surface. We found that the sulfur content may be engineered to form a type II heterojunction, with complementary charge transport channels for electrons and holes, and that sulfur capping is beneficial to lower the nanoparticle gap, with respect to that of NPs embedded in oxide matrices. Our analysis was conducted using density functional theory with local and hybrid functionals and many body perturbation theory at the GW level [6].

2. First principle calculations of transport coefficients in semiconductors

Calculations of thermal conductivity -- We investigated how dimensionality affects heat transport in Si-Ge superlattices (SLs) by computing the thermal conductivity of planar superlattices and arrays of Ge nanowires (NWs) and nanodots embedded in Si [7]. We studied superlattices with ~10 nm periods using a fully atomistic Monte Carlo solution of the Boltzmann transport equation in the relaxation time approximation, and semi-empirical potentials. We found that for periods larger than 4 nm, the room temperature cross-plane conductivity of planar superlattices with equally thick Si and Ge layers is larger than that of their nanowire and dot counterparts of similar sizes (up to 100%), while the trend is reversed below 4 nm. The method developed to study superlattices [7] can be used to compute the thermal conductivity of broad classes of semiconductor nanostructures. We also investigated another type of nanostructured semiconductor: a newly synthesized Si-based ternary clathrate $K_8Al_8Si_{38}$, composed of ~ 1 nm hollow cages with a metal atom inside [8]. This compound contains solely Earth abundant elements. In this case we used ab initio calculations, and we found that, similar to other nanostructured type I clathrates, this system is a semiconductor and has a low thermal conductivity (~ 1 W/mK). It was long believed that the mere presence of rattling centers was responsible for the low lattice thermal conductivity of type I clathrates. We found instead that the cage structural disorder induced by atomic substitution plays a crucial role in determining

the conductivity of these materials, in addition to the dynamics of the guest atoms. Our calculations showed that the latter is substantially affected by the charge transfer between the metal and the cages.

Calculations of Seebeck coefficient and electronic conductivity – In addition to the thermal conductivity, we are studying the electronic transport properties of the clathrates mentioned above (work in progress). Using ab initio calculations and spectroscopic and Hall mobility measurement (carried out in the group of Prof. Kauzlarich at UCD), we showed that $K_8Al_8Si_{38}$ is a promising material for solar energy conversion [9]. We found that this system exhibits a quasi-direct band gap of $\sim$ 1.0 eV, which may be tuned to span the IR and visible range by strain engineering. We also found that upon light absorption, excited electron and hole states are spatially separated in the material, with low probability of charge recombination. Finally, we computed and measured electron and hole and obtained values much superior to those of a-Si and approximately 6 to 10 and 10 to 13 time smaller than those of crystalline. Work is in progress to study transport properties of clathrate superlattices.

Future Plans

Our future plans encompass the calculations of electronic transport coefficients from first principles, including electronic properties obtained within many body perturbation theory and the development of technique to compute thermal conductivities of semiconductors from ab initio calculations. We will focus on nanocomposites, i.e. embedded nanoparticles and solids composed of nanoparticles connected by inorganic ligands.

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NON-EQUILIBRIUM EFFECTS IN QUANTUM COHERENT SUPERCONDUCTING NANOSTRUCTURES

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Project Scope

In this program, we concentrate on quantum kinetic phenomena in superconducting nanostructures. The special focus is placed on the quasiparticles kinetics and on their effect on the dynamics of the superconducting order parameter. Elucidation of the quasiparticles kinetics is important for a broad array of fundamental and applied problems of superconductivity. The non-equilibrium quasiparticles limit the coherence times of the superconducting qubits. The theory being developed within this program aims at mitigating this detrimental effect. The kinetics of quasiparticles also holds a key to the reliable spectroscopy of low-energy localized states: Andreev states at the interface of conventional superconductors and Majorana states at the interfaces involving topologically-nontrivial materials. Observation and characterization of these states is important in the contexts of fundamental and applied superconductivity. The program aims at developing the theory of linear and non-liner responses revealing the low-energy states at the superconducting interfaces.

Recent Progress

Dissipative component of the Josephson current: the resolution of a long-standing "$\cos\varphi$" problem

In contrast to the carefully studied non-dissipative component of the Josephson current, the dissipative one remained a subject of controversy since the seminal 1962 paper by Brian Josephson. His phenomenological theory predicted that the dissipative current across a junction between two superconductors should depend as $\cos\varphi$ on the phase bias between the superconducting leads. Later on, a microscopic theory was developed attributing such term to the presence, at finite temperatures, of equilibrium quasiparticles in the vicinity of the tunnel junction. At low temperatures, the dissipative current is proportional to $(1+\cos\varphi)$. The absence of dissipation at $\varphi=\pi$ can be viewed as a consequence of destructive interference of tunneling of the particle-like and

hole-like excitations across the junction. The experimental confirmation of this effect remained elusive for over 50 years.

Recently, we developed a comprehensive theory of equilibrium and non-equilibrium quasiparticles effect on the qubit relaxation times. (Ref. [1] addressing the T_1 and T_2 times of a superconducting qubit is the latest paper of that cycle.) Our theory relates the qubit relaxation to the impedance of a Josephson junction, thus providing a direct link between the $(1+\cos\varphi)$ dissipative term in the current and the qubit coherence times. During the previous funding period, we also worked on theory which led to the introduction of a new type of a qubit, dubbed "fluxonium". (The latest paper of that cycle is Ref. [2].) The loop-like fluxonium device is largely immune to the parasitic charge fluctuations, while remaining sensitive to the magnetic flux Φ threading the loop. The flux allows one to control the phase bias across the Josephson junction. At half-flux-quantum, the phase $\varphi=\pi$, leading to a minimum in dissipation and to a sharp peak in the T_1 dependence on flux. We developed the theory for $T_1(\Phi)$ dependence necessary for the interpretation of experiment, see Fig. 1. The result of our work published recently in ***Nature*** jointly with the experimental group of Prof. Michel Devoret (Yale University), did firmly establish the $(1+\cos\varphi)$ dependence of the dissipative component of the Josephson current, and allowed us to extract the density of non-equilibrium quasiparticles in the vicinity of the Josephson junction [3].

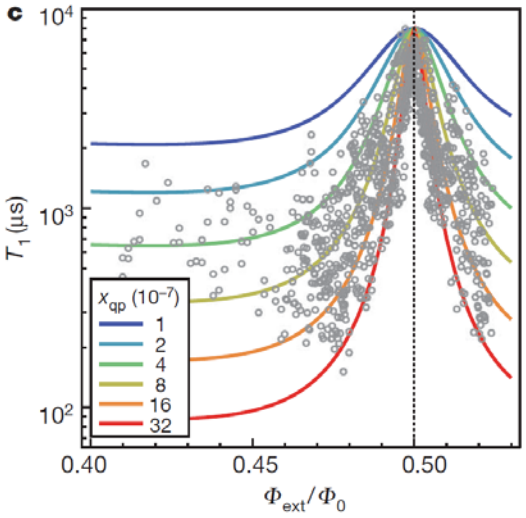

Fig. 1. The dependence of the fluxonium qubit T_1 on the external magnetic flux in the vicinity of half-flux-quantum. The theoretical curves are evaluated for a set of dimensionless quasiparticle densities x_{qp}. The data fits assume the current-phase relation $I \propto (1+\varepsilon\cos\varphi)$ for the dissipative component of current and allow us to establish $\varepsilon = 1$ with an error less than 1% (adapted from Ref. [3]).

Effect of quasparticles occupying Andreev levels on the admittance of a short superconducting weak link

We investigated the linear and nonlinear electromagnetic responses of a nanowire connecting two bulk superconductors. The Andreev states appearing at a finite phase bias substantially affect the finite-frequency admittance of such a wire junction. Electron transitions involving the Andreev levels are easily saturated, leading to the nonlinear effects in photon absorption for the subgap photon energies. We evaluated the complex

admittance analytically at an arbitrary frequency and arbitrary, possibly non-equilibrium, occupation of the Andreev levels [4]. Special care was given to the limits of a single-channel contact and a disordered metallic weak link. The “contamination” of Andreev levels by quasiparticles leads to an increased inductance of the weak link at sub-gap frequencies. Placed in a resonant circuit, weak link makes the resonance frequency dependent on the trapped quasiparticles population. That allows one, in principle, to detect quasiparticles occupying the sub-gap Andreev states by monitoring the resonant frequency.

Our theory worked remarkably well for experiments performed in the group of Prof. Irfan Siddiqi (UC Berkeley) described in our joint publication [5]. In the experiments, a resonant circuit with an Al weak link was investigated. A typical weak link contained over 600 Andreev states. Despite the large number of localized states, contamination of the link by merely one quasiparticle was manifesting itself through a characteristic distortion of the resonance peak in the microwave admittance of the circuit, see Fig. 2. Furthermore, our theory allowed us to understand the effect of high-power microwave pulses applied to the weak link. Such pulses were leading to the temporary restoration of the Lorentzian peak shape, indicating the “evaporation” of the quasiparticles from the Andreev levels.

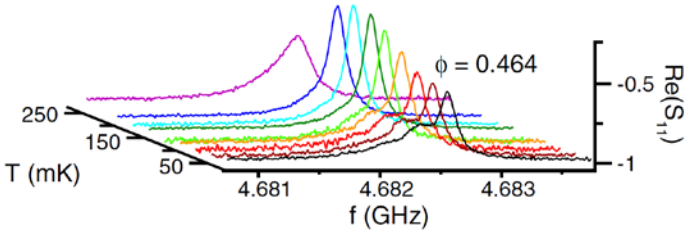

Fig.2. Temperature dependence of the resonance line shape, showing the decrease in trapping of quasiparticles as temperature rises. All data are shown at $\varphi = 0.464$. At low temperature, multiple humps are resolvable, indicating multiple quasiparticles trapping numbers. At higher temperatures, first the 2-quasiparticles and then the 1-quasiparticle peak shrink, leading to a Lorentzian resonance. At even higher temperature (T=250 mK), the resonance broadens, shrinks, and moves to lower frequency; we attribute this to loss originating from bulk quasiparticles transport in the resonator (adapted from Ref. [5]).

Dynamics of Majorana states in a topological Josephson junction

One of the stunning predictions of the theory of topological superconductors is the 4π periodicity of the Josephson current-phase relation, associated with the Majorana states at the interfaces. The apparent contradiction with the conventional 2π periodicity of all observables is resolved by the presence of *two* branches of that relation, shifted by 2π with respect to each other. Generation or trapping of quasiparticles in Majorana states leads to switching between the branches. The generation and trapping processes, at some rate, are inevitable in equilibrium; so, the thermodynamic properties are indeed 2π-periodic. An observation of the unusual periodicity calls for phenomena involving dynamics of the Majorana levels. In our work, we considered two measurable characteristics, the so-called Shapiro steps in the dc current, and the high-frequency

noise spectrum of the Josephson current through a voltage-biased junction [6,7]. Ideally, Majorana states in, *e.g.*, Shapiro steps experiments lead to the absence of all odd steps. We demonstrate that in fact the maximal number of "vanished" odd steps depends on the relation of two rates: the intrinsic for the junction switching rate between the mentioned two branches, and the phase relaxation rate controlled by the external circuit supplying the electric bias to the junction. We developed a theory of the Shapiro steps shape and of the noise spectra accounting for the said relaxation rates.

Future Plans

We continue our theoretical investigation of effects of quasiparticles on the coherence of the superconducting nanostructures. The two closest aims, dictated by the needs of ongoing experiments, are the statistics of generation and recombination of quasiparticles and the effect of vortices on the kinetics of quasiparticles.

Within the first of the two problems, we intend to investigate the kinetics of quasiparticles in structured devices, such as fluxonium, taking advantage of the separation between the time scales for, respectively, generation and diffusion of quasiparticles. The results of the investigation hopefully will help understanding the statistics of transitions ("quantum jumps") between the ground and excited states of a qubit.

In the second direction, we intend to assess the effect of vortices on the qubit relaxation times. We expect that the introduction of vortices may lead to discrete changes in T_1.

We also intend to further develop our theory of Shapiro steps in topological Josephson junctions, by a more detailed accounting for the processes of switching between the Majorana states.

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Simulation of Correlated Lattice and Impurity Systems out of Equilibrium

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8/2/2014

1 Project Scope

Correlated quantum systems out of equilibrium exhibit a wealth of intriguing and unexpected quantum phenomena: Quantum dots at low temperature show Kondo behavior when a bias voltage is applied. Femto- and atto-second pump-probe spectroscopy experiments on Mott-insulating transition-metal compounds reveal a radical change of the nature of the many-body wave-function after a rapid change of interaction parameters, exposing a collapse and reestablishment of insulating behavior. Similarly, the dielectric breakdown of Mott-insulating materials to which a large voltage is applied leads to surprisingly long-lived quasi-static intermediate states. Our theoretical understanding of these phenomena lags far behind our experimental capabilities, as it requires a precise and unbiased solution of the quantum mechanical equations of motion. In this project I propose to develop unbiased, numerically exact methods for correlated quantum impurity and lattice models out of equilibrium.

2 Recent Progress

2.1 Non-equilibrium bold-line Monte Carlo formalism [1]

Obtaining an unbiased solution of a correlated quantum many-body problem requires a numerical method. Several approaches exist. We developed a real-time bold-line [2,3] continuous-time [4] hybridization expansion [5,6] quantum Monte Carlo algorithm [7], and adapted it to obtain the two-time correlation functions.

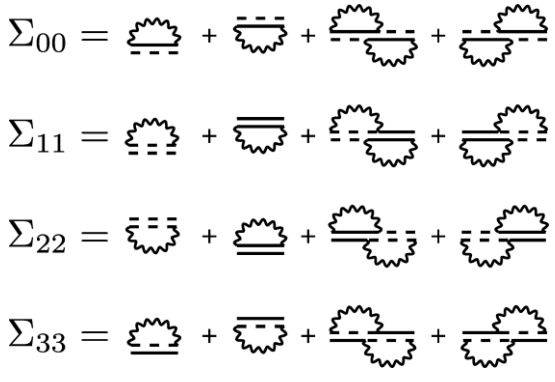

Fig. 1: The matrix elements of the NCA self energy (two terms on the left with a single hybridization line) and of the OCA self energy (all four terms) in diagrammatic form.

The method is based on a stochastic summation of all diagrams containing partially summed ('bold' rather than 'bare') propagator lines and vertex functions. So far, these partially summed propagators have come from the non-crossing or one-crossing approximations (NCA or OCA [8]) but the method is more general: In a first, quasi-analytic step, an underlying diagrammatic approximation selecting some (but not all) diagrams is chosen, and propagators within that approximation are obtained analytically or via the solution of a set of coupled integral equations. In a second step, all corrections to the propagators are summed up using a stochastic Monte Carlo procedure, so that the resulting sum contains all diagrams and therefore becomes numerically exact. The precise choice of the underlying approximation determines the speed of convergence to the exact result, the statistical uncertainty, and the feasibility of the method for any given system, but has no effect on the final answer if convergence is attained.

We consider the single-orbital Anderson impurity model. Here, the non-crossing approximation consists of evaluating the diagrams outlined in Fig. 2.1, and the Monte Carlo algorithm stochastically samples all corrections to all orders to these diagrams.

2.2 Auxiliary lead formalism [9]

The spectral function A can be related to the steady-state current in a weakly coupled auxiliary lead [10,11,12]. In a Monte Carlo simulation, the presence of noise makes the numerical computation of this expression impractical for cases where one is interested in behavior in or near a gap in the lead's spectrum.

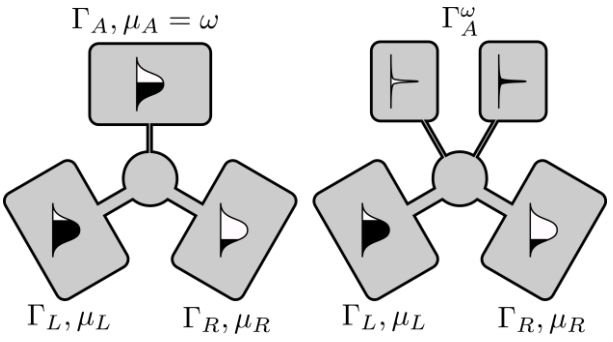

Fig. 2. Left: an illustration of the single probe, wide-band auxiliary current setup. Right: the double probe, narrow-band variation of the auxiliary current formalism. The dot is depicted as the central circle, and is coupled by thick (thin) lines to the physical (auxiliary) reservoirs. The curved region within each reservoir sketches the shape and filling of its coupling density.

In order to overcome this limitation, we propose an alternative double probe scheme, consisting of the unrealistic but convenient choice of *two* auxiliary leads, one empty and one full, set up in such a way that they are coupled to the system at only a single frequency ω'. The assumption made, as in Ref. 11 and 12, is that η is small enough that the properties of the auxiliary lead have a negligible effect on the physical properties of the full system. Two independent calculations, one for an empty lead and a second one for a full lead, provide a setup (see right side of Fig. 2.2) with which the dot spectral function can be obtained.

$$A(\omega) = \lim_{\eta \to 0} -\frac{2h}{e\pi\eta}\left[I_A^1(\omega) - I_A^0(\omega)\right]. \qquad (1)$$

This analytically exact result is not restricted to any particular way of solving the impurity model, and is therefore usable within any formalism where one has access to currents. This includes quantum Monte Carlo but also, e.g., hierarchical equation of motion methods. The introduction of two leads of opposite populations simultaneously helps to conserve current.

These currents also provide direct access to the lesser Green's function $G^<$, providing the full information about single particle correlations even in nonequilibrium situations. Finally, since the auxiliary current lead can be chosen to have any dot orbital matrix structure, it is straightforward to find a choice that allows extracting individual elements of $A_{ij}(\omega)$.

2.3 Equilibrium spectral functions [1]

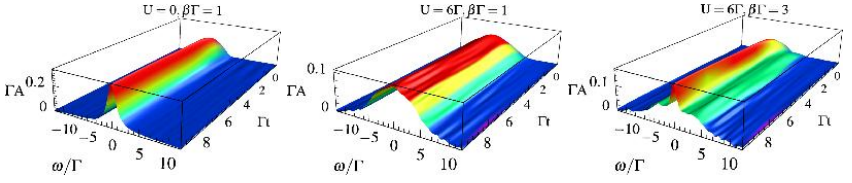

Figure 3: The dependence of the probed spectral function on time and frequency, as obtained from the the auxiliary current method for an initially decoupled quantum dot at Ω_c=10Γ. At U=0 and βΓ=1 (left), a simple Lorentzian shape develops. At U=6Γ and βΓ=1 (center), the interaction distorts and widens the spectrum. At U=6Γ and βΓ=3 (right), the spectral profile typical to the Kondo problem develops, exhibiting a central Kondo peak between two lower Hubbard peaks.

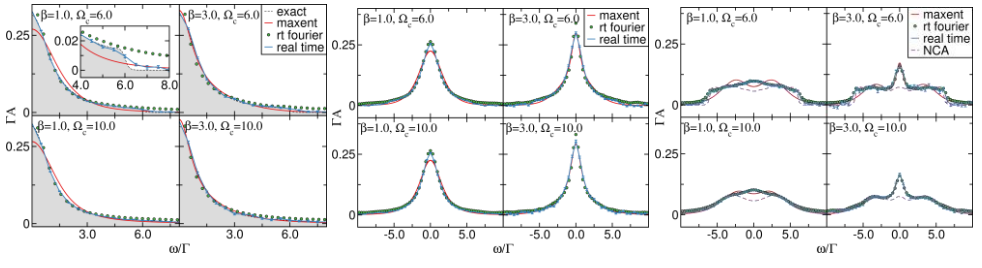

Fig. 4. The spectral function $A(\omega)$ in the non-interacting limit U=0 (left panel), weakly interacting limit U=2 (middle panel), and strongly correlated limit U=6 (right panel) is shown for several combinations of the inverse temperature βΓ and band width Ω_c/Γ. The exact result is shaded in gray for comparison to the imaginary time data analytically continued with Maximum entropy using a flat model (solid red), the result obtained from directly Fourier transforming the real time bold-

line CTQMC correlation function (green circles), and the real time bold-line CTQMC auxiliary current data (thick blue line with error bars). Both real time results are obtained by propagating a decoupled initial state to Γt=10. The inset in the top left panel zooms in on the region near the band edge. Real time NCA data is also shown for comparison (dashed purple line).

Figures 3 and 4 show results for the spectral function of the Anderson impurity model, obtained using bold-line CTQMC and the auxiliary current method and a direct measurement of the time-dependent Green's function. All results are computed with the real time bold-line CTQMC expansion [3,8] built around the one-crossing approximation (OCA) [13] by measuring the current to an auxiliary reservoir defined by

$$\Gamma_A(\omega_A,\omega) = \frac{\eta\beta_A}{\sqrt{\pi}} e^{-[\beta_A(\omega-\omega_A)]^2}, \qquad (2)$$

with $\Gamma\beta_A$=10 and η=$10^{-3}\Gamma$. The dot is initially decoupled from the physical and auxiliary leads, and the coupling is turned on at time zero, after which the system time-evolves according to the full Hamiltonian.

Fig. 3. shows $A(W,t)$ as measured by our virtual probes. Note that a constant-t cut across the surface at long times forms the steady state spectral function, which can be read from the profile of the plots. With the initial (t=0) condition we have chosen, the auxiliary current I_A(t=0) is always zero. With Ω_c set to 10Γ the band is essentially flat over the range of frequencies displayed.

In the left panel of Fig. 3, we display a noninteracting case. Within hybridization expansion CTQMC, the noninteracting case is a stringent test for the algorithm, as it expands about the atomic limit making this exactly solvable limit a difficult case for our approach. First, the final profile has a Lorentzian shape, as expected from a noninteracting dot coupled to a flat lead. Second, the observed relaxation timescale appears to be related to Γ rather than the auxiliary parameters η and β_A. This is typical for charge-related properties in the system, and suggests that we are in fact measuring physical system properties and not properties related to our choice of auxiliary lead. This is expected, since the auxiliary lead is coupled to the system only weakly, so that probing the dot only involves its linear response characteristics.

In the middle panel of Fig. 3, a strong interaction has been turned on, while the temperature is kept rather high. At long times, excitations spread throughout the band, but not far beyond Ω_c. In addition, noise and oscillations in both time and frequency appear, indicating that convergence to the steady state is much slower. However, as before, the time evolution of the spectral function is mostly converged after a time on the order of $1/\Gamma$.

On the right side of Fig. 3 the temperature is lowered while the interaction is reduced. One can observe the formation of a central Kondo peak at the chemical potential and an indication of two side bands.

Within bold-CTQMC two-time correlation functions can also be obtained directly for a given t and t'. Once the equilibrium correlation function $G^r(t-t')$ is obtained in the time domain, a simple Fourier transform takes us to the frequency domain. In practice, since $t-t'$ is limited in range by the maximum t reachable, one must also converge the result of the Fourier transform in t at all frequencies. This proves to be difficult, and the auxiliary current method offers more accurate results. However, for certain nonequilibrium problems, it is often the time-domain function itself that proves to be of interest [12,14].

2.4 Non-equilibrium spectral functions [9]

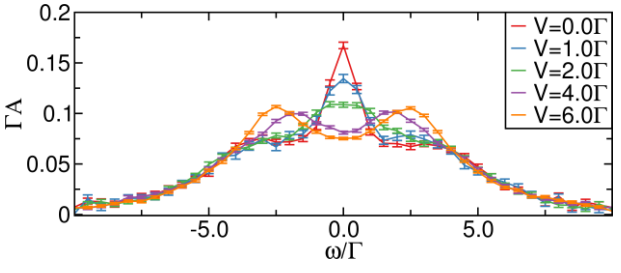

Fig. 5. Steady state spectral function $A(\omega)$ for several voltages. The results are obtained from bold-CTQMC using the double probe auxiliary lead formalism at Γt=10. Error bars estimate statistical Monte Carlo errors.

The effect of voltage on the spectral function is illustrated in Fig. 2.4. At zero voltage the Kondo peak can clearly be seen as it begins to form (the temperature studied is at the upper edge of the Kondo regime). With the application of a bias voltage, the peak lowers, widens and eventually splits. While the magnitude of the Kondo effect decreases when the system is driven away from equilibrium, the effect is obviously not destroyed by the bias, and partial hybridization of the dot with each lead occurs simultaneously. Except at frequencies much higher than the bias, the spectral function is also significantly modified by the nonequilibrium conditions, indicating that the equilibrium spectral function is an inappropriate quantity for the description of nonequilibrium physics.

3 Current and Planned Activity

3.1 Finite temperature solver – Keldysh contour

We are currently extending the bold-line Monte Carlo code to the finite-temperature Keldysh contour. For equilibrium problems, this will allow us to shorten the time needed to overcome the initial transient regime and allow more precise estimates of equilibrium spectral functions. For non-equilibrium problems, this allows the simulation of dynamics of quantum systems prepared in mixed states, in particular driven and quenched interacting systems.

3.2 Dynamical mean field framework

We are currently writing a finite-temperature real-time dynamical mean field framework [15,16,17]. This formalism will enable the simulation of quantum quenches in extended systems and real-time dependent lattice problems within the dynamical mean field approximation, in addition to the quantum impurity problems we have examined so far.

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Theory of Electron Imaging in Small Devices

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Project Scope

The research in this program involves theoretical investigations of the transport of charge in graphene and small heterostructure devices. There is an important trend toward imaging electronic systems in real space, with the goal of understanding the specifics of individual samples rather than settling for ensemble and statistical descriptions. For example one of our goals has been the understanding of scanning probe microscopy (SPM) imaging of systems in which the motion of the carriers is restricted to two degrees of freedom, such as in graphene and the two dimensional electron (and hole) gas (2DEGs and 2DHGs) in GaAs/AlGaAs heterostructures, or when the motion is restricted to one degree of freedom as in nanowires. SPM imaging uses the tip of a movable charged probe to alter the electrons locally, depleting or alternatively increasing the amount of charges in the electron gas just below the tip results in a change to the flow pattern of the charge. Our current research focus is on understanding how the tunable tip affects functional aspects of the device that can be used to understand electronic and transport properties. For instance, scanning over the device while measuring the conductance results in conductance maps, an imaging of the charge transport. This imaging is often 'semi-direct' and requires theory and interpretation to extract all that can be deduced about the underlying physical quantities.

Recent Progress

Stability of semiconductor branched flow

The discovery of the branched electron flow in 2DEG GaAs/AlGaAs semiconductor heterostructures by the Westervelt group and the quantitative explanation of the surprising data by our group, were key discoveries in the physics of electron transport in these iconic semiconductor systems. The electron flow in the 2DEG of high mobility semiconductor heterostructures at low temperatures is strongly influenced by the weak disorder potential and small-angle deflections caused by the impurities. Branched electron flow is the real space manifestation of the specific mechanism by which momentum decorrelates and mobility is limited in the 2DEGs. This discovery is one of the recent rewards of imaging the flow and the associated computations.

Recently, the Goldhaber-Gordon group at Stanford published a report on 2DEG branch stability, making a bold claim that experimentally, and therefore quantum mechanically, branches were relatively stable against changes in the injection point of a quantum point contact (QPC), whereas classically they were expected to be extremely unstable. They concluded that branch stability was a quantum effect. Our group found an alternative explanation for the experimental findings. An adiabatic QPC, when translated sideways

to the flow far enough so that the states inside the middle of the translated QPC do not overlap with the original QPC, can still generate an overlap of 80% or higher out in the more open regions. With such a high overlap, the same branches would have to be seen for the most part. The overlap between two states cannot change if both are propagated in the same Hamiltonian, but *can change if both are propagated under different Hamiltonians*. A QPC and a shifted QPC generate different Hamiltonians with respect to the fixed 2DEG potential! With the 80% overlap, the long-range occupation of the same branches is expected, not unexpected, and indeed is seen. Previous classical simulations did not see this since they injected trajectories from a point like, non-adiabatic port. Our group has been providing theoretical guidance to one of the best SPM imaging groups in the world lead by Prof. Robert Westervelt at Harvard University.

Imaging and theory of transport in graphene

Our theoretical work on SPM imaging strongly connects with ongoing experiments in the Westervelt lab and has contributed to the understanding of electron transport in graphene. We studied conductance fluctuations and the sensitivity of the conductance to the motion of a single scatterer in 2D Dirac systems. Although universal conductance fluctuations (UCF) have been observed by standard conductance measurements, our team managed for the first time to image UCF. Our simulations verified that the measurements are indeed imaging UCF caused by the motion of a single scatterer. The conductance of massless Dirac fermions is indeed sensitive to the motion of a single scatterer, resulting in fluctuations of order e^2/h from the motion of a single impurity by a distance comparable to the Fermi wavelength. The dependence on the Fermi wavelength can be varied widely via gate voltages.

We have also explored the ballistic-to-diffusive transport transition in graphene. The nature of quantum transport is often probed by shot noise and the Fano factor, which unfortunately become nearly useless in the case of graphene both near and away from the Dirac point, because both ballistic and diffusive transport give a Fano factor near 1/3 in both theory and experiments. To address this problem we have proposed a method to study the mechanisms of electronic transport based on displacement conductance, that is, the conductance as a function of the position of the drain lead in a two-terminal device. The method extracts the conductance profile of the charge flow at the edge of the device and it can be applied to discern the mechanism of transport from ballistic to diffusive. Moreover, we simulated SPM measurements for the same devices, to visualize the flow of charge inside the device, thus complementing the transport calculations. We found that both the conductance profile and SPM measurements are excellent tools to assess the transport mechanism differentiating ballistic and diffusive graphene systems.

Control of entangled states in quantum wells

We developed the theory and successful calculations for coherent and high-fidelity quantum control of many-particle states in semiconductor quantum wells. This work uses optimal control theory (OCT) to find optimized optical fields that induce coherent transitions between quantum states. Our approach optimized the optical field by tailoring

the phases and other parameters of the laser, resulting in interferences between two or more possible pathways during the duration of the pulse, and reaching the target states in what could be a new regime of speed (few picoseconds) and fidelity (> 99.9%). Coherent control with THz optics will become feasible in the very near future and we believe that our work is within reach of present experimental capabilities. We hope that our work motivates experiments in the initialization, control, and readout of electric charge in solid-state devices and we will continue to investigate realizable schemes towards advances in quantum information.

Control of charge states in quantum wells

THz time scales are reachable in state-of-the art optical set-ups. However, any gate-voltage control schemes are strictly limited to GHz time scales. In order to overcome this obstacle, we proposed a way to use the SPM tip as a local control gate. Our goal was the application of OCT to optimize the gate voltage pulses necessary to control charge. In this case, we pursue the goals of reducing the time required to reach the target state while minimizing the applied frequency range to realistic (GHz) values without compromising the fidelity of the process.

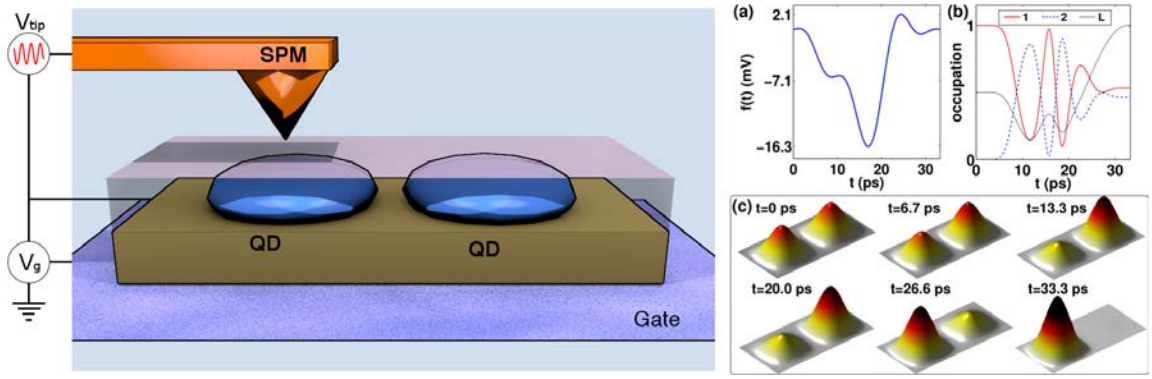

Figure 1: Schematic of the double quantum dot system. Left: Two quantum dots are embedded in a semiconductor heterostructure. A local gate, such as the charged tip of a scanning probe microscope (SPM) capacitively coupled to the system, can change the potential locally. Here, the SPM tip located above one of the quantum dots applies a time-dependent voltage. Right: (a) Voltage applied by the SPM as a function of time. (b) State occupation of the system as a function of time. (c) Snapshots of the charge density in the system showcasing the transition from ground state to left-dot-only state. (Adapted from Blasi, Borunda, Rasanen, and Heller, *Phys. Rev. B* **87**, 241303(R).)

The optimizations resulted in gate voltage pulse sequences for the control schemes accomplished in time scales ranging from 22 to 222 picoseconds. The optimized local fields can be easily reconstructed in the gigahertz regime and are experimentally accessible. The ability to coherently control arbitrary two-electron states while maximizing entanglement and to prepare target states with realistic experimental constraints opens up further perspectives in solid-state quantum information.

Future Plans

For the next years, we plan to continue collaborating with the Westervelt group in our studies of imaging of electron transport in graphene and semiconductor heterostructures. We also have started investigations on the electron-phonon coupling in graphene and related systems from the perspective of Raman scattering. Finally, we plan to extend our studies on optimal control to spin states. The following topics will be investigated:

- Coherent control of the branched flow.
- SPM induced surface deflection and conductance in graphene.
- Studies of imaging electron transport in graphene dots and nanostructures.
- Studies towards imaging branched flow in graphene.
- Theory of electron-phonon coupling and Raman scattering in graphene, graphite, and conjugated polymers.
- Ultrafast spin control for few-electron quantum dots.

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QUASICRYSTALS FROM THE BOTTOM UP: WHERE ARE THE ATOMS AND WHY?

Christopher L. Henley, Cornell University

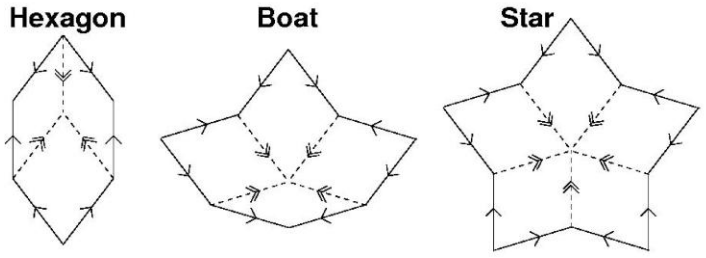
I will survey 25+ years of DOE-grant research on the twin questions in the title, leading up to our current work on these fascinating and solvable problem.

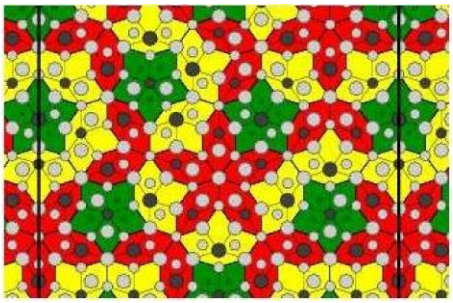
1. Background

Starting in 1987 [1] numerous long-range ordered, equilibrium quasicrysals are known; there are three major classes with different atomic arrangements and compositions. The two major symmetry classes (cutting across the structural classes) are 3-dimensional icosahedral, or decagonal which is a periodic stacking of 10-fold symmetric layers.

But when quasicrystals burst upon physics in 1984 [2,3] ,they were available experimentally only as 10-micron crystallites. Early theories had a dubious connection to real materials, leading the latePer Bak to famously wrote ``where are the atoms?" [4]. In fact we were already piecing together an answer: *approximant* crystals, denoting periodic crystals in which the unit cell is a fragment of quasicrystal [5]. Many long-known complex alloy structures, re-analyze, are build of (2D or 3D) tiles like Penrose's, with each tile tile bearing a fixed pattern of atoms which we call a decoration. These *approximants* are our ``Rosetta stone" from which we can guess the quasicrystal structure, and this continues to be fruitful. Furthermore, the tiling/decoration way of representing the atomic structure has been repeatedly vindicated. The icosahedral structure that we understand are all build from from the ``canonical-cell tilings" [6] with four kinds of 3D-tiles i.e. cells, where the corners are centers of multi-shell icosahedral clusters that decorate this tiling.

The Penroe tiling (figure, left) consists of rhombi with two kinds of markings on the edges that must agree wherever tiles adjoin: this suffices to forces long-range quasicrystal order. The figure shows version with composite talked. Hexagon/Boat/Star, which could economically implements the rules since the outer edges carry just one kind; and most real decagonals or their approximants are actually built from Hexagon/Boat/Star tiles.





It was natural to assume quasicrystals are stabilized by atomic arrangements that somehow implement matching rules [3]. However, the coming "random tiling model" of a kind of entropic stabilization, introduced by Elser, can equally explain quasicrystal order [7], and experiments could not decide between the competing scenaries

2. Our research program

So we were driven, starting in the 1990s, to model quasicrystals "from the bottom up" using multi-scale methods anchored in ab-initio energies,
to resolve the origin of quasicrystal order [8,9]. (All this work was done in collaboration with Dr. Marek Mihalkovic, of the Slokak Academy of Science, and sometimes with undergraduates.) We have multiple levels of description to effective tile-tile interactions and even to the (higher-dimensional) elastic constants peculiar to quasicrystals [10].

A key ingredients in this program were, first, finding a set of pair potentials: the smallest structures of interest consist of hundreds of atoms, which is still forbidding for extensive ab-initio molecular dynamics. We eventually found that ``empirical oscillating pair potentials" [Pub. 2], fitted from an ab-initio database, work extremely well (the key ingredient is allowing Friedel oscillations.) Our methods were tailored to *decagonals* and explained the Ni-rich and Co-rich variants of the best *decagonal*, d-AlCuNi [9,11,12]. On the way, we discovered a structure (with real interactions but somewhat unreal composition) that spontaneously realize a matching up forming exactly Penrose's tiling [13]. (See figure, right. The gray and black atoms stand for Al and Co atoms, with their size indicating which of the two layers they are in, so this image gives an example of a decoration.)

After 2005 we returned to icosahedral quasicrystals. A, striking discovery was that, though these materials built of icosahedral clusters, the
cluster symmetry is spoiled: each has a **non-icosahedral** inner cluster: e.g. a tetrahedron in the Cd-Ca class of quasicrystal (see Pub. 2, 3, 6). Now, *matching rules* (figure left) are markings that propagate information by spoil a motif's internal symmetry. So is conceivable that the orientation degrees of inner clusters can implement *matching rules.*

3. Current directions

We adopted two themes, out of the larger set of quasicrystal interests we were pursuing: (1) How might matching rules be realized microscopically? (2) Truly novel families of quasicrystals.

Matching rules (?) – icosahedral: We focus on i-AlPdMn, the best (stable) icosahedral quasicrystal. Long efforts had been made to get ab-initio c*alculated* energy to indicate stability, as is known experimentally, which forced an understanding of intricate details of the structure [14].
One finds the icosahedral clusters (1) have an irregular 10-atom internal clusters; (2) are smaller in radius by 1/1.6 (i.e. one less shell) than the previously imagined cluster (3) occupy the add sites of a Canonical Cell tiling. This picture was by a diffracting solution of a large-size *approximan*t [15].The question is how orientations on one inner cluster interact with its neighbors, which conceivably could implement a matching rule. We started with an the simplest possible approximant, using Al11Ir4 which has the same clusters [Pub 4], and (in unpublished work) applied the methods from [6] to extract an effective Hamiltonian for the orientation interactions; we are moving to the next two simplest *approximant* crystals.

Matching rules – decagonal: Unfortunately, the Al-Co or Al-Ni structure shown in he figure, with emergent because we artificially forced a 2-layer structure. In real Al-transition metal d*ecagonals*, a subset of Al atoms pucker up or down from the layers, for reasons understood in Ref. [11]. There puckerings form an intricate pattern which one must get right, to have any hope of fining a stable energy (Pub. [1]). We want to find the conditions under which the matching-rule interactions survive the puckering.

Novel compositionis – decagonal: The empirical oscillating pair potentials for the Mg-Rh-Ag system are very similar to those of the best *decagonal* quasicrystal d-AlCoNi [9,11,12,13],leading us to speculate that this will form a quasicry tsal. We are applying the simulation methods we developed for the Al—Co--Ni system the past 15 years to test this conjecture and find the best composition (for d-AlCoNi that we know from experiments), so as to motivate experimentalists to make this material.

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New Parameter Regimes and States of Matter in Strongly Correlated Quantum Systems

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Project scope

A major goal of condensed matter physics is the identification and characterization of new states of matter. Strongly correlated quantum systems, in which interactions among the constituents play a crucial role and lead to numerous incompletely understood phenomena, provide a fruitful setting to pursue this goal. This project aims to explore new parameter regimes of strongly correlated quantum systems, in part to help identify promising candidate systems for new states of matter. Current and recent efforts focus on two classes of systems:

(1) Ultracold fermionic alkaline earth atoms (AEA) in optical lattices. The primary interest in these systems stems from the fact that ultra-cold AEA can have large nuclear spins (up to $I=9/2$) with $J=0$. As a result, to an excellent approximation, a very large SU(N) spin symmetry ($N = 2I+1$) is present. Earlier work of the PI and collaborators pointed out similarities between these systems and more familiar SU(2) frustrated magnets, highlighting the potential richness of condensed matter phenomena in ultra-cold AEA.

(2) *Correlated electron systems with strong spin-orbit coupling.* These systems include iridates and other *5d* transition metal oxides, as well as *f*-electron materials. Such systems are characterized by interplay between strong spin-orbit coupling and substantial electron correlation. This leads to novel magnetic and electronic degrees of freedom that provide a new set of microscopic building blocks, potentially leading to topological and other new states of matter.

Recent Progress

Ultracold alkaline earth atoms

Earlier work by the PI and collaborators showed, based on a large-N solution, that two-dimensional Mott insulators of alkaline earth atoms (AEA) are candidates to realize the long-sought chiral spin liquid (CSL) state. The CSL is a spin-system analog of the fractional quantum Hall effect, and is thus an intrinsically two-dimensional phenomenon, raising the question of the behavior of three-dimensional AEA Mott insulators in the same large-N limit. Rather than forming a uniform spin

liquid state as in two dimensions, we have found a more complex behavior, with spontaneous formation of layered spin liquid ground states, and other lattice symmetry-breaking ground states, depending on system parameters.

Correlated electron materials with strong spin-orbit coupling

One important role for theory in studies of strongly spin-orbit coupled materials is at the level of modeling. In order to provide useful guidance to experiments, as well as to understand likely possibilities for new states of matter and other interesting phenomena, it is useful to have microscopic models that capture the basic ingredients of a material or class of materials in a fairly realistic fashion. The goal is not to develop truly realistic models, which in many cases will be too complicated to be useful, but to provide baseline minimal models that serve as anchors for analysis of experiments and further theoretical work. An important point is that the simplest versions of Heisenberg, Hubbard, and other familiar models are often not adequate for this purpose in *5d* oxides and *f*-electron compounds. Of course, the minimal models to be constructed, just as for better-studied correlated materials, cannot be solved reliably in most cases. But, since the resulting models often have not been studied before, it is possible and valuable to make the simplest statements about their behavior (*e.g.* in tractable limits).

Along these lines, focusing on $R_2Ir_2O_7$ pyrochlore iridates (with R a lanthanide), we studied the role of *f-d* exchange coupling between itinerant *5d* electrons and localized *4f* moments. These are novel "Kondo-lattice-like" systems where both the itinerant carriers and local moments are strongly spin-orbit coupled, and it will be interesting to explore other similar systems in the future. We focused on the Ising part of the *f-d* exchange (which is the only allowed dipolar exchange for non-Kramers *f*-moments), which favors magnetic order that in turn can help to stabilize the Weyl semi-metal phase on the Ir sublattice.

Also in $A_2B_2O_7$ pyrochlores, we realized that strong spin-orbit coupling can lead to a novel type of Kramers doublet for which the Kramers pseudospin is time-reversal odd (as it must be), but does not transform like a magnetic dipole under space group. Instead, the pseudospin has mixed dipolar-octupolar character. This is distinct from the j_{eff}=1/2 doublets that occur in iridates, which have dipolar pseudospin.

Dipolar-octupolar (DO) doublets can occur for $5d^1$, $5d^3$ and various *4f* ions with D_{3d} site symmetry, for instance both the A and B sites in the pyrochlore structure. In fact, there is evidence DO doublets occur for the *f*-moments in A=Nd, Dy pyrochlores. We showed that the most general symmetry-allowed spin exchange Hamiltonian for DO doublets on the pyrochlore lattice is the surprisingly simple

spin-1/2 XYZ model. This model supports two distinct quantum spin ice phases, one of which is a novel "octupolar" quantum spin ice that we identified for the first time.

Beyond these efforts, we collaborated with the Dessau group (ARPES experiment) at Boulder, focusing on understanding the effect of Rh doping in $Sr_2Ir_{1-x}Rh_xO_4$. In particular, we proposed a simple mechanism by which Rh doping may lead to the observed hole doping of the Ir *5d* states.

Future plans

Ultracold alkaline earth atoms

Our earlier theoretical results on alkaline earth atom (AEA) Mott insulators, combined with continued efforts of experimental groups pursuing many-body physics of AEA in optical lattices, highlight the need for reliable information on the properties of realistic models of AEA systems. Such information is difficult to obtain, as even the SU(N) Heisenberg model for the simplest square-lattice AEA Mott insulator has a sign problem in quantum Monte Carlo (for N > 2). Moreover, the large Hilbert space makes exact diagonalization and density matrix renormalization group calculations challenging. We are currently addressing this issue by carrying out high-order high-temperature series expansion calculations for the SU(N) Heisenberg model. This approach can identify finite-temperature phase transitions, and is thus well-suited to search for the CSL, which spontaneously breaks time reversal and has a finite-temperature Ising phase transition. In addition, state of the art experiments on AEA Mott insulators are still at very high temperatures, so our calculations will provide useful quantitative information for current and near-future experiments.

Other ongoing work focuses on AEA Hubbard systems in artificial magnetic fields. Such magnetic fields provide a source of explicit time-reversal breaking, and can help to favor CSL ground states. In addition, the CSL in such systems arises near the Mott transition, where energy and temperature scales are higher than deep in the insulating phase.

Correlated electron materials with strong spin-orbit coupling

In light of our results on DO doublets in pyrochlores, in the coming year we plan to further develop this direction by study of Nd pyrochlores, and via a search for other systems that may support DO doublets or other novel spin-orbit-induced degrees of freedom. In addition, inspired by our work, very recently Melko and co-workers

found evidence via quantum Monte Carlo simulation for a Z_2 spin liquid phase dubbed "quantum kagome ice," in a model of DO doublets on the kagome lattice [1]. We are currently undertaking a theoretical study of this model, in order to shed more light on the quantum Monte Carlo results.

In addition, we are pursuing a new collaboration with the Reznik group at Boulder (neutron, x-ray and Raman scattering experiments). The focus is on understanding selection rules observed in electronic Raman spectroscopy of Sr_2IrO_4.

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(Aug. 2012 – 2014)

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Theory of Novel Superconductors

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Project Scope

The research in this program is devoted to series of problems related to electron pairing, magnetism, and disorder in unconventional superconductors. Studies are directed towards studies directed towards understanding themicroscopic 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. 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.

Recent Progress

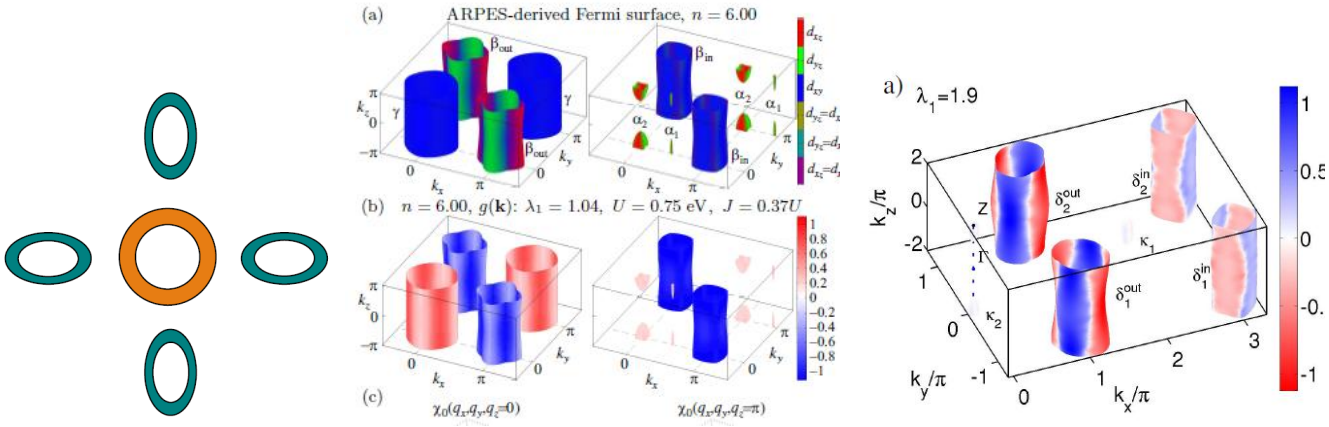

Fig. 1 (Left) Cartoon of $s_{+/-}$ -wave state. Color indicates sign of superconducting gap Δ. (Middle) (a) inner and outer sheets of the Fermi surface; color indicates d-orbital character as in legend; (b) s-wave LiFeAs gap function from theory for parameters in Hubbard – Hund Hamiltonian as shown. (Right) d-wave pairing function in KFe_2Se_2.

THEORY OF SPIN FLUCTUATION PAIRING IN IRON PNICTIDE SUPERCONDUCTORS

Calculations of the superconducting gap and T_c are performed within the Random Phase Approximation (RPA) using DFT-derived 10- and 16-orbital 3D tight-binding models, and Hubbard and Hund's rule interactions on each Fe site. Systems studied recently include LiFeAs, which is unusual for a lack of nesting, and disagreement of angle-resolved photoemission spectroscopy (ARPES) measurements of hole Fermi surfaces with density

functional theory (DFT) calculations. We therefore collaborated with the Dresden ARPES group to fit a band structure to their data, and used it as an input to the calculation of the pairing function, Fig. 1, concluding that a "conventional" $s_{+/-}$ pairing state was likely.

The system KFe_2Se_2 is of great current interest since according to ARPES experiments it has no hole pockets, so that the scenario based on Fig. 1(Left) is apparently inadequate. Indeed in our calculations (Fig. 1 (Right)), we find that the system has d-wave pairing. The 122 symmetry requires quasinodes on the Fermi surface, as seen in the figure, due to hybridization of the electron bands. Work is continuing to improve the method by including states away from the Fermi level and additional scattering processes.

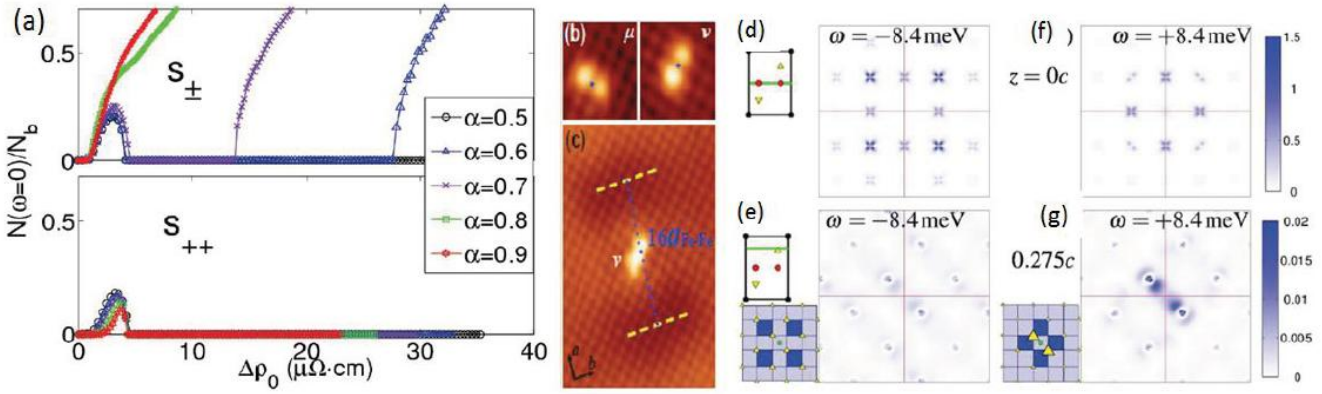

Fig. 2. Novel aspects of disorder in FeSC. a) Top: Fermi level density of states $N_b(0)$ on the band with gap nodes in a nodal $s_{+/-}$ state for various values of the ratio α of inter- to intra-band scattering. Bottom: same, but for s_{++} state. b) ``Geometric dimers" on the surface of FeSe of two different orientations from Song et al PRL 2012. c) larger scale topographic image showing geometric dimer inside ``electronic dimer" structure. d-g): BdG-Wannier results for LDOS of pointlike defect in FeSe of strength 5eV . d,f) Cut through Fe-plane at +/- 8.4 meV. e,g) cuts through plane above upper Se site, same energies. g) shows geometric dimer signature.

THEORY OF DISORDER EFFECTS IN IRON-BASED SUPERCONDUCTORS

Even after several years of intensive study, there is relatively little direct evidence for sign-changing order parameters predicted by theories of pairing due to repulsive electronic interactions. Some theoretical work (Kontani) suggests that orbital fluctuations are important in these systems, and lead to conventional s_{++} symmetry pairing. The critique provided by these alterative approaches includes the claim that impurities are observed to suppress T_c more slowly than one would expect in a system where the order parameter changed sign. To counter this claim, we performed explicit calculations of T_c relative to an experimentally observable measure of disorder, the residual resistivity change, and showed that "slow" suppression observed in transition metal substitutions is quite possible if interband scattering is weak. We also showed that if the s_{+-} order parameter has nodes, a strange evolution of the low-energy quasiparticle structure is possible, whereby the residual DOS at the Fermi level initially increases, then vanishes, then reappears as bound states are formed -- only if the system has average $\langle\Delta\rangle$ of different sign on different bands. This behavior has now been

observed in the magnetic penetration depth of electron-irradiated samples of $BaFe_2(As_{1-x}P_x)_2$ by the Kyoto group, with whom we are actively collaborating.

Recently we developed a method to incorporate the Wannier function information used in the construction of tight-binding models (but discarded in Bogoliubov-de Gennes (BdG) calculations) to reconstruct high-resolution theoretical STS images. Fig. 2 d)-g) shows results for a strong impurity in FeSe which gives rise to a geometric defect structure in the LDOS above the Se atoms closest to the surface. This method takes into account tunneling "filter" effects which have been discussed elsewhere. In terms of both symmetry and higher spatial resolution, the result obtained with the method represents a qualitative improvement over conventional BdG investigations, and opens a new window on the theoretical analysis of atomic scale phenomena in superconductors.

Future Plans

- Studies of pairing in systems with strong residual correlations

Comparison of Fermi surfaces and electronic structure with ARPES suggests that some of the Fe-based superconductors, particularly the chalcogenides, are more strongly correlated thatn the 122 pnictides. This is a priori problematic for our methods, which in the form used until now have been based on the DFT Fermi surface. We have pursued two avenues to address this problem: on one track we simply assume a Fermi surface like that found by ARPES and solving the RPA equations for the superconducting state. In parallel, we have begun testing methods to include correlations by performing LDA+DMFT calculations as input to the RPA pairing, as well as going beyond RPA in calculating both spin dynamics and pairing. We will focus on the fascinating FeSe system, both pressure dependence in bulk crystals and the new high-T_c monolayer systems on strontium titanate substrates.

- Superconductivity and magnetism at the interface of complex oxides

One of the fascinating aspects of LaO/STO interfaces is the recent discovery of robust magnetism persisting to high temperatures whose origin is still unclear. First principles studies have suggested that it is possible to induce a magnetic state at interfaces and surfaces of otherwise nonmagnetic titanates by introducing defects such as oxygen vacancies. We will investigate the effects of disordered O vacancies in this system, utilizing the Wannier function-based disorder method we have applied to Fe-based systems. This will involve extending the method to handle spin-polarized states, which, while straightforward, has not been attempted before. Initial goals will include the calculation of the effective doping of the system due to O vacancy disorder and the determination of the location of the magnetic states relative to the interface. Similar calculations will be performed for FeSe/STO interfaces, where similar questions of doping exist and could be vital to understanding possible 100K+ critical temperatures claimed.

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Title: Topological states in low dimensions

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Project Scope

Many remarkable phenomena in two dimensions, such as the fractional quantum Hall effect (FQHE), topological insulators, anomalous quantum spin Hall effect, Majorana modes and Chern insulators, have topological underpinnings. A general topological classification serves as a useful guide but does not tell us under what conditions the states would occur, and what interesting properties of these states go beyond topology. My goal has been to investigate the experimental realizability of various topological states of matter. This has required detailed microscopic calculations, as well as close collaboration with experimental colleagues. The topics of interest include the physics at the edge of a FQHE state, rapidly rotating ultra-cold atoms, signature of fractional braid statistics, FQHE of composite fermions and of two-component bosons. We have made progress on some of these topics. In collaboration with experimental colleagues at Columbia, we have identified a small skyrmion in the excitation spectrum in the vicinity of the 1/3 state. In collaboration with experimental colleagues at Princeton, we have shown that spin phase transitions are a very sensitive probe of the effect of Landau level mixing. We have also performed theoretical calculations that show that the edge of the 5/2 FQHE is ``reconstructed" for the experimental parameters. Our current research focuses on certain concrete ideas that we believe should make a direct observation of fractional statistics possible in rotating cold atom systems. In addition, we are exploring the possibility of creating a Fermi liquid metal in a system of interacting bosons in two dimensions. We are also in the process of creating a comprehensive catalog of all FQHE states that we can envision at the moment for multi-component systems, which should be very useful for the analysis of FQHE experiments in graphene as well as for identifying new phenomena.

Recent Progress

Here is a brief description of topics (excluding the work that has already been published, listed below) on which have made recent progress.

Edge reconstruction in FQHE: It has been widely believed that the edge of a FQHE state provides a window into its topological structure. In particular, it has been

predicted that the edge exponent (e.g., the power law characterizing the long distance behavior of the equal time Green function along the edge) is quantized, and its value contains information about the topology of the bulk state. We have studied the edge physics of the $\nu=5/2$ FQHE state. We perform calculations in a semi-realistic setup with positive background charge at a distance d, by exact diagonalization both in the full Hilbert space (neglecting Landau level mixing) and in the restricted Pfaffian basis of edge excitations. Our principal finding is that the 5/2 edge is unstable to a reconstruction except for very small d. In addition, the interactions between the electrons in the second Landau level and the lowest Landau level enhance the tendency toward edge reconstruction. We identify the bosonic and fermionic modes of edge excitations and obtain their dispersions by back-calculating from the energy spectra as well as directly from appropriate trial wave functions. We find that the edge reconstruction is driven by an instability in the fermionic sector for setback distances close to the critical ones. We also study the edge of the $\nu=7/3$ state and find that edge reconstruction occurs here more readily than for the 1/3 state. Our study indicates that the 5/2 and 7/3 FQHE edge states are reconstructed for all experimental systems investigated so far and thus must be taken into account when analyzing experimental results. We also consider an effective field theory to gain insight into how edge reconstruction might influence various observable quantities.

Composite-fermion trions in the FQHE: In collaboration with the group of Aron Pinczuk at Columbia and A. Wojs in Wroclaw, Poland, we have identified a new kind of bound state in the excitation spectrum in which three composite fermions form a bound "trion." Certain low lying spin excitations in the lowest Landau level at fillings close to filling factor $\nu=1/3$ revealed in light scattering experiments are interpreted as positively or negatively charged composite-fermion (CF) trions, created when a photo-excited CF particle-hole pair forms a bound state with a pre-existing CF particle (for $\nu>1/3$) or CF hole (for $\nu<1/3$). This identification is supported by an excellent agreement between the calculated and the observed binding energies, and by the disappearance of the mode for $\nu>1/3$ when a transition occurs, upon an increase in the Zeeman energy, from a partially to a fully spin-polarized state. The spectroscopy of trion bound states serves as a sensitive tool for investigating the interaction between composite fermions, which is relevant to the formation of new FQHE states in this filling factor region.

Spin-Polarization of Composite Fermions and Particle-Hole Symmetry Breaking: One of the consequences of Landau level mixing is particle-hole symmetry breaking, which can be incorporated as a three-body interaction term. This symmetry breaking is believed to select one of two candidates, namely the Pfaffian and the anti-Pfaffian wave functions, at filling factor $\nu=5/2$. In collaboration with the experimental group of M. Shayegan (Princeton) and A. Wojs, we have showed that the location of spin transitions is very sensitive to Landau level mixing, and thus can serve as a useful probe into it. The experimenters have studied the critical spin-polarization energy (E_Z) above which FQHE states in two-dimensional electron systems confined to symmetric GaAs quantum wells become fully spin-

polarized. In systems with comparable electron layer thickness, E_Z for fractional states near Landau level filling $\nu=1/2$ is about twice larger than for their hole partners near $\nu=3/2$, suggesting a broken particle-hole symmetry. We have carried out detailed calculations to incorporate Landau level mixing through an effective three-body interaction, as well finite layer thickness. We have showed that these calculations capture certain qualitative features of the experimental results, but also demonstrate the deficiency of the perturbative approach for parameters relevant to typical experiments.

Possible realization of a chiral p-wave paired state in a two component system: There is much interest in the realization of systems with chiral p-wave pairing in two dimensions, because these are believed to support Majorana modes inside vortices. In particular, the so-called Pfaffian and anti-Pfaffian wave functions are believed to provide ideal platforms to look for this physics in two dimensions. While it is believed that the 5/2 FQHE is described by one of these states, the quantitative comparison is not entirely convincing. In a collaborative work with S. S. Mandal, we have considered a system of unequal number of spin-up and spin-down composite fermions and found theoretical evidence that, under certain conditions, the screened interaction between the minority spin composite fermions is such as to produce an almost exact realization of p-wave paired state described by the so-called anti-Pfaffian wave function. We have estimated the parameter regime where this p-wave paired state can be realized.

Future plans

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

Proposal for a direct measurement of fractional braid statistics in cold atom systems: The idea of fractional braid statistics is old but no convincing observation of it has yet been made. The statistics of bosons or fermions manifests through even or odd relative angular momentum of a pair. We have shown recently (a manuscript is under preparation) that a pair of ``impurity atoms" in a FQHE state possesses, effectively, a fractional relative angular momentum, which is a direct manifestation of fractional braid statistics. We propose that the fractionalization of the angular momentum can be detected directly through the measurement of the pair correlation function in rotating ultra-cold atomic systems in the FQHE regime. Such a measurement will also provide direct evidence for the effective magnetic field, resulting from Berry phases arising from attached vortices. We believe that this has the potential to provide a convincing demonstration of fractional braid statistics, and the experimental group of Prof. N. Gemelke at Penn State is currently working on an implementation of this experiment. We plan to work closely with them.

FQHE in multi-component systems: The observation of FQHE in graphene has opened the possibility of FQHE in multi-component systems. The problem of FQHE in the presence of two spin components has been studied previously, and we will perform a comprehensive study of various possible states when several components

are present. The goal will be to make precise predictions that experimentalists can employ in the analyses of their experiments in these systems.

Emergent Fermi liquid metal in a system of interacting bosons: We all know of cases where bosons appear in a system of interacting fermions (e.g. Cooper pairs). Some examples are known where fermion-like objects appear in a system of interacting bosons or spins. Recently, my (outgoing) student Yinghai Wu has made a good case, numerically, that a system of two-component bosons in a magnetic field can produce an emergent Fermi liquid metal. We plan to explore this possibility in greater detail, and, in particular, think about the experimental manifestations of such a metal.

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Network for ab initio many-body methods: development, education and training

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Jeff Greeley, Purdue University
Miguel A. Morales, Lawrence Livermore National Laboratory
Luke Shulenburger, Sandia National Laboratory

Project Scope

This project links the developers of ab initio many-body electronic structure methods, especially quantum Monte Carlo (QMC) methods, and the developers and users of the open-source QMC package QMCPACK[1] to build a next-generation QMC framework that enables science critical for DOE-BES missions and accelerates discovery of advanced materials. The project specifically aims to support QMC methods development and QMC applications, to foster the collaborations among the developers and users of QMCPACK, and to educate and train new generations of computational materials scientists in the US. The intended outcomes include advanced software, efficient workflows, and data repositories, as well as applications of the collaboratively developed methods and software in three areas: (i) heterogeneous catalysis of metallic nanoclusters and nanoparticles, (ii) defect formation, energetics and effects on materials properties, and (iii) phase transitions and properties of materials under pressure.

Recent progress

In order to establish a foundation for future methods development and to help establish standards for databases of QMC simulations, we have performed systematic benchmarks of QMC calculations for a wide range of systems. This includes calculations for a survey of solid-state systems[2], bulk water[3], high-pressure hydrogen[4], and van der Waals interaction dominated materials[5]. The work is enabled by a large INCITE calculation which enables careful and systematic studies of systematic errors such as finite size effects and time step errors, which has historically been prohibitively computationally expensive. The calculations include properties such as lattice constants, bulk moduli, and interaction energies, which together enable a critical assessment of the "standard recipes" for QMC simulation.

Overall our calculations indicate a systematic and globally high accuracy for current QMC methodology when compared with density functional theory (DFT) results. To make further improvement for light element systems will require reduction in the nodal error of the wavefunctions by, e.g., orbital optimization or the extensive use of multideterminants. For heavier systems, such as the late d-block elements used in catalysis, our unpublished calculations – which include equations of state as well as cluster calculations – indicate that additional developments in pseudopotential construction are desirable.

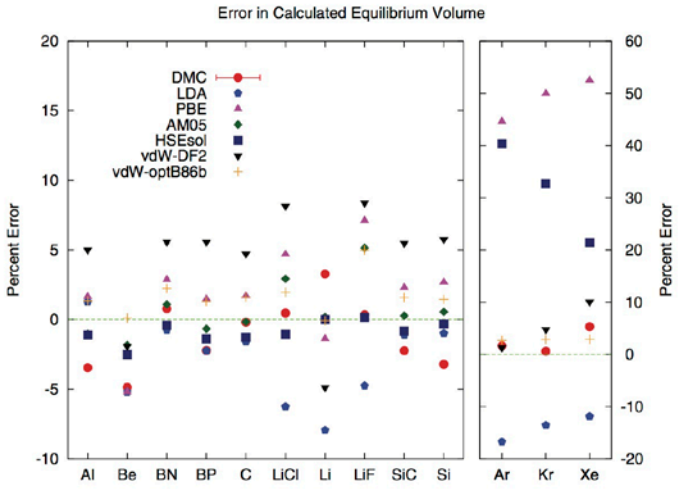

Figure 1: Percentage error in the calculated equilibrium volumes from each of the different theories as compared to experiment. The figure is separated into two panels, one showing the noble gases and one for the other materials because of the disparity in the scales of the error. From [2].

To illustrate the current level of accuracy for solid-state materials we show, Fig.1, the error in the volume calculated[2] using trial wavefunctions with a nodal surface defined by a single determinant of LDA orbitals. This level of theory is sufficient to provide a simultaneous high accuracy for both van der Waals, metallic, ionic, and covalent materials. However, for specific classes of materials some hybrid functionals can be more accurate. Greater accuracy requires the determinants to be optimized.

To illustrate the role of QMC in informing the use of other electronic structure methods, in Fig. 2 we show an application of QMC to atomic hydrogen. This system undergoes a metal-insulator transition with electronic correlations around the transition that are a difficult challenge for electronic structure methods. Using QMC we are able to compute the location of the transition, identifying it as continuous. This is in close agreement with recent G_0W_0 calculations, and the agreement could be further improved by small changes in the U value used in these calculations to improve the DFT starting point and density.

QMC Training Program 14-18 July 2014 – We held a 5-day training program on fundamentals and applications of QMC, with 33 attendees, including students, postdocs, and 1 industrial representative. We received approximately 85 applications for the ∼30 places available. A complete set of lectures and lab materials is now available online[7]. To further increase the accessibility of QMC methods and ease adoption of QMCPACK, all lectures were recorded and will shortly be made available online. After we have fully analyzed the feedback from attendees, we expect to organize another QMC workshop or training in 2015. The newly developed “project suite” automation tool, which can fully automate the DFT through to QMC calculations, was popular in the labs. This suite significantly reduces the degree of human supervision required to perform QMC calculations compared to the historic, burdensome norm. It has permitted postdocs with a

background in electronic structure to transition to using QMC over only a few months.

QMCPACK code release, website and documentation – To increase the user accessibility of QMCPACK we have developed a new website[1] with linked documentation, and made a public release of the code. New releases are expected every 6 months or sooner. In addition to improving the documentation, code, and tools as a result of training feedback, we are developing an extensive test and validation suite for QMCPACK. A significant future focus is the adoption of continuous integration to ensure the quality and validity of the code.

Future plans

To extend our current work[2, 3, 4, 5, 6, 8, 9, 10] we intend to focus on developments that improve the accuracy of standard QMC calculations via improved wavefunctions and pseudopotentials for the specific areas of catalysis, defects, and high-pressure. We will improve the accessibility and practical utility of the QMC method via improvements to the QMCPACK package (emphasizing testing and documentation), and via defined data formats, reproducible workflows, and databases.

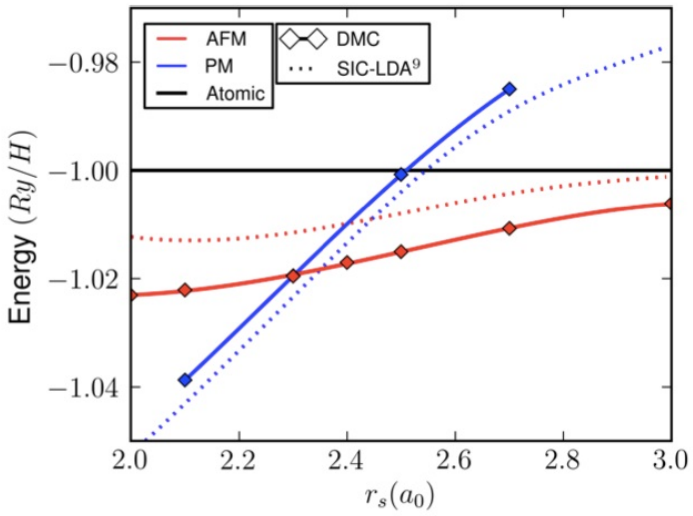

Figure 2: Energy per atom in Rydberg for BCC hydrogen in the anti-ferromagnetic, and paramagnetic phases. The diamonds and solid line are DMC results. The error bars are smaller than the symbols. The anti-ferromagnetic and paramagnetic energies at $r_S = 2.3$ are coincident. The energy of the anti-ferromagnetic phase asymptotes to the atomic limit as $r_S \rightarrow \infty$. From [6].

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Emergence of High Tc Superconductivity out of Charge and Spin Ordered Phases

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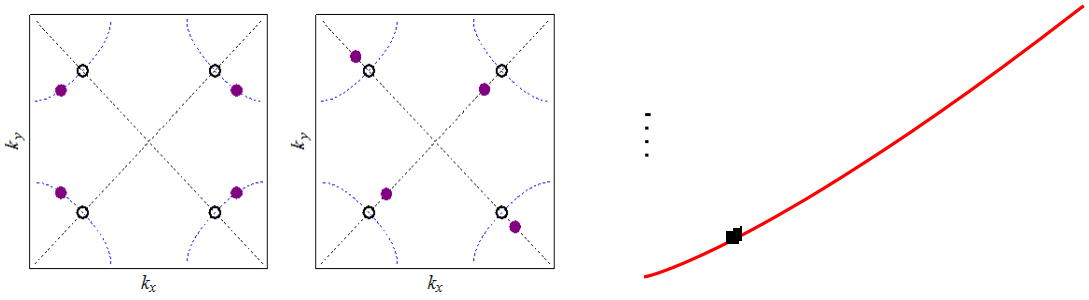
Project Scope

Recent evidence of new forms of charge and spin orders in cuprate largely demystified the psuedogap region, and puts us in a moment of opportunity. The scope of this project is to investigate the mechanisms and roles of charge/spin orders in two classes of high Tc superconductors: I. cuprates and II. Fe-based superconductors(Fe-SC's). Our approach is a symmetry-guided "middle-up/down approach": applying symmetry and quantum field theory based perspective to experimental data and using the results as input to microscopic models that will be studied through a combination of numerical methods. The theoretical advances will be in synergetic relation with rapidly developing experimental discoveries on the subject.

Recent Progress

How quantum critical fluctuations affect penetration depth:

Recent experiments found several families of unconventional nodal superconductors near putative quantum critical points to show anomalous super-linear temperature scaling of low temperature (T) penetration depth (PD). Then a natural question is what is the nature of the quantum critical point, if any, that could result in the observed apparent anomalous scaling of PD. Here we note that the type of quantum critical fluctuations that can affect the T-dependence of the PD are limited to meet two conditions:1) they should carry zero momentum $\mathbf{Q}$=0 and 2) they should shift the position of the nodes. Carrying out a perturbative renormalization group study for the solvable problem of two-dimensional superconductors with point nodes (Figure 1 (a-b)), we showed that such quantum critical fluctuations result in logarithmic corrections to the T-dependence of PD[1]. We further show that although the apparent scaling exponent due to such logarithmic correction is non-universal, fluctuation of the nodes along the Fermi surface would cause sublinear scaling while that away from the Fermi surface would cause superlinear scaling. Our results point to diagonal nematic quantum critical fluctuations as possible source of the observed apparent superlinear scaling of PD (Fig.1 c).

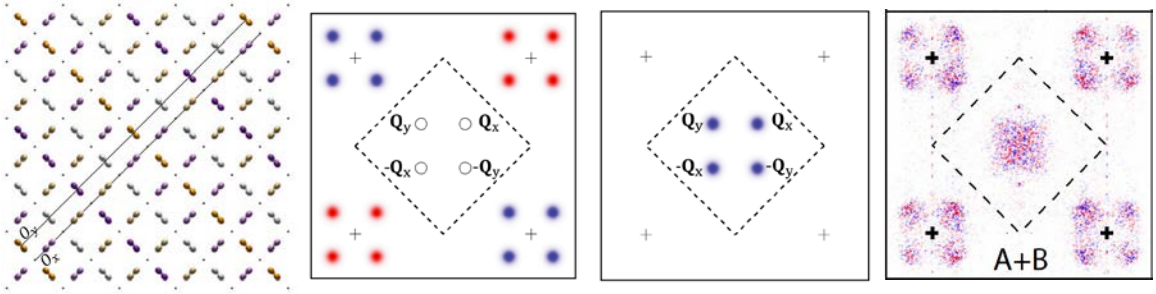


(a) (b) (c)

Figure 1. Effect of Q=0 quantum phase transition and critical fluctuations. (a) and (b) shows how axial nematic (a) and diagonal nematic (b) orders shift the position of nodes in d-wave superconductor. (c) Comparison between measured and calculated temperature dependence of the penetration depth. The calculation was done for diagonal nematic quantum critical point.

Identification of d-form factor density wave in underdoped cuprates:

The key observation underlying this collaboration with J.C. Davis group [2] is the realization that the intra-unit-cell degrees of freedom native to CuO plane implies three inequivalent form factor components in the finite ***Q*** density waves. In Fourier space d-form factor component of the density wave amounts to shifting ***Q=0*** intra-unit-cell nematic to finite ***Q***. In real space the pattern involves the $O_x(r)$ and $O_y(r)$ sublattice images exhibiting a relative phase of π (Fig 2a). The comparison between the Fourier transform of d-form factor component (Fig 2b) and that of s-form factor component (Fig 2c) density wave and that of the scanning tunneling spectroscopy (STS) data (Fig 2d) shows dominance of the d-form factor component in the data. The robustness of the d-form factor at short distance scales suggests microscopic interaction that promotes d-form factor.

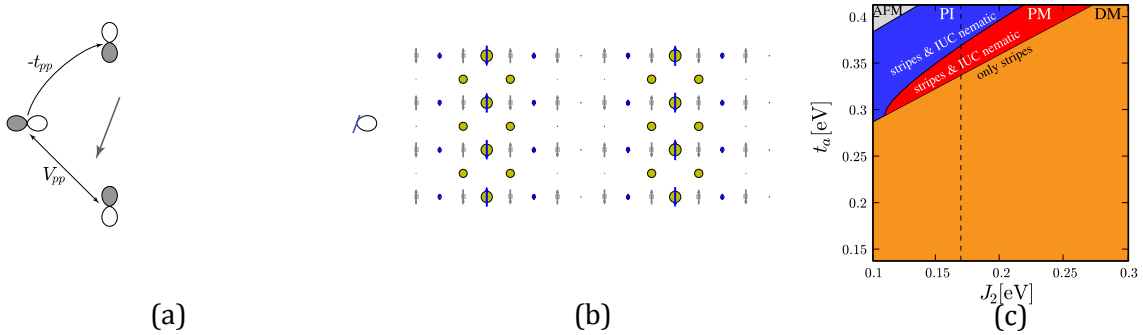


(a) (b) (c) (d)

Figure 2. (a) d-form factor pattern. (b) Fourier transform of d-form factor density wave. (c) Fourier transform of s-form factor density wave. (d) Fourier transform of the $O_x(r)$ and $O_y(r)$ STS data [2].

Nematic and spin-charge orders driven by hole-doping a charge-transfer insulator:

Recent developments in diverse phenomenology of broken-symmetry states raise the question whether a thematic understanding is attainable. We studied a three-band model of the CuO2 plane with Kondo-type exchange couplings between doped oxygen holes and classical copper spins variationally(Fig.3a). Two main findings are 1) that various ordered phases are all accessible microscopically within the model (Fig 3b), 2) many symmetry-breaking patterns compete with energy differences within a few meV per Cu atom to produce a rich phase diagram (Fig 3c). These results indicate that the diverse phenomenology may arise from hole-doped frustration of antiferromagnetism. Further we established oxygen-oxygen repulsion promotes d-form factor observed in [2].



(a) (b) (c)

Figure 3. (a) Three band model of CuO2 plane. (b) Metallic charge stripe exhibiting intra-unit-cell nematic centered at anti-phase domain wall of spin stripe. (c) Phase diagram showing insulating (PI) and metallic (PM) parallel stripes as well as diagonal stripe(DM).

'Fingerprint' of Antiferromagnetic Spin-fluctuations in Iron-Pnictide Cooper Pairing:

Cooper pairing in the iron-based high-T_c superconductors is often conjectured to involve bosonic fluctuations. Among the candidates are antiferromagnetic spin fluctuation and *d*-orbital fluctuations amplified by phonons. Any such electron-boson interaction should alter the electron's 'self-energy', and then become detectable through consequent modifications in the energy dependence of the electron's momentum and lifetime. In Ref.[4] we introduced a novel theoretical/experimental approach aimed at uniquely identifying the relevant fluctuations of iron-based superconductors by measuring effects of their self-energy. We used innovative quasiparticle interference (QPI) imaging techniques in LiFeAs to reveal strongly momentum-space anisotropic self-energy signatures that are focused along the Fe-Fe (interband scattering) direction, where the spin fluctuations of LiFeAs are concentrated. These effects coincide in energy with perturbations to the density-of-states $N(\omega)$ usually associated with the Cooper pairing interaction. We showed that all the measured phenomena comprise the predicted QPI "fingerprint" of a self-energy due to antiferromagnetic spin-fluctuations, thereby distinguishing them as the predominant electron-boson interaction.

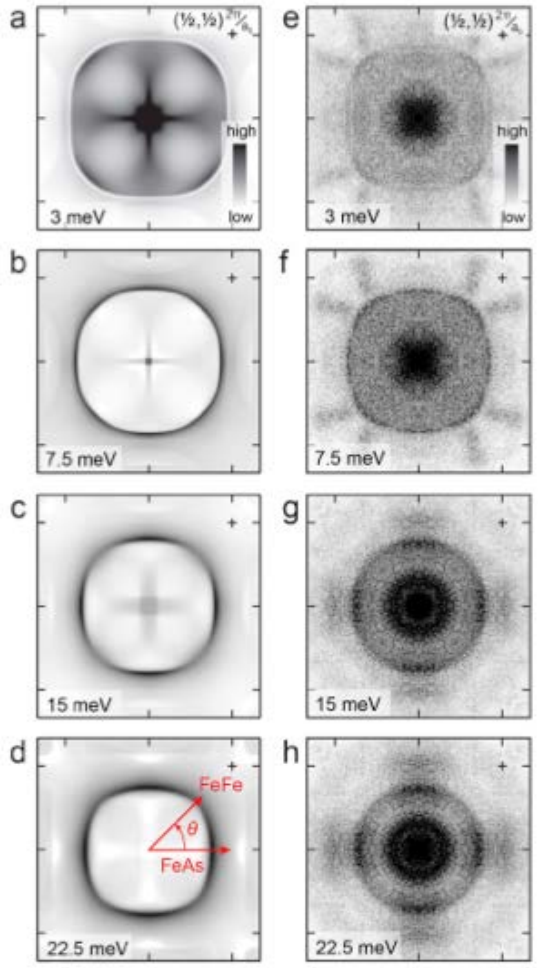


Figure 4. Comparison between the predictions of the anti-ferromagnetic fluctuation driven self-energy effect (left) and the measured (right) quasi-particle interference spectroscopy. [4]

Future Plans

In the near term, we plan to build on our new understanding from the variational study of the three band Kondo type model and from synergetic interaction with Davis group to study the impact of the broken symmetry states and associated quantum criticality on the high Tc superconductivity. These include:

- **Effects of heterogeneous nematicity on the electronic structure of d-wave superconductor**: Although observed local ordering tendencies show short correlation lengths, understanding of implication of such short ranged order on superconductivity and spectroscopic information is lacking. Our hypothesis is that unconventional spectroscopic features such as energy dependent heterogeneity and Fermi arc can be caused by heterogeneous d-form factor ordering tendencies.

- **Explicit solution to the three-band Kondo model [3] combining exact diagonalization and MonteCarlo simulation**: The three-band Kondo model introduced in ref.[3] permits explicit solution when Monte Carlo study of the spin model and exact diagonalization of the fermion problem is combined. The variational study in Ref[3] was conducted as a stepping stone towards such explicit calculation which will be

computationally more costly for large enough systems that can support stripes. We will exploit the understanding of the phase space and the physical range of parameters we gained from Ref[3] to obtain exact finite temperature phase diagram of the model.

- **Investigation of the role of charge fluctuation at the Cu site in the three-band Kondo model [3]**: A key approximation made in the three band model introduced in Ref[3] is to suppress the charge fluctuation at Cu site and to treat the spin on Cu site classically. We plan to investigate the role of charge fluctuation and the possibility of associated Mott transition.

- **Study of commensuration effects in the density waves as detected by scanning tunneling spectroscopy**: The issue of commensurate density wave regions with discommensurations vs incommensurate density wave holds key to resolving the mechanism of the density waves. We plan to develop data analysis schemes to quantify the degree to which scanning tunneling spectroscopy data exhibit locally commensurate regions.

List of Publication

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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, transition metal dichalcogenides, Ir-based correlated spin-orbit coupled 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.

To properly investigate the short-range correlation and disorder effects, both are basically beyond the reach of current first-principles theories, we also develop new theoretical methods that allows including necessarily large length scale and systematic lowering of the energy scale of many-body description. Specifically, we developed a Wannier function-based, beyond-mean-field, non-perturbative treatment of disordered impurities and vacancies in real materials, capable of realizing the important disorder-induced localization that in many cases functionalizes the materials.

Recent Progress

First-principles method to treat disordered impurities in materials

Recently, we have developed a new first-principles method to treat disordered impurities in real materials. This symmetry-respecting Wannier function based method make use of the short-range nature of the impurity potential, and is exact in that in include all order of multiple scattering. This is thus superior to the state-of-the-art coherent potential approximation and any perturbation expansion. In particular, the method allows, for the first time, Anderson localization in the first-principles calculations. The applications of this new method to materials of current interest has lead to publication of four Phys. Rev. Lett, and are expected to revolutionize studies of important physical roles of the disordered impurities, especially in strongly correlated materials.

Effects of disordered impurities in Fe-based superconductors

We investigated several important issues regarding the doping effects of Fe-based superconductors. First, we clarified the widely discussed controversy concerning whether Co substitution of Fe doped the system with additional carriers. Our resulting disordered spectral function indicates clearly that while all the itinerant carriers conspire to accumulate additional density at the Co atom to screen the additional proton, no meaningful localization takes place and each Co substitution does dope the system with basically one more itinerant carrier.

Second, we looked into the puzzling observation of the appearance of heavily electron doped Fermi surface in the *undoped* "245" system that contains 20% Fe vacancy. By assuming some degree of Fe vacancy, our results in Fig. 1 demonstrate a strongly electron doped Fermi surface without actual doping. This beautiful demonstration of "violation" of Luttinger theorem results from an effective strong shift of the chemical potential, due to the large incoherent features in the spectral function originating from the strong repulsive potential at the Se atoms surrounding the Fe vacancy. The same principles and effects are expected in a wide range of materials with vacancy, as contrary to the common practice, most vacancies are very strong scatterers and cannot be treated perturbatively.

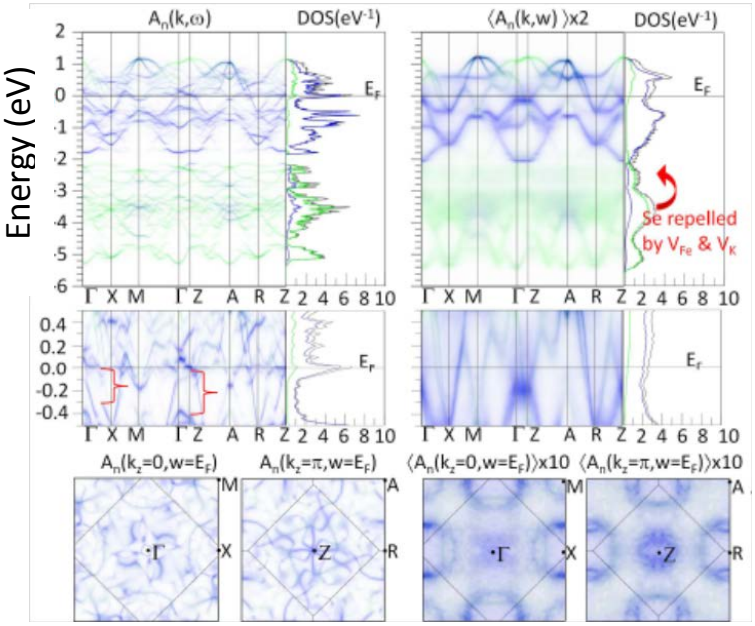

Fig. 1. Band structure (upper panels) and Fermi surface (bottom panels) of fully vacancy ordered (left panels) and disordered (right panels) $K_2Fe_4Se_5$. Even though the system is supposed to be undoped and should contains equal number of electron and hole carriers, the Fermi surface appears to be heavily electron doped. This is a clear demonstration of invalidity of Luttinger theorem in disordered systems.

Third, we investigated the remarkable resilience of superconductivity in Ru substituted Fe-based superconductors, up to 40% substitution. Considering Ru is much heavier than Fe, and thus is a strong scatterer, it is inconceivable that a sign-changing S_{+-} superconducting order parameter can survive such a large amount of substitution. Our analysis shows a perfect cancelation of strong on-site and off-site scattering near the chemical potential, explaining the resilience of the superconductivity and residual resistivity against such a high level of Ru substitution. It turns out that this might be the first realization of the theoretically proposed "superdiffusion" effect in real materials, which bypass the localization even in 1D to give metallic behavior.

Effects of alternating positioning of anion: one Fe vs two Fe picture

We clarify the confusing yet important issue of the alternating anion positioning surrounding the Fe atoms in the Fe-based superconductors. This breaks the translational symmetry of one-Fe unit cell and invalidates the 3D momentum as a good quantum number. We are one of the first to point out that the broken translational symmetry is in fact highly structured owing to the underlying "glide" translational symmetry. Specifically, the translation symmetry breaking potential only couples orbitals of opposite z-parity with respect to the Fe plane, leading to an unusual parity flipping un-folding of the electronic structure. Note that the symmetry breaking potential is not a weak perturbation, but rather of order of eV scale. This is obvious from our unfolded Fermi surface, which contains two incomplete electron pockets, rather than one strong and one weak complete pocket. This realization greatly facilitates the proper interpretation of ARPES and other spectroscopes and explains the lack of signal in certain part of the momentum space. Most significantly, we showed that the heavily discussed electron pockets are in fact only created due to such a alternating positioning.

Magnetic ordering and excitations of strong spin-orbit coupled iridates

We investigated several `spin-orbit Mott insulators' facilitated with strong spin-orbit coupling on the Ir 5d orbitals. First, in a series of collaborated studies with BNL X-ray group, we studied the novel Kitaev spin-liquid state related issues in the $(Li,Na)_2IrO_3$, and suggest the actual magnetic ordering in such a system. We also found that the ferromagnetic state is close in energy, indicating that the spin frustration is still relevant and that how to drive the system to the Kitaev spin liquid regime needs further investigation. Second, we studied the effects of noncubic octahedral distortion in Sr_3CuIrO_6, a model quasi-1D system in which the Ir 5d-5d excitation is dominantly local and relatively easy to be modeled thanks to its special crystal structure. Surprisingly, even for such a system with relatively weaker noncubic distortion, we found a strikingly large noncubic crystal field splitting comparable to the spin-orbit coupling, resulting in a strong mixing of the jeff=1/2 and jeff=3/2 states. In addition, we identified an unusual exchange anisotropy generating mechanism, namely, strong ferromagnetic anisotropy arising from spin-antiferromagnetic superexchange, driven by the alternating strong and weak spin-orbit coupling on the 5d Ir and 3d Cu magnetic ions, respectively. Our results point to unusual magnetic behavior to be expected in mixed 3d−5d transition-metal compounds and opens a new interesting research area.

Propagation of tightly bound excitons

We have been applying our symmetry-respecting energy-resolved Wannier functions to the study of *q*-dependent spectral weight in both X-ray and neutron scattering, and revealed the promising new utilization of large momentum scattering. This allows us to solve an important mystery concerning the missing 70% spectral weight in the neutron scattering of high-Tc cuprates. We have also developed the linear response theory of the LDA+*U* functional within the framework of time-dependent density functional theory, and applied it to the study of hybridization of Frenkel excitons in NiO, using Wannier functions as the basis. Recently, we further complete the theoretical framework by developing the first theory of propagation of local excitations within the density functional theory. By considering the tightly bound local particle-hole pair involving in a local excitation as one composite boson, we were able to define the two-particle kinetic kernel that describes the propagation and decay of the local excitations. This theory effectively integrates out the pair breaking fluctuation and offers a simple and intuitive picture of the propagation of local excitations. It also allows a separation of the non-local propagation from the local many-body problem, thus applicable to systems with strong local correlation. Furthermore, it is computationally much affordable than the typical perturbation theory, the so-called Bethe-Salpeter equation. Using the well-known tightly bound charge-transfer excitons in LiF as an example, we predicted three branches of excitons in LiF, and found that all three branches can be observed partially due to the hybridization between the longitudinal and transverse modes. These predictions are then clearly observed by our UIUC experimental collaborators.

Future Plans

- Methodology development related to disordered impurities in materials
- Effects of disordered impurities in Fe-based superconductors
- Impurity level and band gap bowing in doped semiconductors
- Fluctuating ferro-orbital order and degeneracy lifting in the spectral function
- Interplay of local and itinerant magnetic moments using the spin-fermion model
- Systems with large spin-orbit coupling and local Coulomb interactions
- Novel physics in mixed 3*d*-5*d* transition-metal compounds and superlattices
- Analytical structures of topological insulators and metals
- Strong binding description of high-T_c superconductivity

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Toward High-Accuracy Point Defect Calculations in Materials

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Project Scope

The goal of this project is to study point defects and related properties in materials systems, where the local density approximation (LDA) of density functional theory has significant shortcomings. Our main tool is the linearized muffin-tin orbital implementation of the quasi-particle self-consistent (QS) *GW* method. The advantage of this approach is that the self-consistent energy-averaged self-energy can be represented in a real- space basis set. This suggests a cut-and-paste approach, in which the self-energy for atoms far from the defect is obtained from a primitive cell calculation of the host while the corrections from atoms near the defect are taken from a relatively small defect containing supercell calculation. The possibilities of the LDA+U method for incorporating self-energy effects of the host in defect calculations are also explored. We are particularly interested in ionic and *d*-band systems in which the shortcomings of LDA are more pronounced. We realized that an important question for point defects is to what extent short-range correlation and long-range Coulomb potential screening effects can be separated. A closely related question is the role of lattice dynamics in screening localized excitations such as defect states and excitons. Our main focus has therefore turned from point defects to a broader investigation of *screening and lattice-dynamical effects on electronic structure.*

Recent Progress and Highlights

In year 1 of the project we realized that the method we had initially proposed to represent the self-energy of the host in terms of an LDA+U type ansatz with well-localized *U*-matrices did not work. The self-energy in *GW* contains intrinsically long-range terms, which cannot be represented by on-site *U* terms. Instead the new focus of our project has become how well QS*GW* itself applies to strongly correlated materials systems and what is the role of long-range *vs.* short-range screening and electronic *vs.* ionic screening. Below we describe two materials systems which highlight these questions before we return to the defect topic.

2D layered system V_2O_5: relation of screening to GW gap and phonons

Screening plays a key role in the *GW* method since it involves the screened Coulomb interaction $W=\varepsilon^{-1}v$. It has been pointed out in various recent papers that for 2D materials with ultra-thin few monolayer systems, screening can be very different from the bulk. Vanadium pentoxide (V_2O_5) provides an interesting test case for the study of screening and the validity of the QS*GW* method. It has a layered structure with weakly coupled 1D chains within the layers. It thus presents 1D as well as 2D aspects. The lowest, well separated, conduction band has 1D dispersion and can be expected to exhibit strong correlation effects due to its V-3*d* orbital character. We carried out a study of the electronic band structure, screening and phonons in this material in its bulk and monolayer version. In spite of the weak interlayer interactions, we found strong effects on both the band gap and phonons in this material. At the same time we found that the QS*GW* method overestimates the band gap significantly even for bulk. This points to an underestimate of the screening in the *W* by the random phase approximation used in calculating the polarizability within the *GW* method. We are looking for methods to overcome this by adding local on-site corrections for the *d*-electrons. Lany et al. [1] proposed adding a simple shift of the *d*-electrons. On the other hand, we plan to also test using a modified *W* for the on-site *d*-block of the self-energy Σ. What permits us in principle to do this is that the Σ can be represented in a real-space basis set of muffin-tin orbitals. Meanwhile, we found that while in LDA the monolayer and bulk systems show only a small change in band gap, the latter converges very slowly with the size of the vacuum region separating the monolayers in *GW*. In fact, the gap correction due to *GW* varies as *1/L* with *L* the size of the supercell in the direction perpendicular to the layers as shown in Fig. 1. This in turn is related to the similar dependence of the dielectric response function of the system. We found that the reduced dielectric screening in 2D also strongly affects long-range force cosntants and this ultimately leads to a blue-shift of some of the phonon modes. In the process, we clarified the interpretation of phonon related infra-red and Raman spectra in bulk V_2O_5 and predicted monolayer *vs.* bulk changes in the phonons. The phonon work was published (publication 3) while the band structure work is on-going. Another 2D system we have studied is MoS_2. In particular, we studied strain effects on the spin-orbit splitting in this material (publication 4)

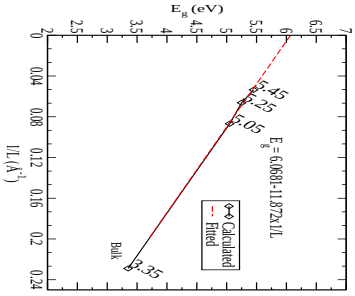

Figure 1: QS*GW* band gap of V_2O_5 bulk and monolayer as function of unit cell size perpendicular to the layers.

Halide perovskites: lattice dynamics and screening of excitons

Halide perovskites such as ABX_3 with X={I, Br, Cl}, B={Sn, Pb} and A=Cs or an organic molecular ion, such as methyl-ammonium (MA) $CH_3NH_3^+$, have recently

[1] S. Lany, Phys. Rev. B **87**, 085112 (2013)

attracted great interest as solar cell materials. We were already interested in the A=Cs, B=Sn family of these materials before this proposal started and were prompted by the recent interest in these materials to accelerate our work on them. We identified the origin of its unusual band structure, which has a strongly Sn-*s* like valence band maximum and Sn-*p* like conduction band minimum. This explains a number of its unusual properties, such as strong optical absorption, anomalous band gap deformation potential, etc. A question related to the main focus of this project is the influence of the lattice dynamics on the screening of the exciton. Should one take into account the phonon contribution to the dielectric constant in determining the exciton binding energy in the Wannier exciton theory or not? In other words, should one use the high-frequency or static dielectric constant? Our view on this is that it depends on the relative time scales of the relative motion of the electron and hole bound in the exciton and the ionic vibrational motions. The unusual circumstance we identified here is that the phonons have rather low frequencies because of the heavy atoms involved. It is thus not *a-priori* clear whether one should include their effect because they might be viewed as too slow to affect the exciton binding energy. We found that without phonon contribution the exciton binding energy is of the same order of magnitude as the highest phonons but the latter already change the dielectric constant significantly in terms of their Lyddane-Sachs-Teller factor and thus need to be included. Including phonon effects, the exciton binding energy becomes very low in apparent contradiction with experimental results. We were able to resolve this discrepancy by noticing that the observed photoluminescence is likely due to a defect bound exciton. This leads us to propose further study of defects in these materials in future work. Meanwhile we undertook a study of the phonons, proposed a new interpretation of the available experimental data and also studied the relations of soft-phonon modes to the phase transitions in these materials. In Fig. 2 we show the predicted infrared spectra for $CsSnI_3$. We find that the unusual circumstance of low phonon frequencies and a low hole mass leads to a significant LO-plasmon coupling even for relatively low carrier concentration. This work was submitted for publication. In Fig. 3 we show the phonon band structure, showing a soft mode related to the phase transitions occurring in this material.

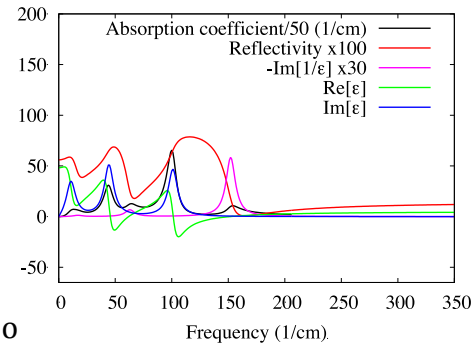

Figure 2: Phonon related spectra in $CsSnI_3$. Note that the highest LO mode seen in the loss spectrum $-\mathrm{Im}\ 1/\varepsilon$ also shows up strongly in absorption. The lowest TO mode (Im ε) on the other hand lies near a phonon DOS peak (see fig. 3) and this leads to broadening of this peak preventing its experimental observation.

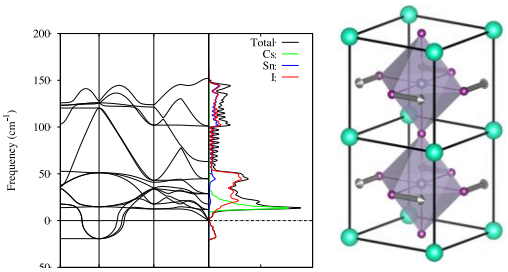

Figure 3: Phonon band structure of $CsSnI_3$: note the soft phonons between M and R corresponding to rotation of the octahedrons shown on the right.

Polarons and defect states in oxides

We have a strong interest in defect related conductivity in oxides. In the first year of this project we studied the possibility of p-type doping of ZnO using Nitrogen. The highlight of this work is that we found the N_2 molecule on a Zn-site to be a shallow acceptor and at the same time identified it with a known electron-paramagnetic center. (Publications 1 and 2.) In the second year, we started some studies of defects in complex perovskite oxides, such as $LaAlO_3$. In particular we studied the possibility of polaron formation within the LDA+U with *U* on O-*p* orbitals. By analyzing the orbital character of the bands we found a way to incorporate the host *GW* self-energy effects in terms of empirical LDA+U shifts and found that this has a strong effect on the nature of the defect states of the oxygen vacancy. This latter work is co-supported by an AFOSR project but the methodological aspects relate to the present project. Further work is required before publication.

Future plans

Recently, our collaborator on the methodology aspects, Mark van Schilfgaarde, has developed a self-energy "editor", which will allow us to return to our original goal of incorporating the host self-energy in defect calculations. It allows one to construct the supercell self-energy from the self-energy of the host primitive cell and to modify the near defect matrix elements. This provides us with the tool we needed to test our ideas on separating the host self-energy from the near defect self-energy effects. We plan to test this method extensively.

Publications

1. Identication of a N-related shallow acceptor and electron paramagnetic resonance center in ZnO: N_2^+ on the Zn site, W. R. L. Lambrecht and A. Boonchun, Phys. Rev. B 87, 195207 (2013)
2. Electronic Structure of Defects and Doping in ZnO: Oxygen Vacancy and Nitrogen Doping, A. Boonchun and W. R. L. Lambrecht, Physica Status Solidi B **250**, 2091-2101 (2013) **Editor's Choice and featured on back cover.**
3. Phonons and related spectra in bulk and monolayer V_2O_5 , C. Bhandhari and W. R. L. Lambrecht Phys. Rev. B **89**, 045109 (2014).
4. Strain effects on the spin-orbit-induced band structure splittings in monolayer MoS_2 and grapheme, T. Cheiwchanchamnangij, W. R. L. Lambrecht, Y. Song, and H. Dery, Phys. Rev. B **88**, 155404 (2013).
5. Lattice dynamics in perovskite halides $CsSnX_3$ with X=I, Br, Cl, Ling-yi. Huang and W. R. L. Lambrecht, submitted to Phys. Rev. B, June 2014.

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

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PROJECT SCOPE

The 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. Nanoscale systems exhibiting unique structures, organizations, stabilities, reactivities, dynamics, and response patterns which endow them with unique physical and chemical properties. These systems are made of varied constituent units and under differing conditions, including: (i) Gas-phase and surface-supported nanoclusters exhibiting structural isomerization transitions that gate their mobility and showing dynamic structural fluxionality that enables their nanocatalytic activity, including nano-catalyzed water splitting and generation of synthetic fuels. (ii) Nanocrystallites with superatom electronic-shell structure stabilities, self-assembled into ordered superlattices, and exhibiting collective response mechanisms to varying pressure and temperature conditions, and unique optical response and transport characteristics.

2. First-principles explorations of bottom-up growth mechanisms of graphene nanosystems and atomically precise graphene nanostructures, including segmented nanoribbons, sGNRs. Investigations (using electronic structure, Greens function transport and relativistic quantum field theory models) of topological effects in graphene nanostructures, including graphene-based topological insulators without spin-orbit coupling, and transport in atomically precise sGNRs.

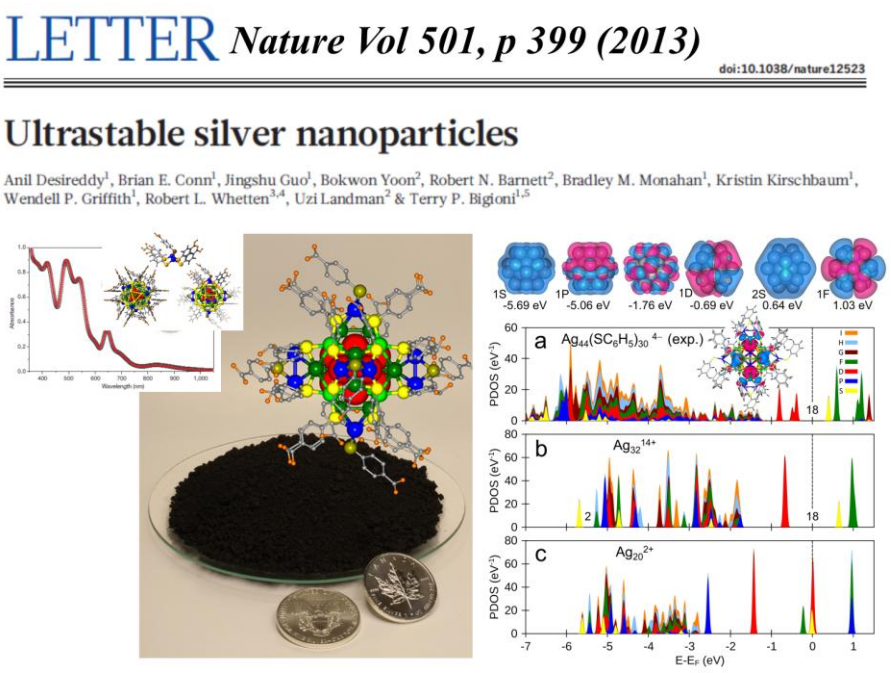
3. Computational explorations (using exact diagonalization) of the properties of confined electron and cold atom trapped systems exhibiting highly correlated states and spontaneous symmetry breaking; semiconducting, metal, and graphene quantum dots (QDs) at field-free conditions and under the influence of magnetic fields; studies of ultra-cold, tunneling-controlled, chemistry, involving development of non-Born-Oppenheimer methodology (quantum electrons and nuclei).

RECENT PROGRESS (see references, [P#], in the list of publications, below)

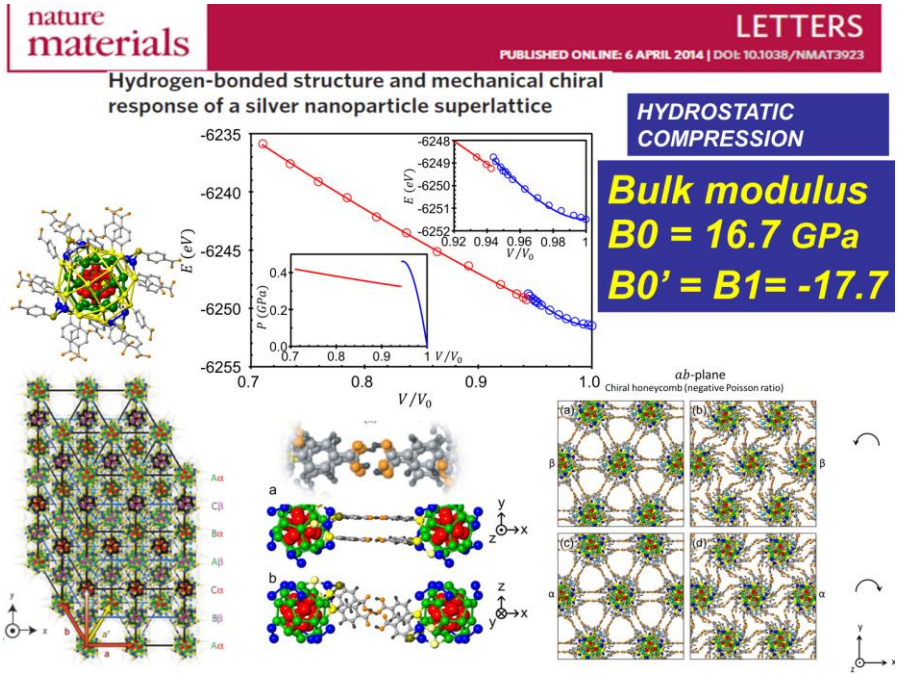
Ultrastable silver nanoparticles - atomic arrangement, superatom shell-structure [P7]

Noble metal nanoparticles have had a deep impact across a diverse range of fields, including catalysis, sensing photochemistry, optoelectronics, energy conversion, and medicine. ultrastable silver nanoparticles as a self-single-sized molecular product in exceptionally large quantities, with quantitative yield and without the need for size sorting. The stability, purity and yield are substantially better than those for other metal nanoparticles, including gold, owing to an effective stabilization mechanism. The particular size and stoichiometry of the product was found to be immune to variations in synthesis parameters. The unique chemical stability and structural, electronic and optical properties are understood using first-principles electronic structure theory based on an experimental single-crystal X-ray structure. Although several structures have been determined for protected gold nanoclusters, none has been reported so far for silver nanoparticles. The total structure of a thiolate-protected silver nanocluster reported here uncovers the structure of the silver thiolate protecting layer, consisting of Ag_2S_5 mounts. The stability of the nanoparticle is attributed to a closed-shell 18-electron configuration with a large energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (see projected density of states on the right in the figure), an ultrastable 32-Ag-atom excavated-

dodecahedral core consisting of a hollow 12-Ag-atom icosahedron encapsulated by a 20-Ag-atom dodecahedron, and the choice of protective coordinating ligands (see figure). The straight forward synthesis of large quantities of pure molecular product promises to make this class of materials widely available for future research & technological development.



Hydrogen-bonded nano-silver superlattice: Structure & mechanical chiral response



Self-assembled nanoparticle superlattice materials made of inorganic cores capped by organic ligands, of varied structures, and held together by diverse binding motifs exhibit size-dependent properties as well as tunable collective behavior arising from couplings between their nanoscale constituents. We reported [**P8**] the single-crystal X-ray structure of a superlattice made in the high-yield synthesis of Na_4Ag_{44}(p-MBA)$_{30}$ nanoparticles, and found with large-scale quantum mechanical simulations that its atomically precise structure and cohesion derive from hydrogen bonds between bundled p-MBA ligands (see Figure). We also found that the superlattice's mechanical response to hydrostatic compression is characterized by a molecular-solid-like bulk modulus B_0=16.7 GPa, exhibiting anomalous pressure softening (B0' < 0) and a compression-induced transition to a soft-solid phase. Such a transition involves ligand flexure, which causes gear-like correlated chiral rotation of the nanoparticles (see Figure). The interplay of compositional diversity, spatial packing efficiency, hydrogen-bond connectivity, and cooperative response in this system exemplifies **[P8]** the melding of the seemingly contrasting paradigms of emergent behavior 'small is different' and 'more is different'.

Graphene - beyond the constant-mass Dirac physics: Solitons, charge fractionization, and the emergence of topological insulators in graphene [P1-P3]

The scientific and technological potential for exploiting charge carriers and quasiparticles with relativistic behavior in tunable condensed-matter and atomic-physics systems is attracting much attention, with a remaining important question: whether quasi-one-dimensional graphene systems support exclusively Dirac-Weyl massless or constant-mass Dirac fermions, or they can induce relativistic-quantum-field (RQF) behaviors requiring the consideration of position-dependent mass terms, reflecting generalized underlying bosonic scalar fields. We have shown that planar graphene nanorings do indeed exhibit a rich variety of physics, ranging from sophisticated RQF regimes to more familiar cases of constant-mass fermions (both in the relativistic and nonrelativistic regimes). The emergence of these physical regimes depends on the specific combination of topological factors associated with modifications of the graphene lattice, such as the type of edge termination (i.e., armchair or zigzag) and the shape (i.e., hexagonal or trigonal) of the graphene ring.

In particular, the behavior found by us for the armchair hexagonal ring is reminiscent of the extreme relativistic regime describing zero-energy fermionic solitons with fractional charge in RQF theory and in the theory of trans -polyacetylene. This regime results from a consideration of a modified (generalized) Dirac equation with a position-dependent mass term . The behavior of the zigzag hexagonal ring resembles the low-kinetic-energy nonrelativistic regime of a lepton-like fermion having a rest mass larger than that of the electron. This behavior contrasts with the relativistic ones found for armchair rings, thus highlighting the compounded topological and edge-termination effects [P2].

In further work that integrates a RQF Lagrangian formulation with numerical tight-binding Aharonov-Bohm electronic spectra and the generalized position-dependent-mass Dirac equation we showed that in contrast to armchair graphene rings (aGRGs) with pure metallic arms, certain classes of aGRGs with semiconducting arms, as well as with mixed metallic-semiconducting ones, exhibit properties of one-dimensional nontrivial topological insulators [P3]. This further reveals an alternative direction for realizing a graphene-based nontrivial topological insulator through the manipulation of the honeycomb lattice geometry, without a spin-orbit contribution

Planned activities: 2014 – 2015

In addition to continuation of our current work (see Project Scope and Publications) we plan the following studies:

1. First-principles DFT simulations (collaborative experiments, TUM, Munich) on growth of graphene and nanostructures from adsorbed small molecules (e.g. ethene, C_2H_4) and precursors, catalyzed on metal surfaces (e.g. Rh(111)). Identification of intermediates and embrionic species underlying growth of graphene, including atomically precise graphene nanoribbons (APGNRs).

2. Investigations using DFT and tight-binding nonequilibrium Green's function calculations and a Dirac continuum model with topological-in-origin reflective mass-barriers, of conductance in APGNRS connected to either graphene or metal leads. Dependencies on the width of the GNRs exhibiting metallic or gapped spectra, and on edge termination (arm-chair and zigzag, with the former showing Dirac electron behavior and the latter Schrodinger-like characteristics) will be explored, including armchair/zigzag/armchair junctions. Explorations of local disorder effects.

3. First-principles DFT simulations (collaborative experiments, Ulm, Germany) of the mechanisms of oxygen exchanges between adsorbed water and skeletal oxygens in the recently X-ray-determined water-oxidizing center (WOC) of photosystem II, consisting of a near cubic $CaMn_3O_4$ cluster tethered to a fourth manganese atom through additional oxo bridges. Next, the pathways of water splitting and O-O bond formation, catalyzed by the WOC unit, will be

investigated theoretically (and explored experimentally). These investigations, starting from the individual, bare, metal-oxide, see **[P15]**, with incrementally added molecular complexity (attached electron and proton "molecular wire" ligands), are steps in a coordinated hierarchial approach to cluster-catalyzed water splitting and energy storage processes, aiming at an effective strategy for a materials design of man-made water splitting & storage system.

PUBLICATIONS

GRAPHENE (1-3); NANOCLUSTERS & ASSEMBLIES (4-14); NANOCATALYSIS (15, 16)

1. "Graphene flakes with defective edge terminations: Universal and topological aspects, and one-Dimensional quantum behavior" I. Romanovsky, C. Yannouleas, U. Landman, Phys. Rev. B **86**, 165440 (2012).

2. "Topological effects and particle-physics analogies beyond the massless Dirac-Weyl fermion in graphene nanorings", I. Romanovsky, C. Yannouleas, U. Landman, Phys. Rev. B **87**, 165431 (2013).

3. ''Beyond the constant-mass Dirac physics: Solitons, charge fractionization, and the emergence of topological insulators in graphene rings", C. Yannouleas, I. Romanovsky, U. Landman, Phys. Rev. B **89**, 035432-1 - 035432-6 (2014).

4. "Size-selected monodisperse nano-clusters on supported graphene: Isomerism and mobility", B. Wang, B. Yoon, M. König, Y. Fukamori, F. Esch, U. Heiz, U. Landman, Nano Letters **12** (11), 5907–5912 (2012).

5. "Total Structure of the Golden Nanocrystal $Au_{36}(SR)_{24}$", C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi, B. Yoon, R. N. Barnett, R. L. Whetten, U. Landman, R. Jin, Angew. Chem. Int Ed. **51**, 13114 (2012).

6. "The Superstable 25-*kDa* Monolayer Protected Silver Nanoparticle: Measurements and Interpretation as an Icosahedral $Ag_{152}(SCH_2CH_2Ph)_{60}$ Cluster", I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R.L. Whetten, U. Landman, Nano Letters **12 (11)**, 5861–5866 (2012).

7. "Ultrastable Silver Nanoparticles", A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R.N. Barnett, B.M. Monahan, K. Kirschbaum, W. P. Griffith, R.L. Whetten, U. Landman, T. P. Bigioni, Nature, **501**, 399 (2013).

8. "Hydrogen-bonded structure and mechanical chiral response of a silver nanoparticle superlattice", B.Yoon, W. D. Luedtke, R.N. Barnett, J. Gao, A. Desireddy, B. E. Conn, T. Bigioni, U. Landman, Nature Materials Online Pub. April 6 (2014), DOI:10.1038/NMAT3923

9. "Fundamental insight into the substrate-dependent ripening of monodisperse clusters", Y. Fukamori, M. König, B. Yoon, B. Wang, F. Esch, U. Heiz, U. Landman ChemCatChem 5, 3330-3341 (2013)

10. "$Au_{67}(SR)_{35}$ Nanomolecules: Synthesis, Isolation, Characterization and First-Principles Theorerical Analysis", P. Nimmala, R.L. Whetten, A. Dass, B. Yoon, U. Landman, J. Phys. Chem. A **117**, 504 (2013).

11. " STEM Electron Diffraction and High-Resolution Images Used in the Determination of the Crystal Structure of the $Au_{144}(SR)_{60}$ Cluster", D. Bahena, N. Bhattarai, U. Santiago, A. Tlahuice, A. Ponce, S. B. H. Bach, B. Yoon, R. L. Whetten, U. Landman, M. J-Yacaman, J. Phys. Chem. Lett. **4**, 975 (2013).

12. "Bare clusters derived from protein templates: Au_{25}^{+}, Au_{38}^{+} and Au_{102}^{+}", A. Baksi, T. Pradeep, B. Yoon, C.Yannouleas , U. Landman, ChemPhysChem **14**, 1272 (2013).

13. "Atomically Precise Silver Clusters as New SERS Substrates", I. Chakraborty, S. Bagchi, U. Landman, T. Pradeep, Phys. Chem. Lett. **4**, 2769-2773 (2013).

14. "High frequency mechanical stirring initiates anisotropic growth of seeds requisite for synthesis of silver Nanorods", M.A. Mahmoud, M.A. El-Sayed, J. Gao, U. Landman, Nano Letters, **13**, 4739 (2013).

15. "Dimensionality Dependent Water Splitting Mechanisms on Free Manganese Oxide Clusters" S.M. Lang, I .Fleischer, T. M. Bernhardt, R. N. Barnett, U. Landman, Nano Letters **13**, 5549-5555 (2013).

16. "Size-dependent self-limiting oxidation of free palladium clusters"S.M. Lang, I. Fleischer, T. M. Bernhardt, R. N. Barnett, and U. Landman, J. Phys. Chem. A (2014), in press.

Properties of Majorana Bound States

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Project Scope

This project explores the properties of majorana bound states (MBS) that may be produced in the laboratory. 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 super-positions 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. In the past several years, several schemes have been proposed to produce MBS in the laboratory and to verify their existence. The aim of this project is to further explore the experimental consequences of these MBS's.

Recent Progress

1. Selective equal-spin Andreev reflections induced by Majorana Fermions [R1]

In this work, we find that Majorana fermions induce selective equal spin Andreev reflections (SESARs), in which incoming electrons with certain spin polarization in the lead are reflected as counter-propagating holes with the same spin. This is in sharp contrast with conventional superconductors where the Andreev reflected holes carry the opposite spin. The spin polarization direction of the electrons of this Andreev reflected channel is selected by the Majorana fermions. Moreover, electrons with opposite spin polarization are always reflected as electrons with unchanged spin. As a result, the charge current in the lead is spin polarized. Therefore, a topological superconductor which supports Majorana fermions can be used as a novel device to create fully spin-polarized currents in paramagnetic leads. We point out that SESARs can also be used to detect Majorana fermions in topological superconductors.

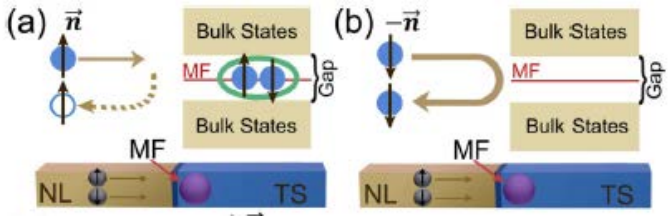

FIG. 1. A paramagnetic normal lead (N) is coupled to a topological superconductor (TS) with Majorana fermion end states. The zero energy MF mode is denoted by the horizontal line inside the bulk gap of the TS. (a) Electrons with a specific spin polarization can undergo equal-spin Andreev reflections in which an electron is reflected as a hole with the same spin. (b) Electrons with opposite spin are totally reflected as electrons with unchanged spin.

2. Proposal to measure the quasiparticle poisoning time of Majorana bound states [R2]

The promise of topologically robust quantum computation has been a major motivation in condensed matter physics over the past decade. In such schemes quantum information is not stored locally but is stored in a global state of the system. In this way systems are protected against decoherence by local perturbations. A simple and potentially realizable platform for nonlocal quantum information storage is in systems with Majorana fermions, which split a single fermionic mode into two spatially separated Majorana bound states.

Systems with Majorana qubits are only protected under perturbations that preserve fermion parity; that is, they only involve the transfer of Cooper pairs. Perturbations that switch the fermion parity of the system, involving unpaired electrons, dubbed quasiparticle poisoning, will change the state of a Majorana qubit. The time scale of this poisoning rate is then a limiting factor for performing quantum computations. Recent theoretical calculations show that this poisoning rate may be problematically large for performing adiabatic gate operations.

In light of this challenge, it is essential to be able to measure this poisoning rate. We propose a method of measuring the fermion parity lifetime of Majorana fermion modes due to quasiparticle poisoning. We model quasiparticle poisoning by coupling the Majorana modes to electron reservoirs, explicitly breaking parity conservation in the system. This poisoning broadens and shortens the resonance peak associated with Majorana modes. In a two-lead geometry, the poisoning decreases the correlation in current noise between the two leads from the maximal value characteristic of crossed Andreev reflection. The latter measurement allows for calculation of the poisoning rate even if the temperature is much higher than the resonance width.

Planned Activities

We are working closely with the experimental group of Jagadeesh Moodera at MIT who is implementing our proposal to use a narrow Au film on a superconductor substrate in the presence of a parallel magnetic field to produce MBS's. We are also planning ahead to come up with schemes to manipulate these MBS's once their existence has been confirmed by tunneling experiments. The flexibility of the thin film fabrication method allows more possible geometries compared with schemes based on nano-wires. We are also discussing with Martin Zwierlein's group at MIT concerning the possibility of realizing MBS's in cold atom systems. The possibility of creating artificial gauge fields and spin-orbit coupling in cold atoms has opened up new domains which are ripe for exploration. Our publication R4 is a step in that direction.

Publications (2012-2014)

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Theory of Materials Program - 2014

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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

Recent activities covered several areas including: topological insulators; many-electron effects in graphene and 2D crystals going beyond graphene; transport through single-molecule junctions; electronic and optical properties of nanostructures; electron supercollimation in 2D Dirac fermion systems; superconductivity; electron-phonon interactions; photovoltaics; strongly correlated electron systems; new theoretical and computational methods. Since 2013, sixty-three (63) papers were published by the program which included 8 *Phys. Rev. Letters,* 7 *Nano Letters,* 2 *Nature Physics,* 1 *Nature Commun., 3 PNAS,* 19 *Phys. Rev. B,* etc. Some selected results are:

- *Explicit formula for optical oscillator strength of excitons in carbon nanotubes*
- *Tuning and control of photoelectron spin polarization from topological insulators*
- *Prediction of novel and diversity of excitons in single layer MoS2*
- *Effects of charge doping and constrained magnetization on electronic properties of monolayer FeSe*
- *Multiple exciton ionization in shallow doped carbon nanotubes*
- *Microscopic coexistence of spin density wave and superconductivity in underdoped NaFe1-xCoxAs*
- *Critical theories of phase transition between symmetry protected topological states and gapped symmetric edges of such states*
- *Theory of satellite structures in the spectral function of 2D electron gas systems*
- *Effects of doping on excitons and quasiparticle lifetimes in graphene*
- *Discovery of electron supercollimation in graphene and Dirac fermion systems using 1D disorder potentials*
- *Development of a general approach to calculate shallow defect levels in semiconductors*
- *Nonadiabatic molecular dynamics simulation for hole transport in organic molecule monolayer*
- *Explanation of highest rectification ratios measured in molecular devices*
- *First hybrid functional for polarization-induced gap renormalization*

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 iron-based superconductors and possible enhancement of superconductivity in monolayer systems, 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 and 2D crystals such as mono- and few-layer transition metal dichalcogenides), defects, nanostructures (sheets, tubes, ribbons), and systems relevant to energy research will be investigated. We will continue development of theories and methods for *ab initio* excited-state calculations, in particular, development of methods appropriate for open-shell systems and those going beyond the standard GW approximation for accurate valence and core spectra, as well as fully selfconsistent solution of the Dyson equation.

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. Develop new algorithm for fast real-time time-dependent DFT calculations, and use it to study dynamic response of nanosystems following optical excitations, and carrier transports. Study transport problems in nanostructures and 2D materials for novel device applications.

Publications from 2013-present

Primary Publications

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CHARGE CARRIER HOLES CORRELATIONS AND NON-ABELIAN PHYSICS IN NANOSTRUCTURES, QUANTUM HALL EFFECT AND HYBRID SUPERCONDUCTOR/SEMICONDUCTOR STRUCTURES.

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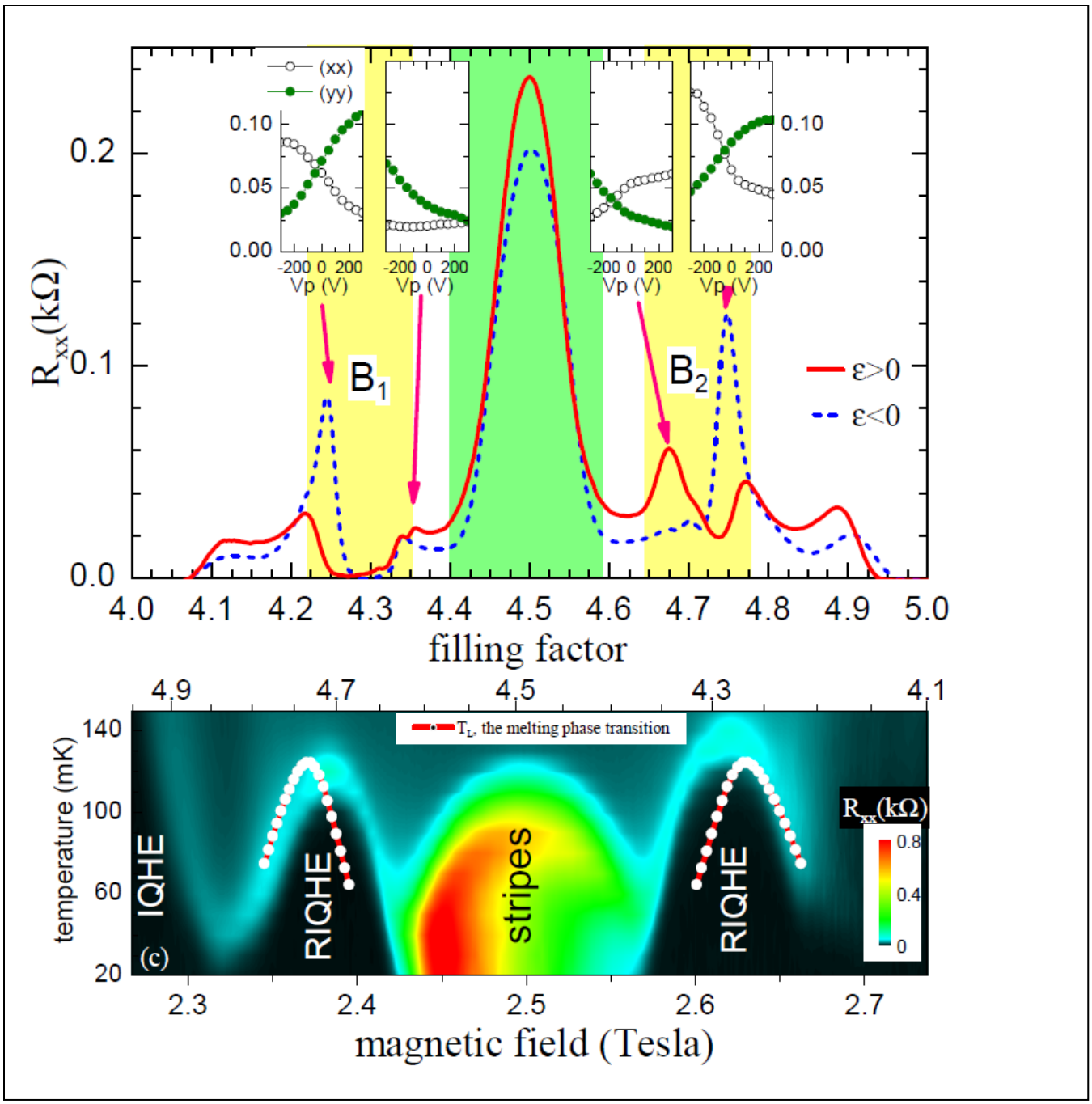
Project Scope.

The project goal is to uncover new non-abelian effects. In the field of Quantum Hall effect, our objectives are investigation of skyrmion charge carrier hole textures at integer filling factors, hole fractional Quantum Hall states, and charge density wave states in high Landau levels. The latter objective include progress in general understanding of charge density wave states of 2D charge carriers in magnetic field, particularly strain effects. One of the unsolved problems that we concentrate on is electric transport in charge density wave regime, and metal to insulator transitions that are experimentally observed with changing temperature and magnetic field.

Recent Progress

Discovery of new topological structures, excitations and melting transitions in quantum Hall systems

Topology and symmetry define states of matter and their responses to external forces. How solids melt and become fluids, or how insulators become conductors is often controlled by excitations rather than by the ground state of systems. Non-trivial topologies of the ground state and non-trivial topology of excitations alter the properties of the system. Topological excitations are notoriously difficult to predict since they cannot be obtained as a perturbation of the ground state. We have investigated Landau level filling factors between integer and half-integer, which exhibit the re-entrant integer quantum Hall effect (RIQHE) with vanishing longitudinal resistance and the Hall resistance quantized to a nearest integer at lowest temperatures (B1 and B2 phases in Fig. 1). Experiments by Csathy [1] and Rokhinson [2] show temperature dependent width of RIQHE with the insulating state bounded by a sharp resistance peak separating insulating and conducting phases in the B-T plane (lower panel). The most striking feature is strain dependence of resistivity: it changes sign across the RIQHE, i.e., $R_{xx(yy)}$ decreases or increases on the two sides of the minima, as shown in the upper panel insets. Theoretical analysis shows the observed sign change is incompatible with the symmetry of the bubble crystal [3] ground state of the RIQHE, or any other state of the interacting electron system known before. We have shown that defects needed to make the system conducting should change symmetry across RIQHE. We have observed that hedgehog and vortex-like distributions

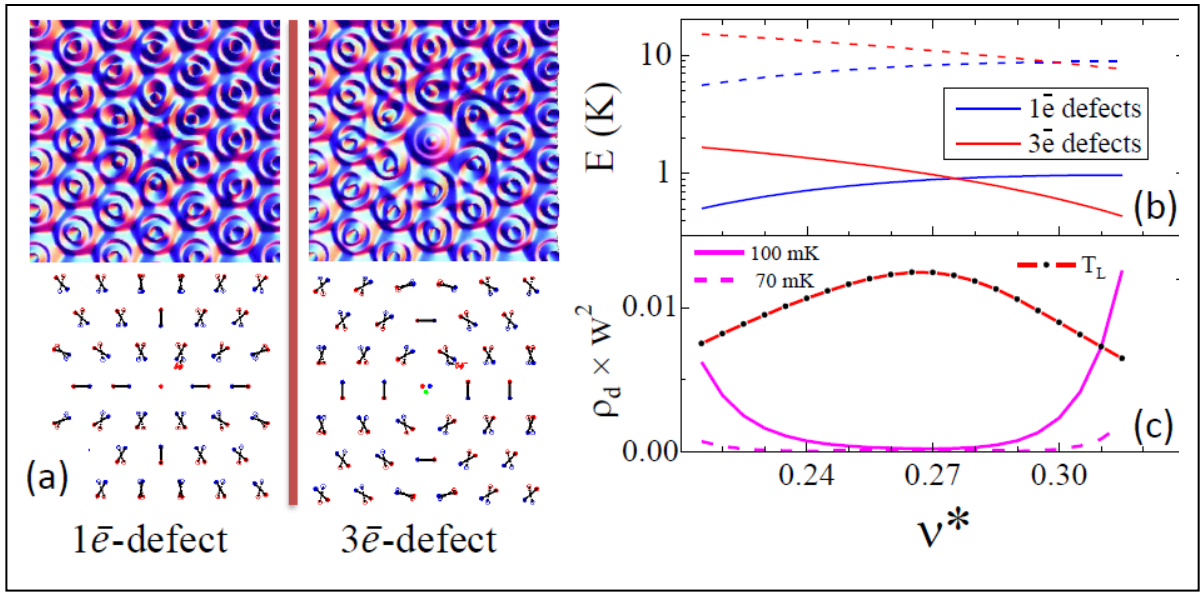


of charge density can be responsible for experimental observations.

We conducted numerical simulations of defects in bubble crystal in the range of filling factors with charge density waves resulting in crystal of two-electron bubbles. We also developed analytical theory based on existence of a small parameter λ/w, where λ is the magnetic length, and w is the lattice constant of the bubble crystal. To simplify our calculations at the first stage, we excluded impurities and smooth potential disorder in a heterostructure hosting 2D electron liquid, and considered only defects of the bubble crystal of guiding centers. Such model explains the data both on insulator to metal transition and on strain dependence of resistivity, by establishing that charge excitations in the RIQHE regime are topologically non-trivial finite size

textures of electron density with charge-dependent symmetry. We find that a charge defect (an extra electron or lack of an electron on a bubble) leads to textured deformation of electron bubbles in its vicinity, thereby lowering its activation energy as shown in Fig. 2. These textures are vortices when electron is lacking and hedgehogs for extra electron on defects. Calculations show that strain dependence of resistivity has opposite signs for vortex and hedgehog textures that dominate two sides of the RIQHE minima.

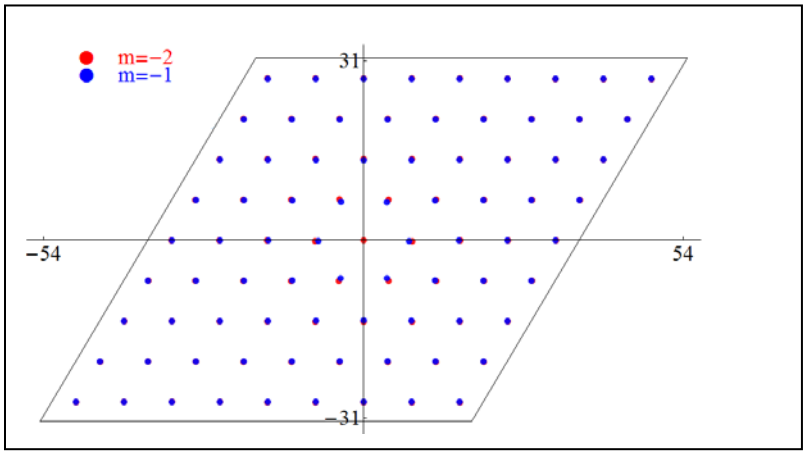
In the absence of heterostructure disorder, the transition from insulating to conducting state is as



follows: at low bubble crystal defect densities, controlled by temperature and magnetic field, textures do not overlap, and extended topological charge defects form an insulating crystal. At high defect density topological defects start to overlap, and we observe that their interactions are described by the XY-model. Such high densities are achieved at temperatures well above the Berezinski-Kosterlitz-Thouless transition, and the crystal of topological defects melts resulting in a sharp insulator-metal transition (see calculation results superimposed on experimental data, Fig.1 lower panel). Such phase transition resembles asymptotic freedom of quarks requiring them to be "squeezed" in order to be freed.

We next include real disorder. Unintended doping always includes both donors and acceptors in quantum well and barriers. At sufficiently low temperatures, electrons go from donors to acceptors, so equal numbers of charged impurities of both signs are present. We found that the presence of charged impurities may result in change of ground state. Indeed, e.g., if negatively charged impurity is in 2D plane, the ground state is the bubble crystal with one-electron bubble defect, which together with impurity effectively forms two-electron object. However if charged defect is far away, the ground state is two-electron bubble crystal [3]. As our numerical simulation shows, at certain intermediate spatial separations between charged defect and the 2D electron plane, negatively charged impurities result in ground state with one-electron defect surrounded by finite-size hedgehog of elongated two-electron bubbles (see Fig.3). In elongated bubbles, electron guiding centers characterized by angular momenta m=-1 and m=-2 are separated. Positively charged impurities result in three-electron bubble defects surrounded by

finite-size vortices of elongated bubbles. Numerical simulation shows that the crystal of finite size hedgehogs of elongated two-electron bubbles becomes a ground state at filling factors closer to integer, and a crystal of vortices is a ground state at filling factors close to half-integer . Physical picture with heterostructure defects demonstrates how defects arise in real structures. Metal-insulator transition in this picture is associated with dislocation- mediated melting of the defect crystal, which frees the charge defects of bubble crystal. Estimate of melting temperature places the transition in the range of experimentally observed values.



Future Work. We will apply Markov chain based Metropolis Monte Carlo algorithm, which has been used for Abrikosov vortex lattice, for evaluation of melting temperature of defect lattice. We will investigate the role played by defect charged bubbles in the melting of bubble lattice itself. We will explore the metal insulator transitions in temperature, filling factor and impurity density phase space. Finally we expect that for charge carrier holes, charge textures in bubble states will be accompanied by spin textures.

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Publications

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Surface and Interface Physics of Correlated Electron Systems

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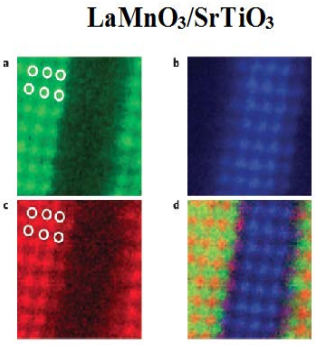
July 17, 2014

Project Summary: *Our group works to develop new theoretical methods for the grand-challenge problem of understanding and controlling the behavior of materials with strongly correlated electron properties and to use these methods to make predictions for the properties of superlattices (primarily involving transition metal oxides) and to understand current experiments. A long-term goal is to design a superlattice with novel correlated electron properties, not available in bulk.*

Scientific Background: Materials with strong electronic correlations exhibit dramatic and potentially useful electronic properties, including superconductivity with unprecedentedly high transition temperatures, colossal magnetoresistance, tunable metal-insulator transitions, high thermoelectric figures of merit, as well as carrier densities, optical gaps and other properties that can be varied over wide ranges by change of chemical doping, pressure, temperature, magnetic field and tuning parameters. If the remarkable properties of these materials can be harnessed, novel and potentially revolutionary devices may be constructed. For this to happen, interfaces and surfaces of the materials must be understood and controlled. As Nobel laureate Herbert Kromer put it, ``the interface is the device".

But surfaces and interfaces also offer a new approach to the grand challenge problem understanding the electronic properties of materials with strong correlations. Atomic-resolution superlattices can now be created and studied (Fig. 1). These are in effect a new class of materials, not previously available in nature. The interplay of theory and experiment required to understand their electronic properties is leading to new insights into basic questions of many-body quantum mechanics and its interplay with crystal structure and lattice distortions.



(a): La (b) Ti
(c) Mn (d) composite

Figure 1: Atomically resolved transmission electron microscopy image of atomic positions in an oxide superlattice. showing density of atoms as indicated From D. Muller et al Nat. Mat. 9 263 (2009).

Energetics of correlated electron materials.
Calculating the energy of an interacting electron system as a function of atomic coordinates is essential for determining structure. In correlated electron systems, properties are sensitively dependent on structure and standard density functional theory (DFT) or corrected (DFT+U) methods can fail to get the structure correctly. A dramatic example is the rare earth nickelates $RNiO_3$, where for some choices of rare earth R a metal-insulator transition occurs in parallel with a large-amplitude two-sublattice `breathing mode'' distortion

of the Ni-O bond lengths, while $LaNiO_3$ remains metallic and undistorted down to lowest temperature. In 2011-12 we solved a decades-old problem, using density functional plus dynamical mean field (DFT+DMFT) methods to show that the insulating phase (previously mischaracterized either as a conventional Mott insulator or as due to `charge ordering') was actually a *site-selective Mott insulator* in which a *hybridization* wave instability caused some Ni atoms to decouple into an S=1 Mott insulating state while others were strongly hybridized with the surrounding oxygens and formed singlets [1] and we showed how this theory had fundamentally important implications for the ability to use atomic scale superlattices to do orbital engineering on the materials [Phys. Rev. Lett. **107** 206804 (2011)]. But this work, like almost all other correlated electron theory, is based on calculations performed at an experimentally determined structure.

<u>*Hyowon Park*</u>, a postdoc in our group now moving to a faculty position at the University of Illinois at Chicago, has succeeded in calculating total energies within the fully realistic DFT+DMFT formalism, opening the door to ab-initio modeling of realistic correlated electron systems [10]. He has validated the formalism on the $RNiO_3$ family of materials, calculating the energy as a function of atomic position and chemical composition by minimizing the energy in an appropriate manifold of states. The results provide the first quantitative understanding of the ground state phase diagram in the space of rare-earth ion R and pressure (Fig. 2), in good agreement with experiment and clearly superior to DFT+U

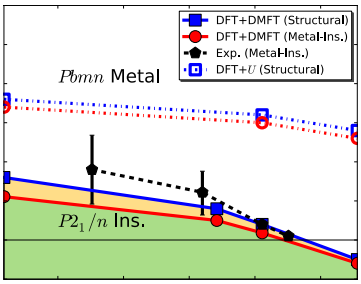


Figure 2: Calculated structural and metal-insulator phase diagram of rare earth nickelates as function of rare earth ion (expressed as tolerance factor) and unit cell volume ;compared to data (black symbols) and DFT+U (dashed lines).

Park's formalism is flexible and general: it works for low symmetry crystal structures (such as $LuNiO_3$) and describes the correlated states with maximally localized Wannier functions which can be constructed from essentially any convenient DFT basis set. Closely related work has been done in the Augsburg group using a simplified formalism in which the correlated subspace is defined only over a narrow energy range near the Fermi energy (PRL 112 146401). *We will next calculate forces within this method. This requires vertex corrections (functional derivatives of the self energy with respect to changes in structure), which can be done relatively efficiently using general methods previously developed in our group [Phys. Rev. Lett. **109**, 106401 (2012)].*

The double-counting correction: Basic to any realistic theoretical treatment of strongly correlated materials is a separation of degrees of freedom into weakly correlated states, which are treated by a computationally inexpensive electronic structure method such as DFT, and strongly correlated (active, in chemist language) states which are treated by a more accurate but much more expensive method such

as DMFT and must be self-consistently embedded in the manifold of weakly correlated states.

In the DFT+DMFT context the key embedding issue is the `double counting' question of how to treat the Hartree shift coming from the correlations included in the DFT calculation. A large (but unknown) portion of this correction is already included in the underlying DFT calculation. We showed [2,9] that standard implementations of the double counting correction predict that many materials known to be Mott insulators are instead metals. Fig. 3 shows as an example the predicted density of states of LaTiO3, which is known experimentally to be a Mott insulator but which the standard theory predicts to be metallic at essentially any value of the on-site iteraction. The issue affects also energetics [10] and applications to molecules and other systems [J. Chen and AJM, unpublished]. We introduced modified double counting formulae with a parameter empirically adjusted to put the oxygen bands at the correct energy and showed that with this double counting the DFT+DMFT procedure leads to results consistent with a broad range of experimental data on many compounds [9,10]. *Future research will focus on placing this approach on a more rigorous and widely phenomenologically supported basis.*

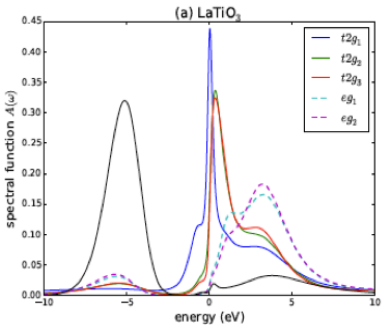


Figure 3 Orbitally resolved many-body density of states computed for LaTiO3 in experimental structure using fully charge self consistent DFT+DMFT with FLL double counting and unphysically large value of on-site correlations.

Charge transfer at Interfaces: A basic question in interface physics is: how much charge flows across the interface from one material to another. In weakly correlated materials charge transfer is controlled by band offsets, calculable to reasonable accuracy by density functional theory (DFT). In strongly correlated materials, bands may not be a useful concept. We used the combination of density functional plus dynamical mean field theory (DFT+DMFT) to calculate the many-body density of states of a superlattices composed of alternating layers of different transition metal oxides., predicting for example that a superlattice composed of alternating layers of $LaNiO_3$ (a metal) and $LaTiO_3$ (a small gap S=1/2 Mott insulator) will be a wide-gap spin-1 Mott insulator [3].

Fig. 4 compares the density of states of a superlattice composed of the `214' Ruddlesden-Popper materials Sr_2MnO_4 and Sr_2VO_4 to the density of states of the component materials. In the superlattice there is a rigid-band shift of density of states such that the oxygen bands (dark brown) of the two different materials align in energy while the charge transfer is controlled by the alignment of the transition metal d-states, whose energies **are fixed relative to the oxygen states**. The charge transfer across interfaces is thus deeply entangled with the double counting correction issue. Also (not shown) our work has found that near-interface lattice distortions fundamentally affect the physics of the interface. *Our future work will*

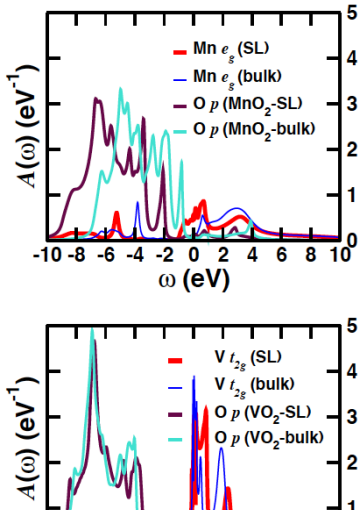


Figure 4 Atomically resolved many body density of states for Sr2VO4/Sr2MnO4 superlattice and for corresponding bulk materials

develop a systematic understanding of charge transfer, lattice relaxation and orbital engineering effects at oxide interfaces, building on and further developing the total energy and double counting work discussed above.

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Optical, transport phenomena, and interaction effects in novel low-dimensional electron systems

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Project scope

Progress of modern day condensed matter physics is to a large extent ensured by the synthesis of new materials. In particular, of special interest are those materials that support chiral electron states, i.e. the states whose properties depend on the direction of electron propagation. Such states exist in a variety of practical realizations: conventional two-dimensional electron gas with spin-orbit interaction, Dirac fermions in graphene and topological insulators, metallic carbon nanotubes, direct-gap semiconducting MoS2 monolayers. While some of these systems are already being extensively investigated, the last one is much less studied. Within this research project we investigate physics of the chiral electron systems. Through a variety of specific projects concerning transport, optical phenomena, and many-body effects, we try to accomplish our main objective, to look for features common to various chiral systems.

Among particular projects addressed are: i) theory of excitons and depolarization effect in metallic carbon nanotubes with the account for the Luttinger liquid dynamics, ii) interaction corrections to the ac conductivity of graphene, iii) possibility of existence of non-RPA polarization waves, iv) resonant impurity-induced states in mono- and bilayer graphene, the latter of particular interest for applications due to the possibility of being gate-controlled, v) collective excitations in MoS2, in particular waves of spin polarization that are expected to have non-trivial spectrum. This project relies significantly upon our previous broad expertise in spin-polarized transport, and many-body effects in low-dimensional systems, both 2D and 1D. The methods to be employed include diagrammatic technique, Luttinger liquid theory, self-consistent approximations, hydrodynamics of electron liquid. Both analytical as well as numerical approaches are utilized. In particular, to study the depolarization effect in nanotubes we will combine the conventional diagrammatic technique with the methods of bosonization, as each method is not sufficient on its own. Another example involves resonant adatoms in graphene known to be strong and attractive: its renormalization due to electron-electron interaction is expected to be so significant as to even reverse the very sign of the coupling. Numerical methods are used to help determine induced charges in the host layer, together with the method of self-consistent non-linear

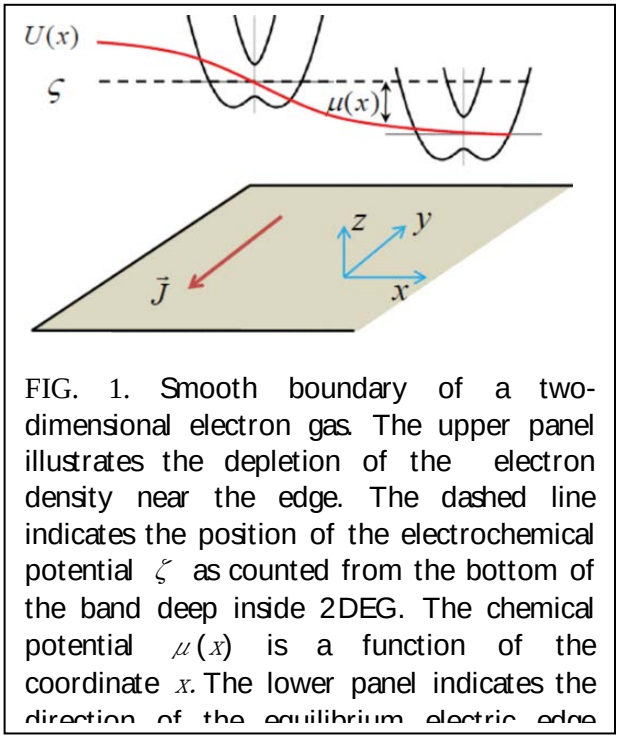

FIG. 1. Smooth boundary of a two-dimensional electron gas. The upper panel illustrates the depletion of the electron density near the edge. The dashed line indicates the position of the electrochemical potential ζ as counted from the bottom of the band deep inside 2DEG. The chemical potential $\mu(x)$ is a function of the coordinate x. The lower panel indicates the direction of the equilibrium electric edge

screening.

Recent progress

Equilibrium currents in chiral systems with non-zero Chern number

Orbital contributions to the magnetization in systems with topologically nontrivial band spectrum represent a relatively new but active field of study. The nonlocal nature of the corresponding quantum operator is one of the obstacles in calculating orbital magnetization of Bloch electrons. We have developed a simple quantum-mechanical approach to calculating equilibrium particle current along the edge of a system with nontrivial band spectrum topology. The approach does not require any *a priori* knowledge of the band topology and, as a matter of fact, treats topological and non-topological contributions to the edge currents on the same footing.

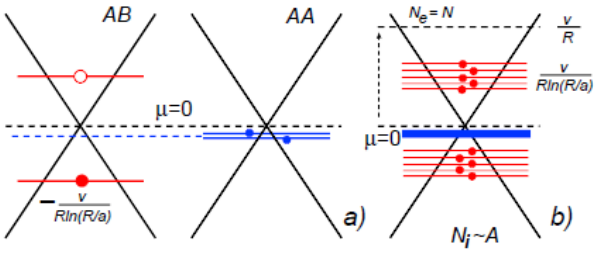

FIG. 2. Energy spectrum of graphene with resonant impurities. a) Two impurities: in the AB-configuration a single-impurity level is split into two. For a fixed chemical potential the upper level is empty, while the lower is responsible for the strong attraction; in the AA-configuration both the splitting and the energies are negligible, the impurity levels stay on the same side of the Dirac point. The interaction comes from the renormalization of the energies of propagating states and is repulsive. In case of many impurities the system the sign of the interaction can change: when chemical potential is zero, the attraction from the negative energy states dominates; if the number of electrons is fixed instead, the states up to the chemical potential v/R are populated, negating the effects of the negative energy states and leading to the repulsion due to the renormalization of the propagating states.

It is based on the equation for the density matrix for the electron system subject to a smooth confining boundary potential, see FIG. 1. We have used our approach to demonstrate the existence of "topologically nontrivial" particle currents along the edges of three different physical systems: two-dimensional electron gas with spin-orbit coupling and Zeeman magnetic field, surface states of a topological insulator, and kagomé antiferromagnet with the Dzyaloshinskii-Moriya interaction. We also developed the relationship of our results to the notion of orbital magnetization.

Another important application of our calculations is the system of cold atoms, where the resulting edge current represents a *mass current*, circulating around the boundary of the system, which should be observable. Such mass current is determined by the gradient of confining potential, which is routinely controlled in cold atom systems. This leads to the realistic possibility of studying current generation in response to a change in the confining potential and/or Zeeman potentials. It can also be detected by a muon spin rotation experiments, like in Sr2RuO4.

Graphene: Attraction-repultion transition in the interaction of adatoms

We studied the interaction of two resonant impurities in graphene, which has been predicted (Shytov, Abanin, Levitov, 2009) to have a long-range character with weaker repulsion when the

two adatoms reside on the same sublattice and stronger attraction when they are on different sublattices. We have demonstrated that this attraction results from a single energy level, see FIG. 2. We also showed that for the ensembles of many resonant impurities the sign of the overall interaction is dependent on whether doping occurs with a fixed number of electrons (grand canonical ensemble, realized for isolated samples) or with a fixed chemical potential (canonical ensemble realized for contacted samples). This finding, contrary to the existing predictions in the literature, has been demonstrated convincingly via both the direct calculations (numerical as well as analytical) and the development of a simple physical picture of the underlying energy spectrum. This prediction opens up a possibility of controlling the sign of the impurity interaction via the adjustment of the chemical potential. For many randomly distributed impurities (adatoms or vacancies) this may offer a way to achieve a controlled transition from aggregation to dispersion.

Plasmonics: Dipole-induced localized plasmon modes and resonant surface plasmon scattering

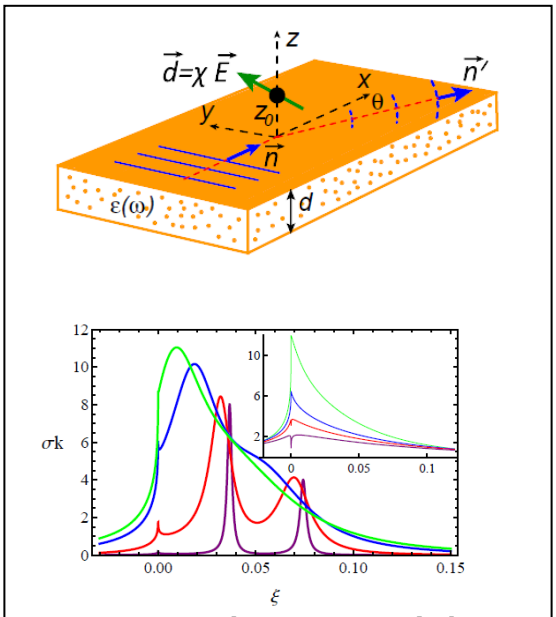

FIG. 3. A nanoobject positioned above a metal film. It acquires the dipole moment in response to the applied electric field. The system depicted here supports a continuum of propagating modes, as well as two localized plasmons. Since the localized solutions overlap with the continuum they acquire a finite width. Conversely, the localized modes show up as resonances in the scattering of propagating plasmons, indicated schematically with (blue) arrows.

We have developed theory for resonant scattering of surface plasmons propagating in thin metal films. A metal film supports the continuum of propagating surface plasmon waves. The interaction of these waves with a dipole (nanoparticle) positioned some distance from the surface of the film can produce well-defined localized plasmon modes whose frequency nonetheless resides inside the continuum, see FIG. 3. This leads to the resonant enhancement of scattering of surface plasmons off the dipole. The maximum of scattering is found to occur when the distance from the dipole to the surface of the film is equal to one-half of the film thickness. The possibility of controllable plasmon scattering could be advantageous for the field of nanoplasmonics.

Planned activities (2014-2015)

1) Following our recently published work we plan to continue investigation of the collective properties of resonant impurities/vacancies in graphene. In particular, we aim to investigate the transport of hydrogen adatoms. According to our preliminary calculations an interesting phenomenon occurs: when an adatom is far from other adatoms its motion on the carbon lattice is slow but relatively unimpeded. Yet, when the second adatom happens to be nearby the motion of both atoms is slowed down significantly. This is the result of the interplay of a) the Casimir-like effective interaction between adatoms, and b) quantum interference due to the honeycomb lattice structure of

graphene. The hopping of hydrogen over carbon sites become inelastic as a result and requires phonon assistance, thus greatly reducing the hopping amplitude. We are going to develop the theory for such "mutual trapping", using both analytical and numerical methods, taking into account the coupling of hydrogen to phonon modes of graphene.

2) As a separate project we are currently conducting studies of many-body effects in carbon nanotubes that involve interaction of the massless electron subbands with the massive (gapped states). This involves a variety of phenomena, known under different terms, such as the Luttinger liquid, zero-bias anomaly, x-ray edge singularity, orthogonality catastrophe, which nonetheless have a unified underlying physics -- a proliferation of the number of modes involved in the low-energy response of (quasi) one-dimensional electronic systems. In particular we are interested in the limitations of the effective electrostatic model of nanotubes treated as metallic cylinders for the purpose of calculating their response to the perpendicularly (to their axes) electric ac field (optical absorption).

Our preliminary results show that the Coulomb interaction with the change of the angular momentum of electrons becomes relevant at low energies. This interaction is always ignored in the theory of one dimensional electron systems, which is based on the standard Luttinger Liquid model. The resulting low-energy behavior is currently being investigated. It is mapped onto a more advanced form of sine-Gordon model.

3) Our last project involves effects of electron-electron scattering on spin diffusion in semiconductors with spin-orbit interaction. Normally, electron scattering off impurities is considered as the source of randomization of electron momenta, with the subsequent precession in momentum-dependent effective magnetic field, originating from spin-orbit coupling, destroying spin coherence. The electron-electron scattering and its ensuing role in the inverse spin-hole effect is, however, much less studied. This in one of our current research objectives.

Recent publications (2013-2014)

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Modeling the Self-Assembly of Ordered Nanoporous Materials

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Project Scope

This project deals with the multiscale modeling of the assembly processes in the synthesis of nanoporous materials. Such materials are of enormous importance in modern technology with application in the chemical process industries, biomedicine and biotechnology as well as microelectronics. An ongoing theme in porous materials science and engineering is the tailoring of pore structure for specific applications. Silicate and aluminosilicate chemistry provides an immensely valuable route to stable nanoporous materials. The number of possible materials structures is almost without limit. The origin of this is the low coordinate bonding in these materials and the unformity of binding energies between different structures that differ primarily through the arrangment of corner sharing silica tetrahedra. We focus on two important classes of materials: i) microporous crystalline materials, such as zeolites, and ii) ordered mesoporous materials. In the first case in which the pores are part of the crystalline structure, while in the second the structures are amorphous on the atomistic length scale but where surfactant templating gives rise to order on the length scale of 2 - 20 nm. Our models are based on the assembly of corner sharing silica tetrahedra in the presence of structure directing agents. We use both on-lattice and off-lattice models and the primary computational tools are Monte Carlo simulations with sampling techniques and ensembles appropriate to specific situations. Our modeling approach is the first to capture silica polymerization, nanopore crystallization, and mesopore formation through computer-simulated self assembly.

Zeolite Nucleation. We are applying both the lattice and off-lattice models to shed new light on zeolite nucleation. The first component of this is the study of silica polymerization across a

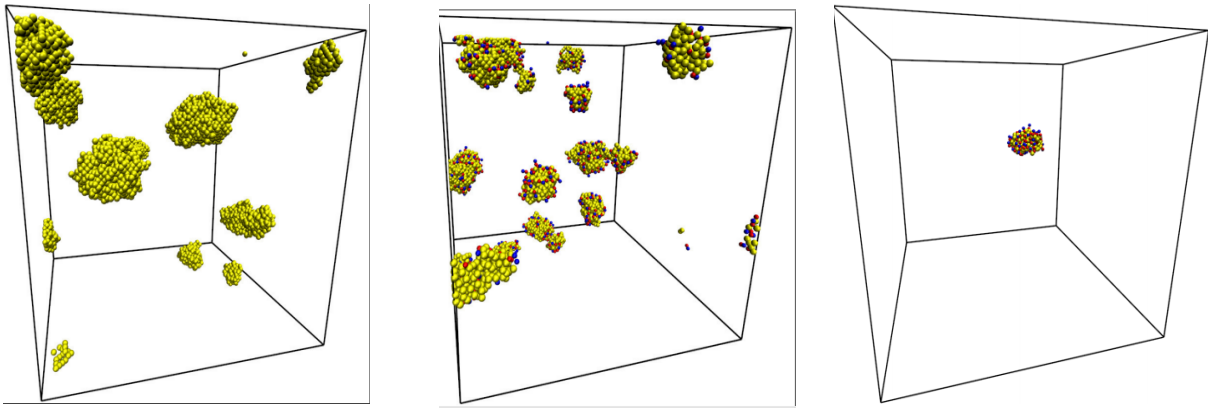

Figure 1: Snapshots of the low concentration system under different cation mole proportions. (a) pH = 2.0, (b) pH = 8.5, (c) pH = 10.5.

broad pH range producing gels at low pH and nanoparticles at high pH. We then consider the

nucleation of all-silica zeolite analogs modeled using transition path sampling applied to our lattice model of silica. The final component involves the study of pathways connecting amorphous and ordered phases.

Ordered Mesoporous Material Formation. We are investigating several effects including the influence of surfactant chain length on the cooperative templating of mesoporous structures. We are also exploring the interplay between silica polymerization and mesoscale surfactant assembly, to identify the most likely mechanism for cooperative structure formation in these materials.

Recent Progress

Modeling silica polymerization across pH spectrum

All-silica zeolite frameworks such as silicalite-1 can be synthesized by sol-gel processing in aqueous medium using a silica source and structure directing agents(SDA). All-silica zeolites fall in the spectrum of sol-gel processing and a central component in their synthesis is the polymerization of silica. We have extended our model of self assembly of corner sharing tetrahedra on a body-centered cubic(bcc) lattice to a wider pH range, especially alkali conditions. Experimental studies have shown gelation at low pH and high concentration of silica and provide a good test for molecular simulations. The low silica concentration and high pH resembles the clear solution synthesis of silicalite-1, the pure form of ZSM-5. Studies of the formation mechanism of silicalite-1 crystals during the clear solution synthesis have shown that the process includes an intermediate nanoparticle phase that is believed to play an important role in the nucleation process of silicalite-1 crystals. At high silica concentration and high pH, the average size of nanoparticles has been observed to decrease with increase in pH, but their structure and morphologies remain unknown.

Lattice Model: Figure 1 shows snapshots of the low concentration system at different pH values (and hence SDA^+ concentrations) going from acidic to basic conditions. We notice nanoparticles across the range of pH with the cluster size not changing significantly. Moreover, we observe nanoparticles having a core-shell structure at intermediate pH values. This is the result of a competition between the electrostatic attraction of $SI\text{-}SDA^+$ and the condensation energy between silica species. The total number of nanoparticles in the system decreases as the SDA^+ concentration is increased due to an increase in the anionic silica species in the solvent to balance the charge of SDA^+.

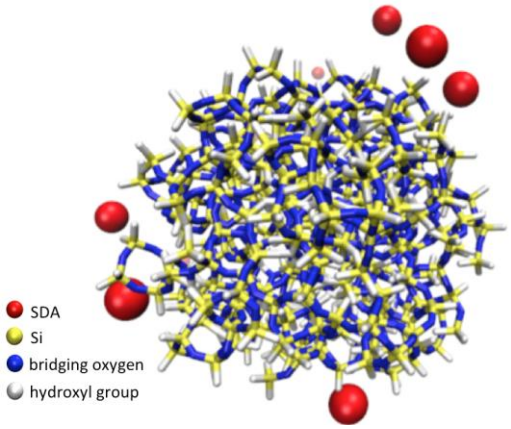

Figure 2. Snapshots of final configurations of the two-step model. The yellow sphere denotes the silica atom, the white sphere denotes the hydroxyl group, the blue sphere denotes the bridging oxygen, and the red sphere denotes the template, respectively.

Off-Lattice Model: We have also continued our investigations with our off-lattice model of silica polymerization where silica condensation states are sampled using reactive Monte Carlo (REMC) simulations. Inspired by our earlier work on mesoporous silica self-assembly it seems plausible that a two-step process occurs in the formation of silica-template nanoparticles. The first step is a rapid agglomeration process bringing silica species together in aqueous solution, driven by van der Waals and hydrophobic forces.

With the two-step formation mechanism, the silica nanoparticles are obtained as shown in figure 2. The nanoparticle has the core-shell structure with most of the silica in the core and structural directing agent on the surface. The cluster size is about 3nm, which is consistent with the experimental data. This is the first instance of off-lattice molecular simulation of the self-assembly of such silica-template nanoparticles, key precursors to zeolite formation.

Templated Assembly in Synthesis of Zeolites

In a previous study, we had applied our lattice model to study the microporous crystalline ground state structures (zeolite analogs) of a system containing only neutral silica molecules. With the help of Parallel Tempering Monte Carlo (PTMC) algorithm, we were able to simulate the self-assembly a variety of crystalline zeolite-analog structures, chalcogenides and layered materials. We are now extending the study to include structure directing agents (SDAs) in the simulations. To keep the model simple, we have considered a spherical SDA with near neighbor repulsions to account for its finite size. Figure 3 shows a fully connected framework on an 8x8x8 bcc lattice with a 12-ring channel where we see a fully connected crystalline microporous material formed in the presence of the template.

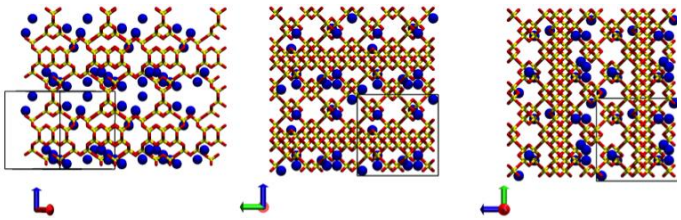

Figure 3: Different views of a three-dimensional connected materials in the presence of a structure directing agent.

Further studies are required to investigate the effect of the size of the SDA on the crystalline structures. In order to systematically study the effect of composition under the influence of the SDA, we plan to extend the Monte Carlo tempering algorithm to tempering in the chemical potential of the species in the Grand Canonical ensemble. This latter feature will allow us to search for ground states without assuming a density. We have also begun to extend this work to our off-lattice silica model, including development of a PTMC simulation method that includes the REMC algorithm.

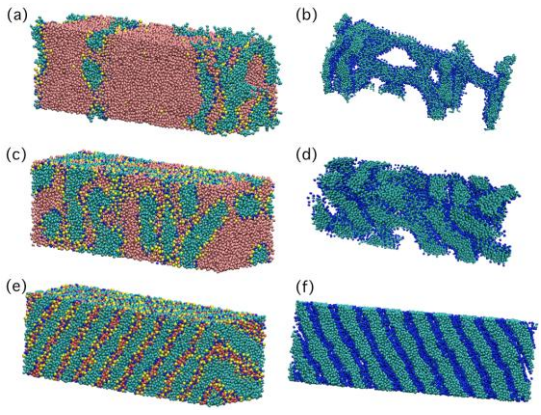

Figure 4. Snapshots of the obtained structure with different ratio among SI, CTAB and Water after 1.5μs. The dark blue, blue, yellow and red spheres indicate surfactant head groups, surfactant tail groups, silicic acid and water, respectively. The pictures on the right have the water removed to show the structure more clearly.

Ordered Mesoporous Materials Formation

In this part of the work is to combine the off-lattice model of silica polymerization and coarse-grained model of the surfactant to elucidate the formation mechanism of silica mesoporous materials. We are developing a hybrid MD/MC simulation in which the mesoscale structure is evolved using MD while the silica condensation is evolved with REMC.

Some initial results are shown in Fig. 4. These results show how different mesoporous structures can be obtained via changing the ratio between different species. In particular, our results show that the addition of silica

species promotes the formation of rods and gyroid structures. We also found a lamellar structure from this surfactant-silica-water system. It is observed from the simulation that adding silica into the system causes a morphology change in the system.

Future Plans

We anticipate progress in the following areas over the next year:

- We will complete our work on using PTMC studies of our lattice model ground states in the presence of templates and move to a study of templating mechanisms under synthesis conditions, including the incorporation of path sampling simulation techniques as necessary
- We will complete our studies of silica polymerization over the range of pH with our off-lattice model. This will be followed structural characterization of the silica materials produced and comparison with experiment
- We will further the develop the reactive parallel tempering simulations of the ground states of our off-lattice model of silica and begin the incorporation of templates into these calculations
- We will continue studies of the off-lattice model of ordered mesporous materials synthesis, with incorporation of silica polymerization in our MD/MC approach. New, important information about the synthesis mechanism the structure of these materials (pore wall structure, microporosity in the walls, etc.) will emerge from these studies

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Non-Equilibrium Physics at the Nanoscale

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Project Scope

The PI's long-term program objective is to create a comprehensive theoretical framework to describe the emergence of complex non-equilibrium phenomena at the nanoscale, and their evolution across the meso- to the macroscale. The specific objectives are (a) to identify the key elements that govern non-equilibrium charge and energy transport in nanoscopic systems, such as strong correlation effects, topological interactions, and disorder, (b) to determine how these elements shape the relation between local and global transport properties, and (c) to identify new methods for manipulating and quantum designing transport at the atomic scale. Investigating the emergence of complex non-equilibrium phenomena at the nanoscale will shed fundamental insight into the microscopic origin of charge and energy transport at the meso- and macroscale, providing unprecedented possibilities to optimize the development of new functional and smart materials for applications ranging from energy research to quantum computing.

Recent Progress

1. Spin Diodes in Topological Insulators

Breaking the time-reversal symmetry of topological insulators (TIs) gives rise to exotic quantum states with potential applications in fields ranging from quantum computation to spintronics. The PI recently demonstrated that nanoscopic TIs can be employed to create spin-diodes yielding nearly fully spin-polarized currents [1]. Such spin diodes utilize the existence of spin-polarized edge currents in TIs, schematically shown in Fig. 1A, in conjunction with magnetic defects, which break the time-reversal symmetry of the TI. Due to the finite size of a nanoscopic TI, the density of states exhibits a discrete set

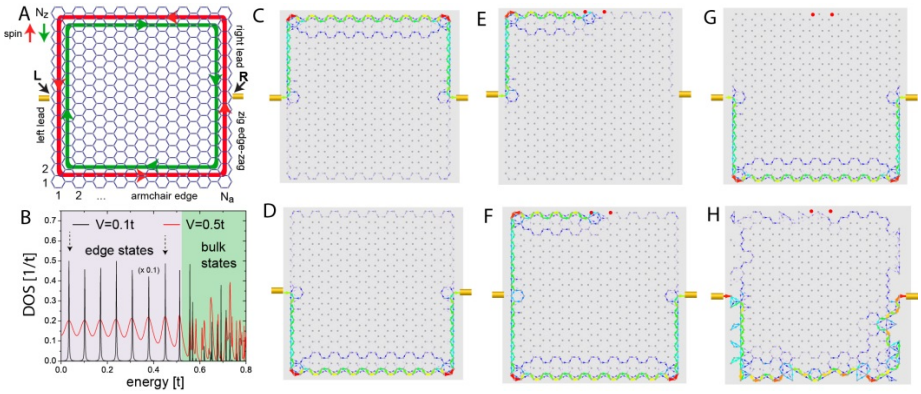

Fig.1 **A** Spin-resolved edge states in TIs. **B** Density of states, and **C**,**D** spatial current patterns of edge states in a clean TI. **E**,**F**,**G** Spatial current patterns in the presence of magnetic defects, and **H** edge roughness.

of states (Fig. 1B). The spatial current pattern for the spin-↑ and spin-↓ bands, shown in Figs. 1C and 1D, respectively, demonstrate the counter-propagating nature of the two edge states. When magnetic

defects (denoted by red dots in Fig.1) are placed in the path of one of the two spin-currents, as shown in Fig. 1E for the spin-↑ current, electrons are scattered into the opposite spin band, leading to an almost complete conversion of spin-↑ current into spin-↓ current [Fig. 1F]. As a result, the total current through the TI, shown in Fig. 1G, is nearly fully spin-↓ polarized. When the voltage across the TI is reversed, the spin-polarization of the total current is reversed as well, implying that such a TI can be utilized as a spin-diode. The extent of the spin-diode effect remains unaffected by the presence of wide-leads, or of edge roughness, Fig. 1H. These results demonstrate that by breaking the time-reversal symmetry of a nanoscopic TI, novel non-equilibrium quantum states emerge with nearly fully spin-polarized currents and spin-diodes effects which are a crucial building block for many spintronics applications.

2. Direct Evidence for a Magnetic *f*-Electron Mediated Cooper Pairing Mechanism of Heavy Fermion Superconductivity in $CeCoIn_5$

Understanding the microscopic origin of unconventional superconductivity in general, and that in heavy fermion materials in particular, is one of the most important open problems in condensed matter physics. We recently proposed a novel theoretical approach to identify the microscopic mechanism of heavy-fermion Cooper pairing [2,3]. By extracting the momentum form of the magnetic interactions between f-electron moments in $CeCoIn_5$ from experimental QPI results, Fig. 2A, we obtained a crucial element for investigating magnetically mediated Cooper pairing as the origin of heavy-fermion superconductivity. Specifically, this approach allowed us to solve the superconducting gap equations, yielding quantitative predictions for the symmetry and magnitude of the superconducting gap Δ_k, [Fig. 2B], the critical temperature T_c, the Bogoliubov and phase-sensitive QPI spectra [Fig. 2C], the spin-lattice

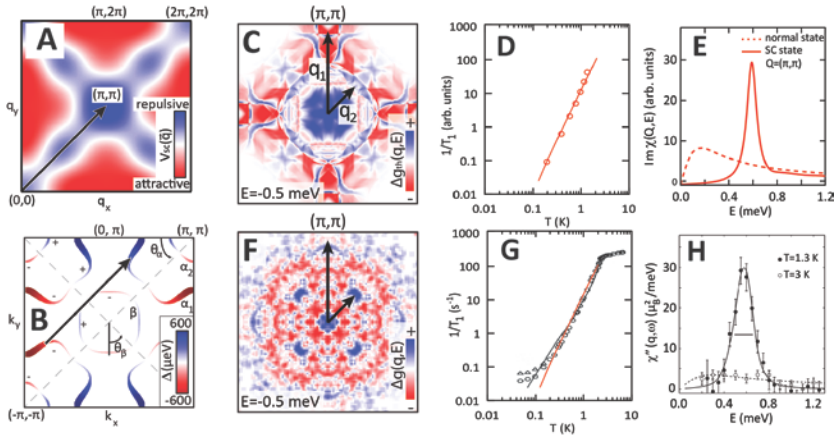

Fig.2 **A-E** Theoretical and **F-H** experimental results in $CeCoIn_5$

relaxation rate [Fig. 2D], and the magnetic resonance peak, Fig. 2E]. All of these results are in very good quantitative agreement with experimental measurements [Fig. 2F-H], providing strong and direct evidence that the heavy-fermion Cooper pairing is mediated by f-electron magnetism, and *lifting the fog of complexity* [4] surrounding this material.

3. Noise-Enhanced Quantum Transport in Photosynthetic Complexes

We recently proposed a novel theoretical framework based on the Keldysh Green's function formalism to investigate the role played by quantum coherence in the highly efficient exciton energy transport through the photosynthetic Fenna-Matthews-Olson (FMO) complex -- a major unsolved problem in the

study of light-harvesting complexes [5]. By relating the spatial exciton flow patterns [Fig. 1A] to the total exciton flux through the FMO [which varies non-monotonically with exciton dephasing, arising from the coupling to a noisy environment, Fig. 1B], our approach directly demonstrated how the interplay between dephasing, disorder and exciton coupling controls the relation between the FMO's local and global non-equilibrium transport properties. In addition, we demonstrated that the nature of the noise-enhanced quantum transport is only weakly affected by the specific spectroscopic distribution of phonon modes, demonstrating the robust nature of this phenomenon [6]. These results provide important insight into the transport mechanisms of biological systems and open a new approach for controlling excitonic flow in photovoltaic materials, such as the hybrid perovskites.

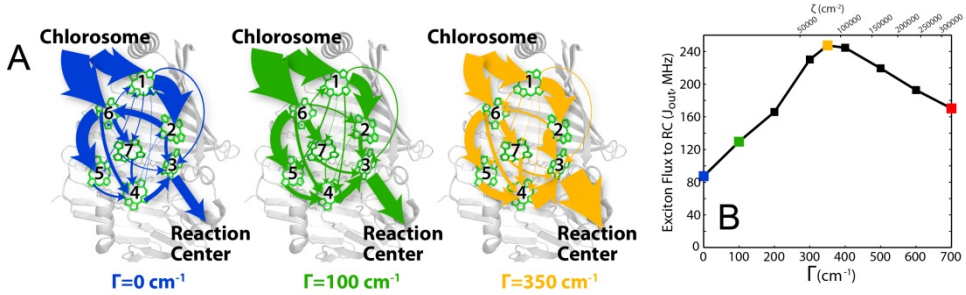

Fig.3 **A** Spatial excitonic flow patterns, and **B** total exciton current in the FMO complex.

Future Plans

1. Effects of Disorder and Strong Correlations on the Non-Equilibrium Transport in nanoscopic Kondo systems

How the interplay between defects and strong correlations determines the local and global transport properties of strongly interacting electron systems in general, and heavy fermion materials in particular, is an important, yet unresolved problem. To address this question, we are currently employing the slave-boson approach to the infinite-*U* Anderson model to investigate the effects of defects, magnetic interactions, applied bias, and dephasing on the local electronic properties, conductance and spatial current patterns in nanoscopic Kondo system. We have shown that the onset of Kondo correlations strongly modifies not only the conductance of the system, but also the spatial current patterns, opening the possibility to use the latter as *spatial footprints* of strong correlation effects [7]. Moreover, we have succeeded in self-consistently computing the changes in the local hybridization and spatial current patterns with increasing voltage bias, and are currently investigating the spatial correlations between these two quantities. As the next step, the PI intends to study how the spatial flow of currents, and the spatial form of shot noise around defects changes with the onset of Kondo screening and (magnetic) non-local correlations, and how these changes are reflected in the overall conductance and shot noise.

2. Veselago Lenses and Fictitious Magnetic Fields in Nanoscopic Graphene Lattices and Topological Insulators

The electronic structure of graphene gives rise to a plethora of intriguing physical phenomena, such as current focusing in *Veselago lenses*, or the emergence of fictitious magnetic fields in strained graphene lattices. The experimental realization of *molecular graphene* has raised the intriguing possibility to study some of these unconventional phenomena at the nanoscale. We are therefore currently investigating

how Veselago lenses affect the spatial current patterns and conductance of nanoscopic graphene lattices and topological insulators. In addition, we are investigating the signatures of strain-induced fictitious magnetic fields on the spatial current patterns in nanoscopic graphene lattices. Of particular interest is here the question of whether the current patterns in strained graphene differ from those in the presence of real (externally applied) magnetic fields.

3. Quantum Design of Transport

In many areas ranging from energy research to spin-based electronics and quantum computation the question of how one can *quantum design* the most efficient or stable system is of paramount importance. This question can be cast in terms of an inverse optimization problem: how can one optimize the geometry or size of a system to realize a specific set of target properties, such as an *I-V* curve or spatial form of currents? We are currently investigating two types of quantum design problems pertaining to nanoscopic system with specific transport properties, and to excitonic networks which exhibit highly efficient and long-range energy transport and are robust against disorder. As the first step in this project, we are developing fast algorithms to compute the transport properties of nanoscopic networks – conductance and spatial current patterns – from the connectivity matrix describing the electronic structure of the system.

Publications

[1] *Magnetic Defects and Spin Diodes in Topological Insulators*, J. Van Dyke and D.K. Morr, in preparation.

[2] *Imaging Cooper Pairing of Heavy Fermions in $CeCoIn_5$* ,M. P. Allan, F. Massee, D. K. Morr, J. van Dyke, A.W. Rost, A. P. Mackenzie, C. Petrovic and J. C. Davis, Nature Physics **9**, 468 (2013).

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Abstract: Studies of the Marginally Jammed Solid

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The University of Chicago
Andrea J. Liu (DOE award #: DE-FG02-05ER46199)
The University of Pennsylvania

Project Scope:

At the jamming transition, a collection of soft, repulsive particles attains rigidity due to an infinitesimal confining pressure. Is the rigid solid formed in this way similar to or different from a solid created by crystallization? This is the main question that has defined the scope of our project.

Accompanying the jamming transition, we have identified diverging length scales that lead to qualitatively new physics. As a result, a rigid packing at the zero-temperature jamming transition represents an extreme limit of a solid in several ways. In a well-defined sense, such a marginally jammed solid is the epitome of disorder; it lies at the opposite pole from a zero-temperature crystal where order is perfect. Moreover, at the jamming transition, the response to shear is infinitely weaker than the solid's response to compression. This is similar to the response of a liquid and distinguishes the jammed solid from a perfect crystal, where the ratio of the shear to bulk modulus, G/B, is of order unity. Building on our previous work, our present focus has been to investigate to what extent an ordinary solid can be described as lying between the two extremes of perfect order and complete disorder; can it be coherently described by perturbations around each limit?

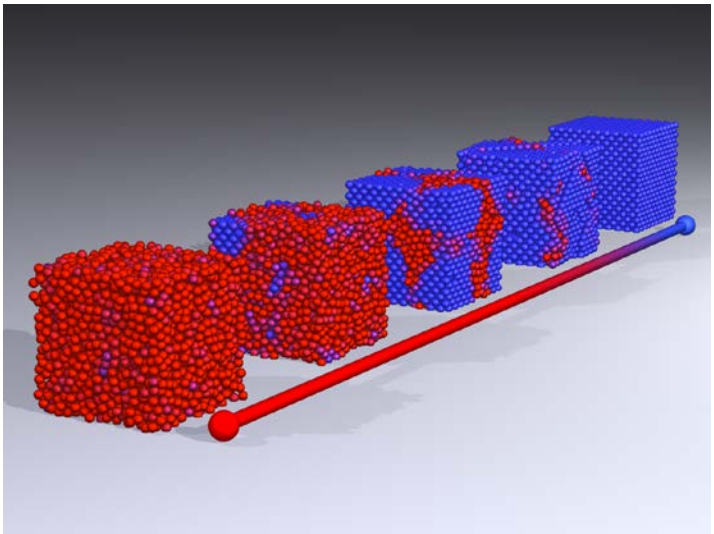

Fig. 1 Examples of solids with different degrees of disorder. Colors represent the degree of local order: blue represents particles with local FCC crystalline order, whereas red represents particles that are in the jamming limit with no crystalline order.

The question we address is to what extent the intermediate cases are best described by starting from a crystal or by starting from the opposite pole of jamming.

Recent progress:

Jamming as the pole of complete disorder

On first being introduced to solid-state physics, we typically learn about ideal perfect crystals. We are taught to describe real solids, which must always have imperfections, in terms of perturbations about crystalline order. However, such an approach only takes one so far: a glass, another ubiquitous form of rigid matter, cannot be described in any meaningful sense as a crystal with defects. Is there an opposite extreme to a crystal, an idealized solid with "complete

disorder," that can be used as an alternate starting point for understanding real materials? We argue that the solid made of particles with finite-ranged interactions at the jamming transition constitutes such an extreme limit. It has already been shown that the physics associated with this transition can be extended to interactions that are long ranged. We have now demonstrated that jamming physics is not restricted to amorphous systems but dominates the behavior of solids with surprisingly high degrees of order. Much as the free-electron and tight-binding models represent two idealized poles from which to understand electronic structure, our findings identify the two extreme poles of mechanical behavior. Thus, the physics of jamming can be set side-by-side with the physics of crystals to provide an organizing structure for understanding the mechanical properties of solids over the entire spectrum of disorder.

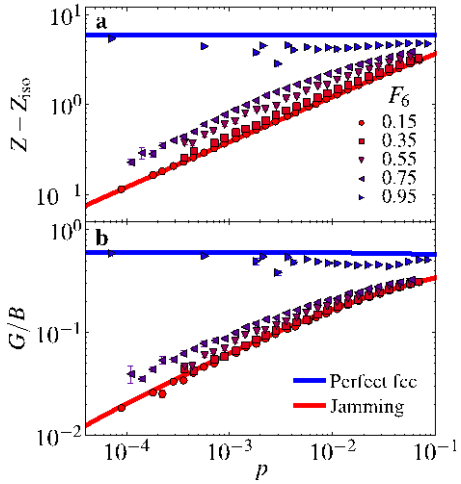

Fig. 2 The crossover from jamming physics to crystalline physics. (a) The excess contact number versus pressure at different values of the order parameter, F_6. The blue line shows the constant $Z - Z_{iso}$ behavior for a perfect fcc crystal, while the red line shows the behavior at jamming. (b) The ratio of the shear modulus to bulk modulus, G/B, for the same systems. Only for systems with very high values of F_6 do the properties have the pressure independence expected for a crystal.

The jamming transition can be studied in its purest form at zero temperature in disordered packings of spheres interacting via finite-range, repulsive interactions. At the transition, the packing fraction is just sufficient to cause unavoidable contact between particles. The marginally- jammed state at this transition represents an extreme limit of solids – the epitome of disorder – in several ways. (1) For a perfect crystal, the ratio of the shear to bulk modulus, G/B, is of order unity while for a liquid, G/B = 0. At the jamming transition, the response to shear is infinitely weaker than the response to compression. That G/B vanishes at the jamming transition implies that the marginally jammed solid lies at the extreme edge of rigidity. (2) Any crystalline solid supports sound modes at sufficiently low frequency; since the wavelength of sound is long enough to average over microscopic details, the crystal, even with defects, is well approximated as an elastic medium. At the jamming transition, however, there are diverging length scales that exceed the wavelength of sound, even at arbitrarily low frequencies. This leads to qualitatively new physics: a new class of vibrational modes that overwhelms plane-wave behavior.

Linear response and diverging length scales in jammed solids

The harmonic approximation of an energy landscape is the foundation of much of solid-state physics. While the harmonic approximation is not exact and breaks down for large perturbations, the existence of a linear regime is essential to our understanding of ordered solids. Our prior work has led to significant progress towards uncovering the origin of commonality in disordered solids [A. J. Liu, S. R. Nagel, *Annual Reviews of Cond. Mat. Phys.* **1**, 347 (2010)]. Specifically, we have discovered that near this jamming transition, the shape of the landscape near each minimum is essentially the same within the harmonic approximation. As a result, linear response properties such as the elastic constants can be characterized by a single property of the minimum,

such as its energy, pressure or contact number, which quantifies the distance from the jamming transition for that state. This powerful property forms the basis of the jamming scenario, which has been shown to explain similarities in the mechanical and thermal properties of many disordered solids. According to the jamming scenario, we have established that the commonality that is observed in a wide range of glassy solids originates in the existence of two diverging length scales at the jamming transition: the "cutting length," l^*, which was previously understood in terms of a counting argument, and the "transverse length," l_T. Both of these diverging length scales govern the mechanical response to changes in boundary conditions. In particular, the transverse length, l_T, is the minimum size of a system whose boundary conditions are changed infinitesimally away from periodic ones.

Energy Loss at Propagating Jamming Fronts in Granular Gas Clusters

From the patterning of sand dunes to the intermittency of avalanches, the physics of granular materials depends on the complexities of inelastic interactions between neighboring particles. The influence of inelastic effects is perhaps most dramatically illustrated in the dynamics of a seemingly simple dilute gas of granular particles; even without any attractive interactions, dense particle clusters form due solely to energy loss during collisions. These clusters subsequently collide and fragment. There has been much theory and simulation outlining the many different regimes for the dynamics in such gases. However, there has been significantly less experimental work due to the difficulty of obtaining systems that do not immediately sediment due to gravity. We have studied one previously unappreciated regime, which can be studied by experiment as well as by theory and simulation, in which energy decays due to the collision of particle clusters. We have explored the initial moments of impact between two dense granular clusters in a two-dimensional geometry. The particles are composed of solid CO_2 and are levitated on a hot surface. Upon collision, the propagation of a dynamic ''jamming front'' produces a distinct regime for energy dissipation in a granular gas in which the translational kinetic energy decreases by over 90%. Experiments and associated simulations show that the initial loss of kinetic energy obeys a power law in time $E = -Kt^{3/2}$, a form that can be predicted from kinetic arguments.

Collision dynamics of particle clusters in a two-dimensional granular gas

In a granular gas, inelastic collisions produce an instability in which the constituent particles cluster heterogeneously. These clusters then interact with each other, further decreasing their kinetic energy. We reported experiments of the free collisions of dense clusters of particles in a two-dimensional geometry. The particles were composed of solid CO_2, which floated nearly frictionlessly on a hot surface due to sublimated vapor. After two dense clusters of ≈100 particles collide, there are two distinct stages of evolution. After a "jamming front" sweeps across each cluster, the kinetic energy decreases more slowly as the particles approach the container boundaries. In this regime, the measured velocity distributions are non-Gaussian with long tails. We compared our experiments to computer simulations of colliding, two-dimensional, granular clusters composed of circular, viscoelastic particles with friction.

Multiple transient memories in sheared suspensions

Multiple transient memories, originally discovered in charge-density-wave conductors, are a remarkable and initially counterintuitive example of how a system can store information about its driving. In this class of memories, a system can learn multiple driving inputs, nearly all of which are eventually forgotten despite their continual input. If sufficient noise is present, the

system regains plasticity so that it can continue to learn new memories indefinitely. We had previously shown how multiple transient memories could be generalized to a generic driven disordered system with noise, giving as an example simulations of a simple model of a sheared non-Brownian suspension. We have now, with computational support from DOE, further explored simulation models of suspensions under cyclic shear, focusing on three main themes: robustness, structure, and overdriving. We showed that multiple transient memories are a robust feature independent of many details of the model. The steady-state spatial distribution of the particles is sensitive to the driving algorithm; nonetheless, the memory formation is independent of such a change in particle correlations. We demonstrated that overdriving provides another means for controlling memory formation and retention.

Future Plans

As described above, we have found that the physics of jamming is important also for systems with a high degree of positional order. We are continuing to ascertain the limits of this behavior by studying the density of states of normal modes and the bulk and shear moduli of *polycrystalline* materials. We will be varying the size of the individual grains (and thereby change the overall amount of order) to see over what range jamming physics will still be important.

We will continue our earlier study of anharmonic effects near the jamming threshold. In particular we are interested in seeing how the stability of the amorphous solid is influenced by the anharmonic properties. The data that we find will then be compared with the situation in crystals. This will also involve a study of how defects are initiated by normal mode vibrations in crystals.

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Condensed Matter Theory

Lead PI – Mike Norman
Co-PIs – Olle Heinonen, Alex Koshelev, Ivar Martin, Kostya Matveev
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Project Scope

Condensed matter theory research programs are carried out in the areas of superconductivity, magnetism, and low dimensional systems, with an emphasis on interaction with various experimental programs at Argonne. Our long-term goal is to make fundamental advances in condensed matter physics as it relates to BES mission goals. In particular, we desire to make a major impact in a number of important endeavors, including the understanding of high temperature cuprate and pnictide superconductors, other transition metal compounds with novel properties such as quantum spin liquids and charge density waves, topological properties of metallic and nanostructured magnets, quantum phase transitions in strongly correlated electron systems, and transport in quantum wires, quantum dots, and spintronic devices. We are also developing as a center for theoretical analysis of spectroscopic and imaging data, not only within the context of MSD programs, but also those at the Advanced Photon Source and Argonne's Center for Nanoscale Materials, as well as other DOE national laboratory programs.

Recent Progress

Low-Dimensional Systems

Quantum Wires: The conventional Luttinger liquid theory states that the excitations of a one-dimensional system of interacting electrons are bosons with a linear dispersion. It is known that in this approximation, one can alternatively describe the excitations in terms of fermionic quasiparticles. As long as the electron dispersion is approximated as linear, the description of the excitation spectrum in terms of bosonic or fermionic excitations are equivalent. The finite curvature of the dispersion results in decay of the bosonic excitations with a rate that scales with energy as ε^2. We have studied the decay of the fermionic quasiparticles and discovered that their decay rate is proportional to ε^8. This means that the fermionic quasiparticles are more robust than the bosonic ones at low energies. As a result, the picture of fermionic excitations is more appropriate for studying the low-energy properties of one-dimensional systems beyond the linearized spectrum approximation, such as thermal transport in quantum wires. Our results are also applicable to the case when the physical particles constituting the Luttinger liquid have bosonic statistics. Furthermore, our conclusions hold for any interaction strength.

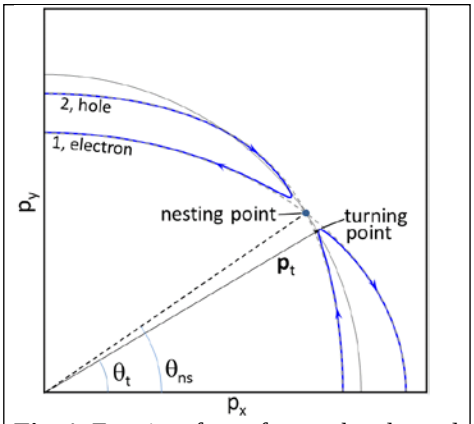

Fig. 1. Fermi surface of a two-band metal reconstructed near the nesting point by SDW order. Arrows illustrate orbital motion in a magnetic field.

Superconductivity

Magneto-transport in multiband metals: Almost all of the iron-pnictide compounds with spin density wave (SDW) order have an extended range of linear magnetoconductivity that is usually attributed to Fermi pockets with a Dirac-like

spectrum. We found, however, a simpler and more natural explanation of this behavior. The SDW transition strongly modifies the electronic spectrum near the points where the Fermi surfaces folded by the SDW wave vector cross (nesting points, Fig. 1). It is difficult for the electrons to pass through these points during their orbital motion in a magnetic field. As the Fermi momentum range over which an electron can cross the turning point is proportional to the magnetic field, this mechanism leads to a linear magnetoresistance. The crossover between the quadratic and linear field regimes takes place at a field scale determined by the SDW gap and the scattering rate.

Magnetism

Ferromagnetic resonance in height-modulated permalloy thin film nanostructures: A 100 nm thick Permalloy film was sputtered onto a colloidal crystal with individual sphere diameters of 200 nm, and its magnetic modes studied using broadband ferromagnetic resonance techniques and micromagnetic modeling. Two primary spin wave modes were seen experimentally. Modeling shows that both modes are nodeless in the unit cell but reside in different demagnetized regions of the unit cell. New, higher order topographically modified spin wave modes are also predicted (Fig. 2). The work demonstrates that topographic modification of magnetic thin films opens new directions for manipulating spin wave modes.

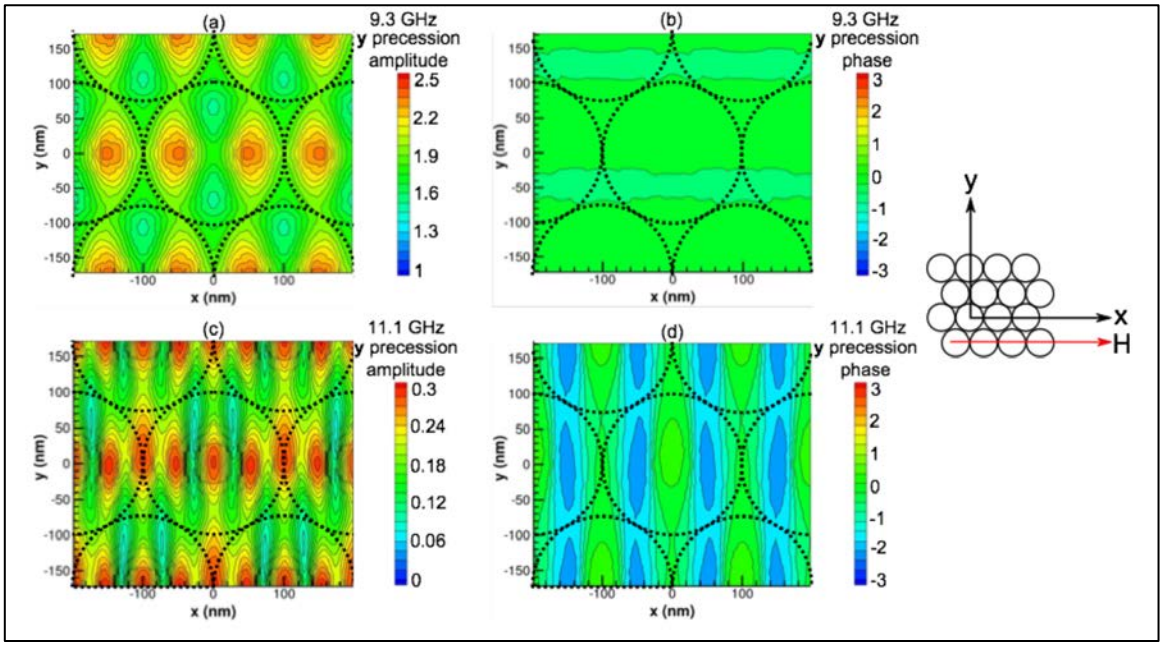

Fig. 2. Calculated magnon precession amplitude (left panels) and phase (right panels) with a field of 1000 Oe along the x-axis. The hexagonal topography is indicated with dashed circles. The figures cover two unit cells of the 2D hcp lattice.

Future Plans

Low Dimensional Systems

Physics of quasicrystals: In quasicrystals, matter self-organizes into states that are ordered in momentum space, but only quasiperiodic in real space. The practical importance of quasicrystals lies in their high mechanical strength and very unusual electronic and heat transport properties. As we have recently shown, quasicrystalline order can also emerge in quantum coherent cold-atom systems. We considered quasi-two-dimensional dipolar Bose gases in which the bosons experience Rashba spin-orbit coupling. We showed that the degenerate dispersion minimum due to spin-orbit coupling, combined with the long-range dipolar interaction, can stabilize a variety of quantum crystalline and quasicrystalline ground states, including striped states. We estimated that the crystalline and quasicrystalline phases should be detectable in realistic dipolar condensates and discussed their symmetries and excitations. The qualitative features of our analysis apply beyond the specific example of cold atomic gases. Armed with the developed intuition, we are now ready to address the long-standing problem of the stability of quasicrystalline alloys, which until now has defied unambiguous resolution. Quasicrystalline alloys are composed of two or more atomic species, which have approximately equal ionic radius, but different valence. Thus, by varying the composition, one can adjust the ratio of electronic and ionic densities, *e/a*. It has been empirically found that many stable quasicrystals arise in rather narrow ranges around "magic" values of *e/a*. This strongly suggests an electronic mechanism of their formation. However, despite the superficial simplicity of the system (a mixture or atoms and electrons), there is no explicit derivation of an effective theory. Instead, there are arguments, based on postulated Ginzburg-Landau (G-L) functionals, or density functional calculations with a large unit cell. To fill this gap in our understanding, we are developing an effective G-L functional in terms of the ionic density by integrating out the electrons. This effective description will allow one to predict the stable ionic configurations, and will then be used to simulate the thermodynamics and the kinematics of the quasicrystalline phase transitions.

Magnetism

Spin Liquids: We would like to understand the role that defects play in spin liquids. One of the postdocs in the Emerging Materials Group, Harry Han, has taken extensive neutron scattering data on the proposed spin liquid material $ZnCu_3(OH)_6Cl_2$ (herbertsmithite), where the Cu ions sit on a Kagome lattice. The data indicate a continuum of magnetic excitations over a broad range of momentum and energy. Recent low energy neutron data have been interpreted as due to interchanges between Cu and Zn sites, and we have shown that this gives rise to a specific heat in remarkable agreement with thermodynamic data (Fig. 3). Based on this, we would like to calculate the neutron spectra directly based on site diluted spin models such as those used to explain quantum criticality in heavy fermion metals. We would also like to also study the influence of longer range spin correlations, as the structure factor found in experiment cannot be fit with just near-neighbor spin interactions.

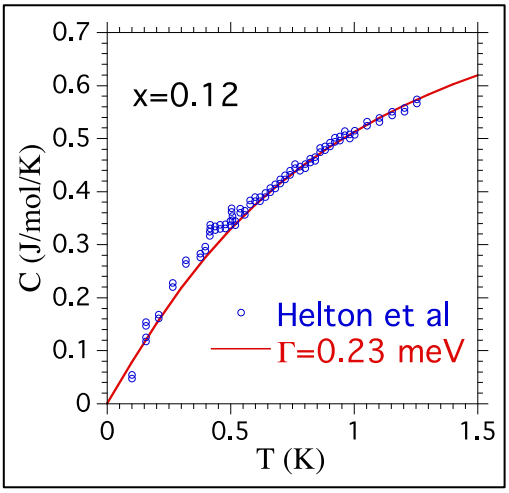

Fig. 3. Specific heat C of herbertsmithite compared to that calculated from a quasielastic Lorentzian of 0.23 meV based on low energy neutron data with an assumed impurity concentration of 12%.

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SPIN-ORBIT TAILORING OF MATERIALS PROPERTIES

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Project Scope

Spin-orbit coupling (SOC) rose in visibility almost a decade ago with the discovery of topological insulators (TIs) based on SOC and inverted bands. SOC connects the direction of the electron's orbital moment with that of its spin moment, while having an effect on both and coupling to magnetic order and to the lattice. For TIs the impact is qualitative – a matter of fact rather than one of magnitude, and small couplings may still be important. For most other areas of application of SOC (and for TIs as well) the magnitude is important. The magnitude of *just what* is one issue. 4-5 years ago we discovered computationally surprisingly large orbital moments in 3d oxides, values from 0.2-0.7 μ_B, an order of magnitude larger than in most 3d systems. It is also evident that moving to 4d and 5d systems will result in much large impact of SOC. We have pursued both limits: 3d and 5d oxides during the past year, and have uncovered new characteristics arising from SOC, e.g. the orbital moment of a 3d ion at a low symmetry site can be very sensitive to several factors, a behavior that may be useful for tuning properties. For each project summarized below, we begin by listing one of the important (usually surprising) findings.

Recent Progress

An **invited overview** [1] titled *Magnetism at the Edge: New Phenomena at Oxide Interfaces* was published in the December 2013 MRS Bulletin. That the invitation was extended to this PI was based on ~15 papers our group has published on oxide interfaces and heterostructures (or very closely related natural materials) in the past eight years.

An **extended overview** on charge states (equivalently, oxidation states) was published in a special issue of *J. Phys.: Condens. Matt*. (2014).[2] We had established in several *charge order* or *charge disproportionation* systems that the two charge states in the ordered phase, e.g. $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$, contain the same 3d occupation – the same charge. This revelation is disturbing, first because there are several paradigmatic metal-insulator transitions that suddenly are no longer understood, and second because the concept of "charge state" underpins our basic understanding of strongly correlated transition metal oxides. We are in the process of rebuilding a quantitative understanding of charge states in terms of occupied Wannier functions. This overview described the basic conundrum and a beginning of the resolution.

1. LNO/LAO multilayers. [3] *Finding: numerous broken symmetries in the ground state* of ultrathin $LaNiO_3$ (LNO) layers confined within $LaAlO_3$ (LAO) slabs with (111) growth orientation. Nearly all of the many studies of oxide heterostructures and interfaces to date have addressed (001) grown films. In our new work various broken symmetry two-dimensional ground states are predicted in (111)-oriented $(LNO)_N/(LAO)_M$ superlattices,

based on density functional theory calculations including a Hubbard U term. M=5 is sufficient to enforce 2D character of the LNO layers. In our results, the LNO bilayer with graphene-like topology (N=2) displays a switchable multiferroic (ferromagnetic [FM] and ferroelectric) insulating ground state with inequivalent Ni sites and thus two inequivalent "interfaces." An unanticipated Jahn-Teller distortion with d(z^2) orbital polarization and a FM Mott insulating, and again multiferroic, phase emerges in the N=1, M=1 (alternating layer) case, which is actually the double perovskite structure usually pictured as (pseudo)cubic. With its strong response to strain, this system has a higher potential for orbital engineering of behavior than the more heavily studied (001) superlattices. The confined LNO slab undergoes a metal-to-insulator transition through a half-semimetallic phase beyond N=3 with conduction originating from the interfaces.

This work built on our 2013 *Physical Review Letter* [4] on $LaAlO_3/SrTiO_3$(111) interfaces involving t_{2g}, rather than e_g, orbitals. The dominating features making (111) growth a richer platform for competing (and finally broken symmetry) ground states are: (1) triangular and hexagonal symmetry rather than tetragonal, and (2) dissonance between threefold growth symmetry and (approximate) fourfold local symmetry of the perovskite lattice.

2. The heptavalent Mott insulator $KOsO_4$. [5] *Finding: substantial orbital moments can arise in e_g subshells*. Applying the correlated electronic structure method based on DFT+U calculations we have investigated the tetragonal scheelite structure Mott insulator $KOsO_4$, whose e_g^1 configuration should be affected little by spin-orbit coupling (SOC). This work is done in collaboration with K.-L. Lee (Korea University). The method reproduces the observed antiferromagnetic Mott insulating state, populating the Os d(z^2) majority orbital. The quarter-filled e_g manifold is characterized by a small symmetry breaking due to the structure, and a relatively small crystal field splitting considering the high formal oxidation state Os^{7+}. The small magnetocrystalline anisotropy before including correlation (i.e. in the metallic state) is increased by more than an order of magnitude in the Mott insulating state, a result of interplay between large SOC and strong correlation. In contrast to conventional wisdom that the e_g complex will not support orbital magnetism, we find that for the easy axis [100] direction a large Os orbital moment $M_L \sim -0.2\ \mu_B$ compensates half of the Os spin moment $M_S=0.4\ \mu_B$, leaving most of the net moment lying on the oxygen tetrahedron. The origin of the orbital moment has been analyzed, with spin-orbit lowering of symmetry being the substantial factor. Further interpretation was assisted by analyzing the spin density and the Wannier function when SOC is taken into account.

3. The ferromagnetic insulator Ba_2NaOsO_6 (BNOO). [6] *Finding: manipulating direction of spin (and orbital) moment can control a metal-insulator transition*. With the Na+ ion being an onlooker, this osmate double perovskite compound consists of weakly coupled OsO_6 clusters, and of course Os has large SOC. It has several unusual characteristics: a ferromagnetic insulator (very unusual); a very high oxidation state Os^{7+} (also unusual); an open d^1 shell with no Jahn-Teller splitting (peculiar); an anomalously small Os moment. Our hybrid functional + SOC calculation models this compound's behavior well, including that [110] is the magnetic easy axis. Our calculation of the (spin+orbital) susceptibility and the NMR screening fraction will be compared with experimental data of our collaborators (Curro, UC Davis; Fisher, Stanford).

4. The complex quadruple perovskite $CaCo_3V_4O_{12}$ (CCVO). [7] *Finding: large orbital moments (arising from SOC) may feed back and affect the magnitude of the spin moment*. The new quadruple perovskite compound $CaCo_3V_4O_{12}$ (CCVO) was pressure-synthesized by the

Dresden group (which included as coauthor our former theory student Deepa Kasinathan!), and its Curie-Weiss susceptibility requires large orbital moments on Co as an explanation. Postdoc HB Rhee has performed the first electronic structure calculations on this material, which became a challenging task due primarily to the very narrow Co 3d bands and the very low Co site symmetry. This compound has the same structure as $CaCu_3Ti_4O_{12}$ whose ultrahigh dielectric constant ~10^5 attracted much attention a decade ago (it was found to be an extrinsic effect) including work of our group.

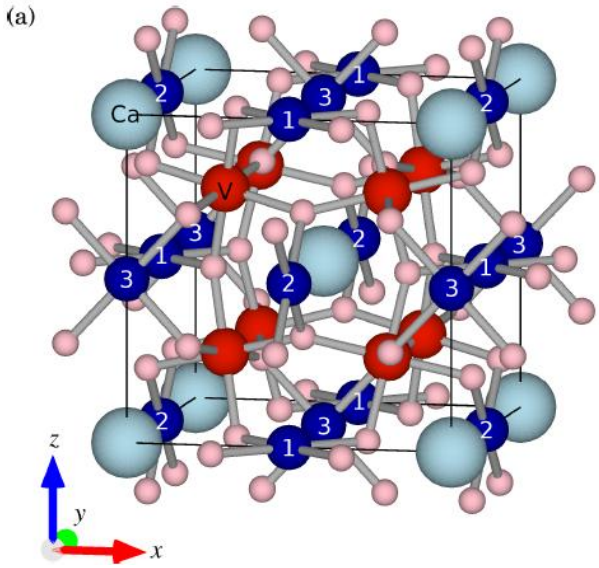

Figure 1. The crystal structure of the overall cubic compound CCVO, with the Co ions in a very low symmetry sites, centered in a rectangular O_4 plaquettes oriented perpendicular to the three cubic axes. V ions are located in oxygen octahedral with roughly (locally) cubic symmetry. The low symmetry of the Co site (labeled by 1, 2, 3) leads to behavior of the spin-orbit-coupling induced orbital moments that have not been seen in the more commonly studied t_{2g} and e_g (pseudo)cubic symmetries.

We studied the electronic and magnetic structures and spin and orbital moments of CCVO in a systematic way, using a selection of methods from density functional theory. Implementing the generalized gradient approximation and the Hubbard U correction (GGA+U), ferromagnetic spin alignment leads to half-metallicity rather than the observed narrow gap insulating behavior. Including spin-orbit coupling (SOC) produces a half semimetallic spectrum that is practically Mott insulating. Evidence was obtained of the large orbital moments that have been inferred from the measured Curie-Weiss constant. Switching to the orbital polarization (OP) functional, GGA+OP+SOC also displays clear tendencies toward very large orbital moments but gives behavior that is substantially different. In both approaches application of SOC, which requires specification of the direction of the spin, introduces large differences in the orbital moments of the three Co ions in the primitive cell. For more clarification we studied a fictitious cousin compound $Ca_3CoV_4O_{12}$ (Ca replacing two of the Co atoms) to probe in more transparent fashion the interplay of spin and orbital degrees of freedom with the local environment of the planar CoO_4 units. The observation that the underlying mechanisms seems to be local to a CoO_4 plaquette, and that there is very strong coupling of the size of the orbital moment to the spin direction, points to a non-collinear alignment of the 3 Co moments, and also of the 4 V moments, each with its own <111> symmetry direction. Full understanding of this material provides a challenge for the future.

Future Plans.

- Our studies of 5d d^1 systems will be followed by study of additional t_{2g} systems containing d^2, d^3, and d^5 ions, where studies in each case have shown unusual magnetic behavior. Example: the d^3 ion (half filled, high spin) would seem to be simple, so why is the magnetic behavior of La_2NaTO_6 (*T*=Ru, Os) peculiar? This work will be done in collaboration with K.-L. Lee (Korea University), just beginning a sabbatical year in our group.
- The complex behavior of the Co^{2+} ion in the low symmetry site in CCVO open unanticipated questions about the origin and magnitude of orbital moments, and on their effect on the spin moment. Another low symmetry compound will be chosen to provide additional insight into this new issue.
- The unusually intricate broken-symmetry ground states obtained in transition metal oxide nanostructures with (111) growth direction will be extended in work with our collaborator R. Pentcheva (University of Duisberg).

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The "to be submitted" manuscripts below are in essentially final form.

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Complex (anti)ferroic oxides: statics and dynamics at finite temperatures

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Project Scope. Complex oxides that exhibit ferroic, antiferroic or multiferroic properties are of extreme fundamental and technological importance. Fundamentally such materials are very attractive because they exhibit delicate energy competitions which result in appearance of some spontaneous property (magnetization, electric polarization or strain) or particular type of ordering. Technologically they are in the heart of numerous applications. A few examples include memory applications, pyroelectric sensors, pressure sensors, capacitors, optical communications, ultrasonic motors, phase-array radars, ultrasound imaging and actuators, thermistors, filters, light detectors, high-power microwave devices, and many others. However, despite of their special role in both fundamental and applied sciences, many such materials and their properties remain rather poorly understood. Some examples include statics and dynamics of antiferroelectrics and relaxors, exotic energy conversion mechanisms in (anti)ferroics, fundamental intrinsic dynamics of such materials, and (anti)ferroic phenomena at the nanoscale. Such lack of understanding critically hinders both scientific and technological progress, especially as it applies to the nanoscale.

The ultimate goal of this project is to achieve a fundamental understanding of statics and dynamics of complex oxides that exhibit ferroic, antiferroic, multiferroic or relaxor properties at both macro- and nano-scales through state-of-the-art computer simulations.

Recent progress.

Soft mode dynamics in $PbTiO_3$ from atomistic simulation.

$PbTiO_3$ is regarded as a model ferroelectric perovskite with mostly displacive first-order phase transition associated with softening of the relevant phonons. A microscopic explanation derives its origin from the competition between the short-range interaction which stabilize the paraelectric phase and a long-range interaction which stabilizes the ferroelectric phase. Near the Curie point the short- and long-range interactions compensate each other in such a way that the

frequency of a transverse optical phonon approaches zero. Interestingly, while $PbTiO_3$ indeed provides one of the best examples of the displacive phase transition associated with softening of polar mostly underdamped modes, the possibility of an additional excitation associated with order-disorder mechanism has been considered in the literature. However, despite considerable efforts towards a better understanding of the soft mode dynamics and nature of the phase transition in this material the issue remains controversial.

To address the nature of phase transition in $PbTiO_3$ from atomistic simulations we developed a first-principles force-field that allows simultaneously accurate description of both static and dynamical properties of $PbTiO_3$ at finite temperatures. Figure 1(a) shows the dependence of the soft mode frequency on the temperature obtained from our computations. Experimental data from the literature are given in the same figure for comparison. The figure demonstrates a very good agreement between computational and experimental data.

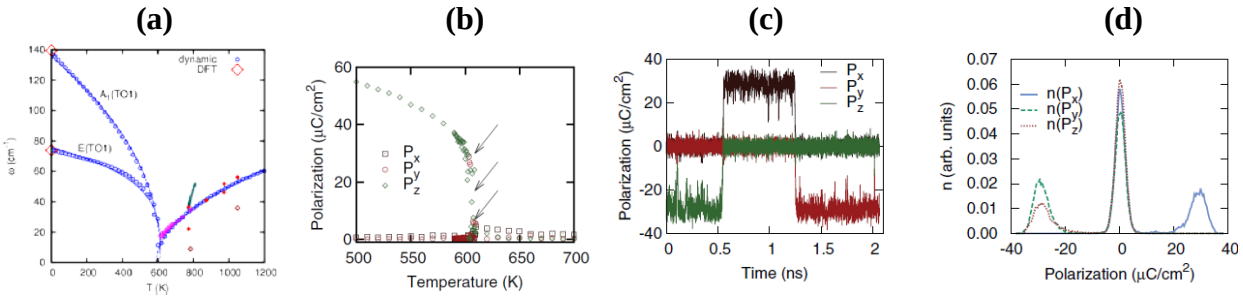

Fig. 1. (a) The soft mode frequency as a function of temperature. The blue symbols indicate our computational data; the large red diamonds give first-principles data, while the rest shows experimental data from literature. (b) The Cartesian components of the polarization vector as a function of temperature in the vicinity of the phase transition. The arrows indicate fluctuations. (c) The time evolution of the Cartesian components of the polarization at 603 K as obtained from a 2.1 ns Molecular Dynamics run. (d) The probability distribution of the Cartesian components of the polarization at 603 K as obtained from data given in panel (c).

Next we used the newly developed force-field to address the nature of phase transition in $PbTiO_3$. Figure 1(b) shows the dependence of the polarization vector components on the temperature. Interestingly, we found that there exists a narrow region of temperatures in the vicinity of the phase transition where the polarization exhibits drastic fluctuations in both magnitude and direction. Such behavior seems to suggest the existence of an order-disorder component to the phase transition in the sense there exists large thermal hopping between multiple states. To gain further insight we followed the time evolution of the polarization during 2.1 ns for a few temperatures in the vicinity of the phase transition. Figure 1(c) shows our

computational data and reveals large amplitude thermal hopping between states associated with different polarization. The probability distribution function associated with this time evolution plot is given in Fig. 1(d). The presence of multiple peaks unambiguously demonstrates the order-disorder mechanism associated with this temperature. We concluded that while ferroelectric phase transition in $PbTiO_3$ is mostly driven by the soft mode, there exists a narrow temperature region in the vicinity of the Curie point where the order-disorder mechanism is present.

The role of mechanical boundary conditions in the soft mode dynamics of $PbTiO_3$.

In most ferroelectrics the transverse optical soft mode is strongly coupled to the acoustic phonons giving rise to a coupled ferroelectric structural phase transition. Such coupling makes soft modes very sensitive to mechanical stresses and strains. In other words, the dynamics of the soft mode will exhibit a strong dependence on the mechanical boundary conditions such as pressures, stresses and strains. For example, the soft mode frequency typically decreases as a function of hydrostatic pressure and can be well described by the Curie-Weiss pressure law. The law states that the square of the soft mode frequency is proportional to the applied pressure. Such sensitivity of the soft mode dynamics to the mechanical forces is very attractive since it allows: 1) manipulation of the soft mode dynamics via an appropriate choice of the mechanical boundary conditions; 2) uniquely identifies boundary conditions by the change in the soft mode dynamics. The latter one turned out to be very useful in studies of residual stresses in ferroelectric thin films and superlattices. Interestingly, however, many such studies relate the change in the soft mode dynamics to the residual stresses on the basis of the Curie-Weiss pressure law. One may wonder, however, whether the Curie-Weiss pressure law is applicable to study the residual stresses and strains in ferroelectric nanostructures. To answer this question we carried out simulations of soft mode dynamics in $PbTiO_3$ under a variety of mechanical boundary conditions.

Figure 2(a) shows the dependence of the soft mode frequency squared on the hydrostatic pressure for a few temperatures in ferroelectric P_{4mm} phase. From the graph we notice that our data are in good agreement with experimental findings and that they follow the Curie-Weiss pressure law in the pressure and temperature range investigated. Furthermore, we note that in P4mm phase the frequency of the soft mode *decreases* under compression. Figure 2(b) shows similar data but when $PbTiO_3$ is subjected to biaxial strains. From the data we conclude that

there exists Curie-Weiss strain law that relates the soft mode frequency to the biaixal strain. Interestingly, however, we find that in ferroelectric P_{4mm} phase the soft mode frequency *increases* under compression. Note that negative strain indicates compression. This is just the opposite of what we observed under hydrostatic pressure and suggests that the Curie-Weiss pressure law may not be applicable for studies of residual stresses and strains in ferroelectric nanostructures.

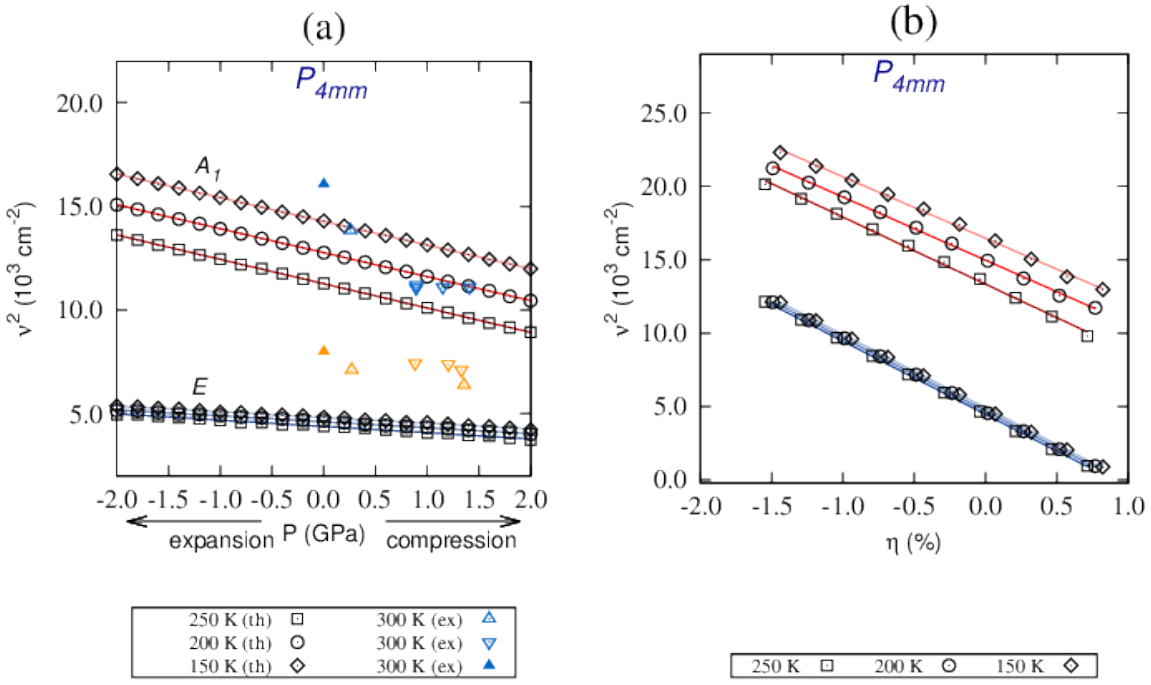

Fig. 2. Dependence of the soft mode frequency squared on the hydrostatic pressure (a) and biaxial strain (b). In panel (a) triangles indicate experimental data from literature.

Future plans.

In future we plan on studying antiferroics, multiferroics and relaxors. In particular, we will focus on developing of a force-field and studying finite-temperature properties of antiferroic $PbZrO_3$ in bulk and nanostructures. Another research direction is the dynamics of partially compensated nanostructures and multiferroics.

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Emergent properties of highly correlated electron materials

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Project Scope

The primary goal of this program has been to explore robust low energy properties of correlated electron materials in the context of simplified effective model systems. These effective models include simplified Hamiltonians and effective field theories. They are sufficiently simple in that they involve far fewer microscopic degrees of freedom than are present in an actual material. This in turn allows us to identify well-controlled solutions to the theory in various limits; the qualitative, robust features present in such solutions that may carry over to real materials, and by finding many soluble limits, we are able to "triangulate" a complex many-body problem. Examples of phenomena studied include unconventional superconductivity, novel broken symmetries in correlated electron materials, topological phases and phase transitions, and non-Fermi liquid behavior. Specific issues that have been addressed in this project so far include: 1) identifying new qualitative strategies for raising the transition temperature of unconventional superconductors, 2) phenomenology of the spin-triplet superconductor Sr_2RuO_4, in particular on the absence of observed edge electrical currents, 3) phenomenology of the pseudogap regime of hole-doped cuprate superconductors, in particular the consequences and nature of charge order in the pseudogap regime, 4) phenomenology of heavy fermion materials, and 5) new descriptions of metals in the vicinity of continuous zero temperature phase transitions.

Recent Progress

Below are some highlights of progress made in the past 2 years (a more comprehensive publication list is appended below the highlights).

Bandstructure effects on unconventional superconductivity – the PI, in collaboration with Weejee Cho (graduate student), Ronny Thomale (former postdoc, currently a faculty member at Wurzburg), and Steven Kivelson, considered the role of competing orders and perturbations to the bandstructure on the paring scale and pairing symmetry of unconventional superconductors. In this project, several general design principles were uncovered by studying the system in a controllable weak-coupling limit. Several examples include: 1) observation of a phase transition from d-wave to sign-changing s-wave superconductivity in a bilayer model as a function of interlayer tunneling, 2) role of CDW on the pairing symmetry, in particular in changing the pairing symmetry from B1g to B2g symmetry as a function of the CDW amplitude, 3) smooth evolution of the d-wave gap

function in a square lattice to a sign-changing s+d solution in a quasi-one dimensional system as a function of increasing nematicity.

New strategies for raising T_c of unconventional superconductors – the PI, in collaboration with Ted Geballe and Ronny Thomale considered the role of screening of longer ranged interactions on raising the transition temperature. He considered the role of long range interactions in the weak-coupling limit, where the induced non-local attractions by particle-hole fluctuations have to overscreen long range repulsive forces. This was studied in the context of extended Hubbard models in the weak-coupling limit using both perturbative renormalization group as well as functional RG techniques. The role of long range interactions in lowering T_c in the strong coupling limit was studied using slave boson mean-field theories and in all cases, the PI concluded that if correlated metals were embedded in a highly polarizable solid-state environment which would aid in screening away long range coulomb forces, the result would be a substantially enhanced transition temperature. The analysis led to the argument that charge reservoir layers in multi-layered cuprates may play a role akin to a highly polarizable medium.

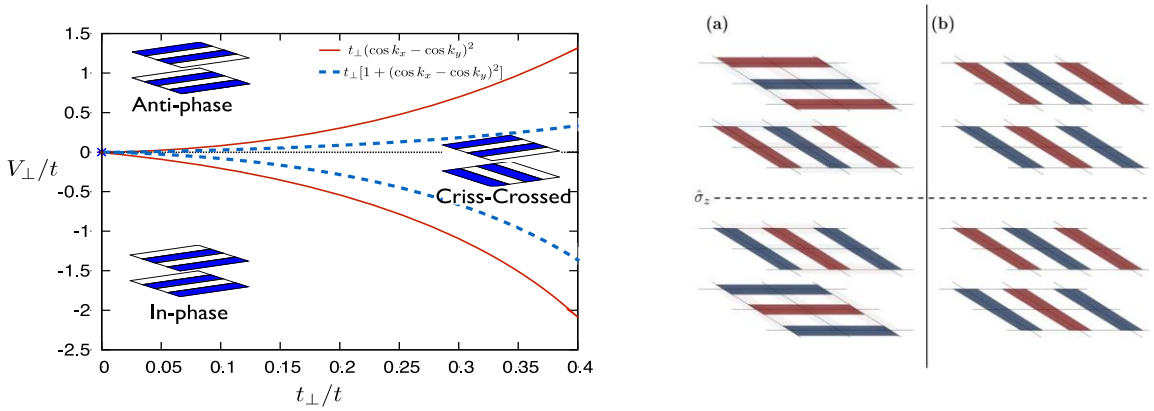

Figure 1 (left) Phase diagram as a function of interlayer tunneling and interplane Coulomb interactions. There is a crisscrossed phase, which breaks mirror symmetries in addition to translation symmetry. (right) proposed structure of charge order in the crisscrossed phase (a) and in the striped phase (b).

Phenomenology of the pseudogap regime of hole-doped cuprate superconductors – The PI, along with his student Akash Maharaj and his postdoc Pavan Hosur considered the role of interlayer tunneling and interlayer Coulomb interactions on the charge order of YBCO. The main conclusions of this study was that due to the momentum dependence of the interlayer tunneling, there is a regime in which the charge order becomes "cris-crossed", breaking vertical mirror symmetries in addition to translational symmetries (see Fig. 1). The pattern may naturally account for the fermiology observed in quantum oscillation measurements of YBCO, it can account for recent THz regime transmission measurements in films, and has predictable experimental consequences in terms of transport in the presence of strain. The paper has been submitted to the Physical Review, and the PI and his group members are currently studying phenomenological consequences of the theory, making predictions for elastoresistivity measurements.

New descriptions of non-Fermi liquids at quantum critical points – The PI, with his colleague Shamit Kachru has developed new approaches to the old problem of quantum phase transitions in metals. Specifically, he has formulated and studied low energy effective field theories of metals near continuous zero temperature Pomeranchuk instabilities, and studied the destruction of the Landau quasiparticle in such theories. By departing from the standard approach to this problem, and treating the fermions and bosons (order parameter fields) on a completely equal footing, the PI and his collaborators have looked for new soluble limits that shed light on the scaling behavior of this system. The particular new aspect to this work involves new large-N limits, which are soluble and which allow for strongly overdamped *fermion* modes. The solutions are complementary to the present approaches to the problem, in which predominantly the order parameter modes are strongly overdamped. Among the physical outcomes of this theory are: 1) strong dressing of the fermions near the Fermi surface – renormalization of and vanishing of the Fermi velocity (i.e. effective mass divergence) and branch cut propagators (which would produce broad incoherent spectral functions), 2) strong instabilities towards charge density wave in an SU(N) large N theory, and 3) strong instabilities towards superconductivity in an SO(N) large N theory. We are currently investigating the possibility of obtaining high temperature superconductivity out of an incoherent normal state in the context of such simplified effective field theoretic models. We have also studied the problem using scaling and renormalization group techniques (see Fig. 2) to produce descriptions that are identical to the solution of the theory in large N limits. (See below for a list of publications that resulted in this project). Our strategy has been to take a purely Wilsonian approach, never to integrate out gapless degrees of freedom in a renormalization group treatment.

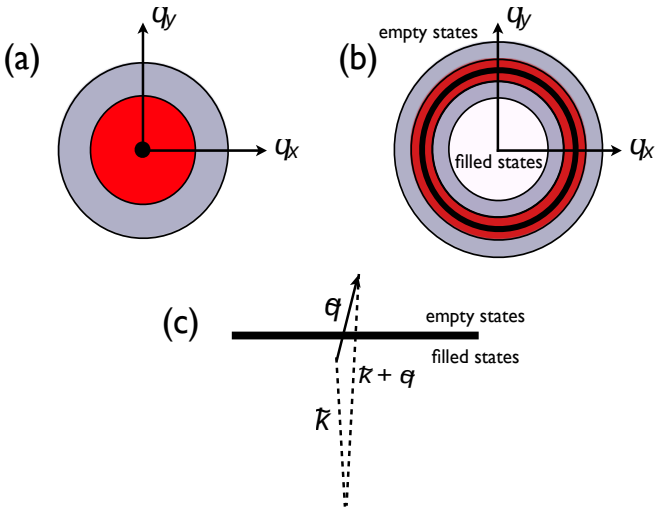

Figure 2 Scaling near in the vicinity of a metallic quantum critical point associated with a Pomeranchuk instability. The order parameter fields are bosons whose low energy locus is a point in momentum space (a) whereas the fermions occupy a Fermi surface in momentum space. The vastly different kinematics in this problem in addition to the requirement that the coupling between the two sets of particles (c) must conserve momentum and energy poses a considerable challenge. High energy modes eliminated in the RG are denoted by blue, whereas the low energy degrees of freedom are in red.

Future Plans

Raising T_c via screening by a proximate polarizable medium – the PI will study the question in the context of quasi-one dimensional solids such as the Bechgaard salts, which

have quasi-one dimensional crystal structures. He will investigate the role of longer ranged interactions on T_c in these materials. The advantage of quasi-one dimensional systems is that they allow for a more controlled non-perturbative approach via bosonization techniques. The PI will also consider experiments in multilayered cuprates and the role of dissipation as a complementary aspect of screening in raising the transition temperature by suppressing phase fluctuations.

Non-Fermi liquids – the PI will study the onset of antiferromagnetism in metals using the techniques he developed with Kachru and co-workers in the context of Pomeranchuk transitions in metals. He will study the problem using Eliashberg theory and consider both overdamped fermions and bosons and their consequence for superconductivity as well as charge density wave instabilities.

Unconventional superconductivity – the PI, in collaboration with Ross McKenzie and Weejee Cho (graduate student) is developing and analyzing superconductivity in purple bronze. Preliminary findings involve the prediction of spin triplet pairing in this system. Publication is in preparation.

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4. A. Maharaj, R. Thomale and S. Raghu, "Particle-hole condensates of higher angular momentum in hexagonal systems," Phys. Rev. B **88**, 205121 (2013).
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9. H. Watanabe, S. Parameswaran, S. Raghu, and A. Vishwanath, "Anomalous Fermi liquid phase in metallic skyrmion crystals", Phys. Rev. B, in press.
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12. A. Maharaj, P. Hosur and S. Raghu, "Criss-crossed stripe order from interlayer tunneling in hole-doped cuprates," arXiv:1406.4154, submitted to PRB.

Theory and Modeling of Optical and Magnetic Properties of Functional Nanomaterials

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Project Scope

Our work focuses on understanding structure-function relationship in nanomaterials so as to enable the long term goal of rational material design. We are particularly interested in understanding factors that control the magnetic and optical properties of these materials and their response to ultrafast external fields. We thus develop and apply techniques which provide accurate description of excited and bound states, correlation effects and non-adiabatic, non-equilibrium behavior of nanosystems. Our efficient Density Functional Theory + Dynamical Mean-Field Theory (DFT+DMFT) algorithm allows proper incorporation of electron-electron interaction. While our density matrix version of Time-Dependent Density Functional Theory (TDDFT) makes feasible examination nonlinear effects (e.g. trions, biexcitons, exciton-plasmon and plasmon-phonon coupled states) in nanostructures. For nonequilibrium phenomena we construct exchange-correlation functionals by merging DMFT and TDDFT. Our systems of interest include transition metal nanoalloys and dichalcogenides and magnetic nanoparticles.

Recent Progress

Non-adiabatic Time-Dependent Spin-Density Functional Theory for strongly correlated systems: We have developed a methodology for examining the spectral properties and nonequilibrium response of strongly-correlated electron systems within multi-orbital time-dependent spin-density functional theory. The key element of the theory – exchange-correlation (XC) kernel - is derived from the expression in dynamical mean-field theory (DMFT) for two-particle susceptibilities and the electron self-energy for the effective Hubbard model. We demonstrate that the appropriate description of strongly-correlated materials requires a non-adiabatic (time non-local) XC kernel, though the spatial locality in general is not necessary. As in dynamical mean-field theory, in TDSDFT such interaction defines the main properties of correlated systems, including satellite Hubbard peaks in the electronic spectrum. We find that the corresponding nonadiabatic XC kernel reproduces main features of the spectrum of the Hubbard dimer and the infinite-dimensional Hubbard model, some of which are impossible to obtain within the adiabatic approach. We test the theory by applying it to several strongly correlated materials, including the spectral properties of cerium and $YTiO_3$, and establish that the method is capable of describing both metallic and insulating systems. In addition, we present results of the nonequilibrium response of $YTiO_3$ under an applied short laser pulse. In particular, we analyze the role of inter-orbital interactions in the relaxation dynamics of the system.

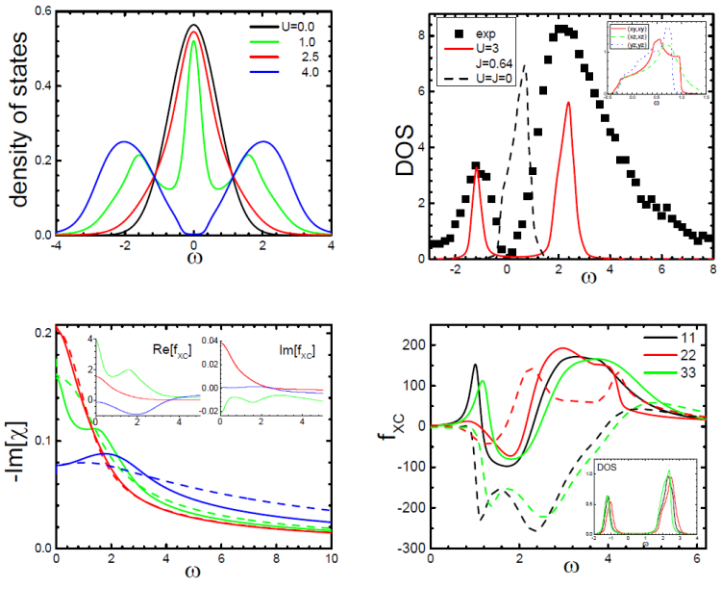

Fig. 1 Left(top): The DMFT DOS for the one-band Hubbard model at different values of the Coulomb repulsion; left (bottom): the corresponding TDDFT excitation spectrum (the inset graph shows the frequency dependence of the XC kernel). Right (top): The LDA results for the projected DOS for the t_{2g} electrons (top) and the NA-TDSDT results for the total DOS together with the DMFT and experimental data (Arita et al., 2007) (bottom) for $YTiO_3$.

***A DFT + Nonhomogeneous DMFT approach for finite systems*:** We have developed a code which combines DFT and dynamical mean-field theory (DFT + DMFT) and is feasible for application to non-homogeneous systems containing few hundred atoms. The single impurity problem in DMFT involves finding of the single-electron Green's function for the given site/orbital by treating the rest of the electrons in the system as a bath. We have used Iterative Perturbation Theory (IPT) approximation for the solver in which the expression for the single-electron self-energy is a function of second order in the local Coulomb repulsion parameter and it is chosen such that the resulting self-energy satisfies correctly known limiting cases (such as the high-frequency and large-Coulomb repulsion limits). The main advantage of the approximation is its simplicity which speeds up the calculations. We have applied the code to investigate the role of electron-electron correlations in determining the magnetic properties of Fe nanoparticles containing 11 to 147 atoms, which we believe is the first calculation of the kind. We demonstrate that experimentally observed non-monotonous dependence of the magnetization as function of cluster size can be better reproduced within DFT+DMFT than by DFT+U.

Magnetocrystalline anisotropy of FePt nanoparticles: We have carried out theoretical investigation of Magneto Crystalline Anisotropy (MCA) of L10 FePt nanoparticles which have alternating Fe and Pt plane along (001). Structural relaxation and magnetic moment of the clusters are evaluated using spin polarized *ab initio* density functional theory, and the MAE is calculated using two approaches: (i) self-consistent inclusion of spin-orbit coupling in DFT and (ii) the torque method. The clusters studied have 3(4) planes of Fe and 2(3) planes of Pt atoms and vice versa. We find an enhancement of MCA for the FePt clusters as compared to that of pure Fe nanoparticles with the same size and geometry and bulk L10 FePt. We trace this enhancement to the increased spin and orbital moment of Pt atoms which raises the spin-orbit coupling constant. We also find that nanoparticles with Pt atoms in the central layer have larger MCA than the corresponding ones whose central layer is Fe. This is due to the fact that when Pt is in the central layer it has more Fe atoms around so it more strongly hybridized resulting in higher orbital moments than that of Pt atoms in other layers. Detailed investigation of electronic structure of atoms in different position on the clusters is also performed.

A DFT study of geometric, electronic, and magnetic properties of Fe_xAu_{113-X} (x=23, 56, 90) core-shell nanoparticles: We have performed spin dependent DFT calculations for Fe_xAu_{113-X} (x=23, 56, 90) nanoparticles to find that these nanoparticles prefer the formation of core-shell structure and the Fe core of the nanoparticles maintains almost constant magnetic moment of ~2.8 μ_B regardless of the Fe content, which is 27% enhancement from the bulk value, in agreement with previous studies. The local magnetic moment of Fe atoms are correlated with the local coordination of Fe atoms and the enhanced magnetic moment is a result of charge depletion from Fe to Au atoms. We find that the more the depleted charge, the larger is the induced magnetic moment. This indicates that electron depletion is crucial for the enhancement of the induced magnetic moment for Fe atoms. The case of $Fe_{90}Au_{23}$ is interesting as only a partial Au shell can be formed owing to the lack of the sufficient number of Au atoms in the cluster. This core-shell structure is more stable than the segregated phase consisting of two Fe and Au nanoparticles. Segregation between Fe and Au phases may be driven by large surface energy mismatch and core stress, but another important factor for the formation of the core-shell structure could be low surface tension in the Fe-Au interface (i.e., strong Fe-Au interfacial interaction), which we attribute to the large charge transfer at the interface.

***Tuning plasmon excitations in transition-metal doped arrays of noble-metal nanochains*:** We apply time-dependent density-functional theory to study the absorption spectrum of arrays of nano-scale pure noble and transition metal (TM) chains. We find 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 more than 10 atoms. We also find collective excitations (plasmons) in arrays of TM chains: a behavior distinct from bulk TM systems. Doping noble metal chains with TM atoms leads to additional plasmon peaks close in energy to the main one for the undoped case. We 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 the multi-chain case, the response is very sensitive to the position of the doped atoms. We argue that the origin of the additional modes is charge oscillations around the impurity atoms. Finally, we analyze the effect of interaction of excitonic modes created in infinite chains with plasmons in neighboring nanochains, including the possibility of resonance excitations and their trapping by the TM impurity atoms.

Trions and other excitations in monolayer transition-metal dichalcogenides: We applied our TDDFT formalism to study trions (two electrons and a hole) and excitons in monolayer MoS_2, $MoSe_2$ and WSe_2. The binding energies of these states were obtained using several different types of exchange-correlation kernels: local, including LDA and GGA kernels, and long-ranged kernels, such as Slater. Good agreement with experimental results (hundreds and tens of meV for exciton and trion, correspondingly), was obtained only in the presence of long-ranged kernels, showing the importance of long-range features of the inter-particle interaction (Coulomb type). Our results are the first consistent TDDFT calculations of the trion energies, which give theoretical confirmation of the experimentally found large binding energies of the electron-hole states in TM dichalcogenides. The relatively large values of these binding energies, suggest possible technological applications at room temperature.

***Effect of monolayer substrates on the electronic structure of single-layer MoS_2*:** We have performed first-principles calculations based on DFT to examine structural and electronic properties of a single layer of MoS_2 deposited on single-layer substrates of hexagonal boron nitride (BN), graphene and silicene. All have a honeycomb structure; hence the formation of heterostructures is expected. Since the lattice mismatch between MoS_2 and these substrates is large, we have considered different periodicities among layers so as to reduce, as far as possible, the incommensurability between the lattices. Our results show that BN barely affects the electronic structure of isolated single-layer MoS_2; the DFT gap remains ~1.8 eV. Graphene and silicene severely modify the electronic structure introducing additional states within the optical gap. Adsorption on graphene turns the system into a zero band gap semiconductor, bringing the conduction bands of MoS_2 down to the Fermi level of graphene. Adsorption on silicene shifts the MoS_2 valence and conduction bands towards the silicene Fermi level, in addition to inducing a gap of 55 meV in the silicene itself. We present analysis of possible charge transfer in these systems and discuss the relevance of these hetero structures for practical applications.

Electron-Phonon Coupling and Photoluminescence in monolayer MoS_2: We have carried out first principles calculations of the photo-luminescent properties of monolayer MoS_2 using DFT. In particular, we have analyzed the role of electron-phonon interactions in the photoluminescence process. Phonon dispersion curves calculated using DFPT served as the basis for the evaluation of the system electron-phonon coupling, which in turn was used to calculate the electron self-energy and the electron spectral function within the Eliashberg approach. We find that the resulting photoemission spectrum is in good agreement with experimental data. We pay special attention to the ultrafast relaxation of the electron system as manifested by the electron-phonon coupling and evaluate the ultrafast photoluminescence of the excited system by using the two-temperature model. It is shown that similar to graphene, MoS_2 may demonstrate significant ultrafast photoluminescence.

Future Plans

Some future directions:

• Application of TDDFT formalism to study other types of coupled excitations in arrays of noble and transition metal nano-chains and other structures, including exciton and polaritons and phonon-plasmon and exciton-polaritons interactions. The analysis of these types of excitations will lead to a more complete understanding of possible excitations and potential tunability of the optical absorption spectrum of TM-doped systems by changing their size, shape and chemical composition. Other systems of interest are monolayers of several dichalcogenides and BN.

• Further optimization of the DFT+DMFT code will allow application to more complex systems, for example, magnetism and magnetic anisotropy in Fe_2O_3. Our interest is also in magnetic states in layered structures and possibility to tune magnetic anisotropy with slab thickness.

• TDDFT+DMFT analysis of the excitations in strongly correlated nanostructures is one of our main targets. Also study of spatially nonhomogeneous breakdown of Mott insulator phase in the nanostructures in the presence of strong local external field, which may have many potential applications in nanoelectronics. We have in mind VO_2, Ce_2O_3 and $YTiO_3$ nanostructures.

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Extending the reach of computational-theoretical methods to materials at the energy frontier

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Co-PI's G. Malcolm Stocks, Markus Eisenbach and Jaron T. Krogel

Project Scope

This program is designed to overcome challenges in materials theory that are both at the frontier of basic research and beyond standard theoretical and computational capabilities. Our overarching goal is to significantly improve our description and understanding of electronic correlations and magnetic interactions 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 allow us to test new methods and extend *ab initio* results to larger systems. A priority is to develop, improve and implement in computer codes new theories that take advantage of current high performance computers (HPC). 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.

Some Recent Progress

QMC calculations in Cuprates:
To achieve the dream of designing theoretically new materials with desired properties, we must first describe existing materials with accuracy consistent with technological specifications. In the transition metal oxides (TMOs), errors in DFT approximations, presumably due to self-interaction errors, have precluded reaching agreement with experiment. Empirically adjusting DFT, while valuable to support and explain experiment, lacks of predictive power. These limitations can be overcome by performing highly accurate *ab initio* many-body calculations on target systems with Quantum Monte Carlo (QMC) to be used as benchmarks for DFT. This approach is now being used

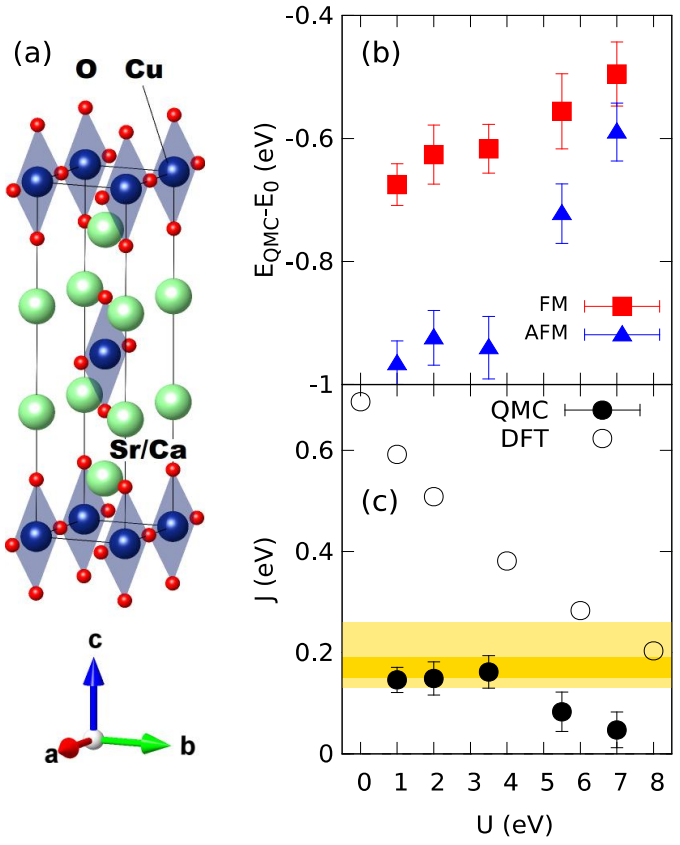

Figure 1: a) Unit cell of Ca_2CuO_3 and Sr_2CuO_3. (b) QMC energies of the AFM and FM states of Ca_2CuO_3 as a function of the parameter U of LDA+U used to alter the trial phase. The energies are shifted by E_0 = 34705 eV. (c) Nearest-neighbor Cu spin super-exchange coupling J of Ca_2CuO_3 calculated with WEIN2k (DFT) and FP-DMC as a function of U. The light gold band represents experimental estimates.

in this project to study some of the most challenging oxides. In Fig. 1 we show the results obtained for a "one dimensional" cuprate of the exchange coupling constants of Cu atoms resulting from total energy differences obtained with QMC. The results have been recently published in Physical Review X.

In Fig. 2 we show the energy differences of the hole quasiparticle energies obtained with QMC for the superconducting cuprate $Cl_2Ca_2CuO_2$ for special points as a function of the in-plane strain. The lines are fits with LDA+U. We find that U=3 best reproduces the valence band structure but fails to open a gap.

An important fraction of the literature surrounds the idea that superconductivity arises as quasiparticles interact via spin excitations. The calculations of the spin excitations and hole quasiparticles is a necessary step for a better understanding of superconductivity.

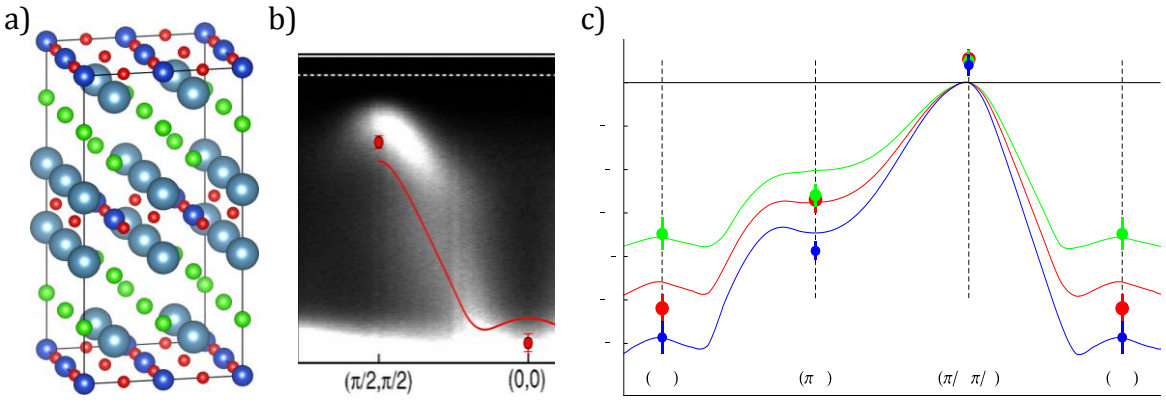

Figure 2: (a) Structure of $Cl_2Ca_2CuO_2$ (QMC calculations: 8 unit cells, 520 e-) (b) ARPES experiments Ronning et al. PRB 71 094518 (2005). (c) Relative energies of the hole quasiparticle excitations for high-symmetry k points for 3% compressed, experimental and 4% expanded structures (in-plane). Points denote DMC results, lines LDA+U (U=3).

Point defects and doping in ZnO

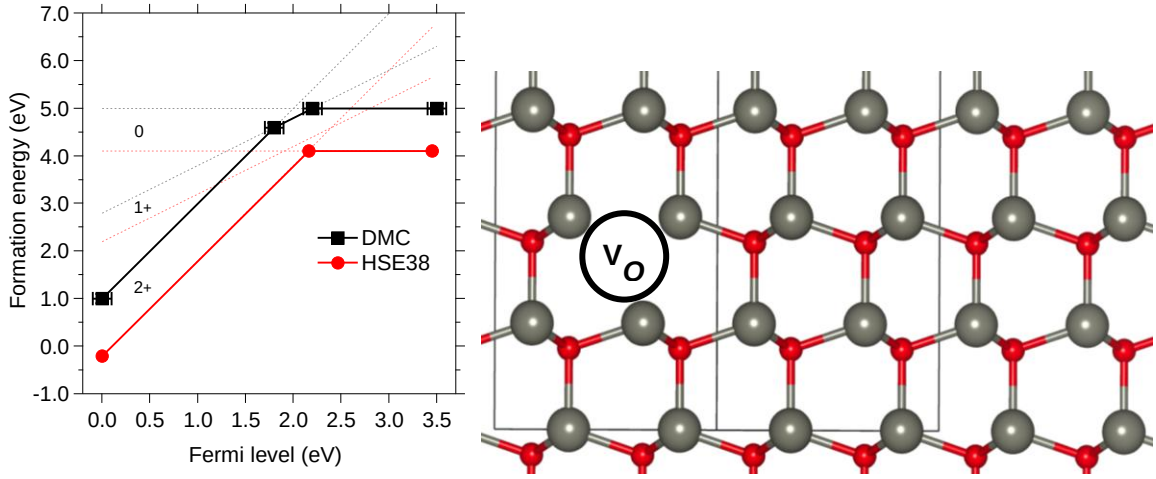

Figure 3: Thermodynamic transition levels of the O vacancy evaluated with DMC and HSE (a = 0.375). Finite size effects extrapolated from LDA. The Fermi energy is calculated relative to the valence band maximum of ZnO in DMC. The last point is the position of the calculated band gap.

The prediction of gaps and doping remains a challenge for most TMOs. We have recently reported energy gaps and defect formation energies for ZnO which has been shown to be particularly problematic for DFT approximations.

Magnetism at finite temperatures within DFT:
We have further expanded the capabilities for first principles based statistical physics of magnetic systems within our Wang-Landau – Locally Self-consistent Multiple Scattering (WL-LSMS) framework: Previously our code only sampled the magnetic moment directions and neglected the fluctuations in the moment magnitude. We have now implemented longitudinal moment fluctuations in WL-LSMS. This new capability in WL-LSMS has been implemented and allows the calculation of magnetic moment fluctuations in materials that deviate from a rigid spin Heisenberg model. This will lead initially to the calculation of the Curie temperature of Ni, a still outstanding problem in understanding magnetism. We performed first principles calculations using frozen potentials without moment magnitude fluctuations as well as model calculations including varying moment magnitudes. Additionally we have investigated the performance of the recent parallel replica exchange Wang-Landau algorithm for model systems [Zhao2014] and we have implemented this algorithm inside WL-LSMS to ensure the continued scaling on massively parallel architectures.

Publications 2014

"*Ab initio* Quantum Monte Carlo Calculations of Spin Superexchange in Cuprates: The Benchmarking Case of Ca_2CuO_3" Kateryna Foyevtsova, Jaron T. Krogel, Jeongnim

Kim, P. R. C. Kent, Elbio Dagotto, and Fernando A. Reboredo Phys. Rev. X **4**, 031003 (2014) .

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Next Generation Photon and Electron Spectroscopy Theory: Satellites and the Cumulant Expansion

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Project scope

The primary goal of our DOE BES Grant is to develop improved theoretical methods for quantitative calculations of photon and electron spectroscopies over a broad spectrum, from the visible to x-ray energies. Our approach is based on theories of excited states and response functions, e.g., real space Green's function (RSGF), GW/Bethe-Salpeter Equation (BSE) methods, and beyond. Our research has led to highly successful codes such as FEFF, which are used worldwide to interpret x-ray spectra. Our recent work has focused on treatments of many-body effects such as inelastic losses, which are essential in quantitative calculations. In particular we have developed cumulant expansion methods that go beyond the GW approximation and have yielded breakthroughs in the treatment of multi-electron excitations and satellites. These advances provide an improved methodology which may be advantageous in future investigations of complex materials.

Recent progress

Cumulant expansion for the one-electron Green's function

One of the key signatures of many-body correlation effects is the satellite structure in the spectral function $A_k(\omega) = (1/\pi)$ |Im $G_k(\omega)$|, where $G_k(\omega)$ is the one-electron Green's function. Many body interactions generally lead to the replacement of sharply defined one-particle states, $A_k(\omega) = \delta(\omega-\varepsilon_k)$, by a broadened quasi-particle peak together with satellites that characterize excitations in the system. The usual approach for calculating $A_k(\omega)$ uses an expression for $G_k(\omega)$ in terms of the one-electron self-energy $\Sigma_k(\omega)$, *i.e.*, $G_k(\omega) = [\omega - h - \Sigma_k(\omega)]^{-1}$. Typically Σ is calculated to first order in the the screened Coulomb interaction W with the GW approximation of Hedin, i.e., $\Sigma=iGW$. While the GW approximation (GWA) usually gives good quasi-particle properties, it is known to give a poor approximation for the spectral function. For example, the GWA sometimes predicts spurious plasmaron peaks and cannot produce multiple plasmon satellites. In an effort to overcome these limitations, our recent work has focused on the cumulant expansion, a powerful many-body approach based on an exponential representation of the time-dependent Green's function $G(t)=G_0(t)e^{C(t)}$. Here the cumulant $C(t) = \int (\beta_k(\omega)/\omega^2)(e^{i\omega t}-i\omega t-1)\, d\omega$, and $\beta_k(\omega)$=|Im $\Sigma_k(\omega+\varepsilon_k)$| is the quasi-boson excitation spectrum. The cumulant approach builds in dynamic vertex corrections and yields multiple-peaks in $A_k(\omega)$ consistent with experiment, thus improving on the GWA without additional computational effort. Some of our work on this topic has been carried out in collaboration with the Reining group at the Ecole Polytechnique, Paris. This work has already been successfully applied to number of systems (see [1] and references therein) and sets the stage for many other developments.

Intrinsic and extrinsic losses and interference

Physically the satellites in the spectral function arise from many-body excitations in a system and are often dominated by plasmons and particle-hole excitations. Mathematically, such neutral excitations can be treated on a common footing within the quasi-boson approximation of Hedin. Their energies correspond to peaks in the electron energy loss function $L(\omega)=(1/\pi)$ |Im $\varepsilon^{-1}(\omega)$| . These spectral features characterize the inelastic losses, and are essential for a quantitative description. Of these losses, the *intrinsic losses* arise from the creation of a hole and *extrinsic losses* from excitations created by a propagating photoelectron; additionally *interference* terms reduce the loss. Our group has found that the satellite lineshapes of these contributions are similar, and hence one can approximate the total loss by renormalizing the intrinsic satellite intensity. Similarly, the total spectral function can be calculated with a cumulant $C(t)$ as defined above, but with $\beta_k(\omega)$ replaced by a renormalized excitation amplitude $\gamma_k(\omega)$ that includes extrinsic and interference terms (see [1] and references therein). In related work on molecular systems in collaboration with the Uppsala group, the combination of extrinsic, intrinsic and interference terms was successfully applied to understand *nonstoichiometric intensities* in core photoelectron spectra [2,3].

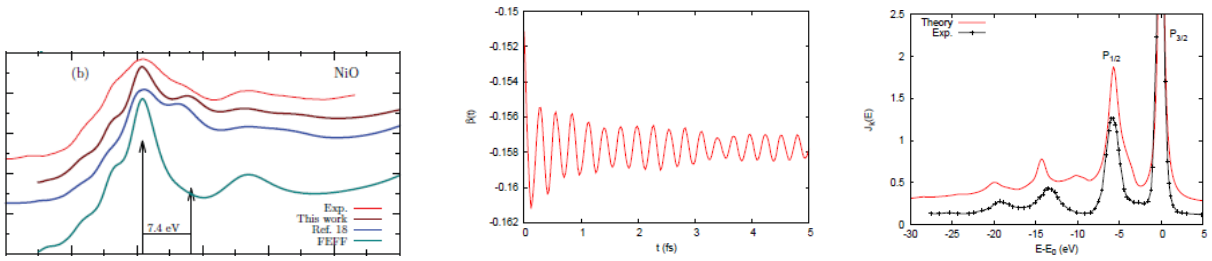

Fig. 1. (left) CT satellite effects (indicated by arrows) in the XAS of NiO calculated with the model of Lee et al. [4]; (middle) the real-time TDDFT response function $\beta(t)$, and (right) associated spectral function of TiO_2 compared with experiment [5]. Note the two CT satellites about 13 eV below the two spin-orbit split peaks at 0 and -6 eV in the Ti L_{23} XPS.

Charge-transfer satellites in correlated systems

Strongly correlated materials such as transition metal oxides (TMOs) exhibit large satellites in their x-ray spectra which heretofore have been difficult to calculate from first principles. These satellites arise from localized *charge transfer* excitations that accompany the sudden creation of a core hole. Recently we have made significant progress in understanding these effects. First, we implemented the tight-binding model of Lee, Gunnarsson and Hedin to achieve a semi-empirical treatment of charge-transfer satellites, with parameters obtained from fits to XPS experiment [4]. In this approach the XAS is given by a convolution of an energy dependent spectral function representing the localized CT processes, and the effective, quasi-particle XAS obtained from our RSGF code FEFF9, $\mu(\omega)= \int A(\omega,\omega') \mu_0(\omega-\omega')d\omega'$. More recently, we have developed a cumulant approach for CT satellites based on a real-time, time-dependent density functional (TDDFT) approach [5], with a spectral function obtained from the core-Green's

function $G_c(\omega)$ (Fig. 1 right). We have shown that the excitation spectrum $\beta_k(\omega)$ is given by the Fourier transform of the transient, oscillatory, response of the local charge distribution to the creation of a core-hole. Physically the CT satellites are characterized by the density-density response function. Remarkably the approach yields a semi-quantitative treatment and interpretation of CT satellites measured in XPS. This development also illustrates the significant advantages of real-time approaches in calculations of excited states and spectra.

Retarded cumulant expansion

Despite the above successes, the conventional cumulant expansion based on the time-ordered Green's function can be problematic. In particular, the approach ignores terms that give rise to satellites both above and below the quasi-particle peak, making a pure exponential representation impossible. This problem is particularly severe near the Fermi level or for systems with particle-hole symmetry. Remarkably, however, we have found that many of these pathologies disappear if one uses instead, a retarded Green's function, yet the computational effort is similar to that in the GWA. The approach also leads to fractional occupation numbers n_k and gives good results for correlation energies [6] within the Galitskii-Migdal approximation. An extension to phonon contributions to the spectral function is under development.

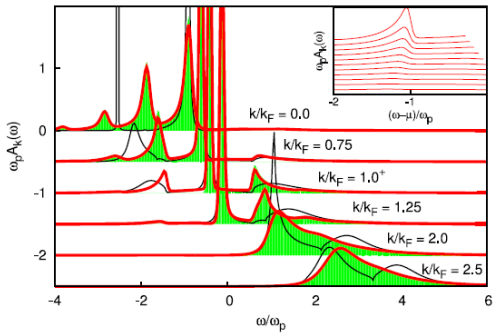

Fig. 2. Spectral function for the homogeneous electron gas from (red) retarded and (green) time-ordered cumulants and (black) the GW approximation. Unlike the retarded cumulant, the GWA fails to produce multiple-satellites, and the time-ordered cumulant only has satellites on one side of the Fermi energy ($\omega=0$) [6].

Future Plans

During the next year we plan to continue our development of advanced theoretical methods and their implementation in our spectroscopy codes, particularly with cumulant expansion methods which offer many opportunities for further development. Our efforts will include:

- Extensions of the retarded cumulant method to include self-consistency, off-diagonal contributions, finite temperature correction, total energies, phonon-contributions and applications to various systems.
- Extensions of our GW/BSE codes OCEAN and AI2NBSE including improved parallelization, larger basis sets, better pseudopotential support, and code-integration to facilitate efficient, large scale calculations. Some extensions are now in progress [7].

• Extensions of our RSGF codes to include improved treatments of many body effects, e.g. satellites and Hubbard corrections for *d*- and *f*-electron systems.
• Development of real-time approaches for x-ray spectra, including our RT-TDDFT cumulant method and correlation functions, and their implementation in a code RTXS.

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STRONGLY CORRELATED ACTINIDE MATERIALS

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Project Scope

The project involves the theoretical investigation of the electronic, magnetic and structural properties of strongly correlated actinide materials, such as uranium, plutonium and related compounds. The investigation is focused on the effects introduced by strong coulomb interactions. In particular, we investigate mechanisms whereby the correlations minimize the interactions, the competition between the different mechanisms and the emergence of novel states of matter.

Recent Progress

Hidden Order in URu2Si2

URu2Si2 is a particularly interesting material, in that it is a heavy fermion compound which undergoes a second-order phase transition at 17.5 K to a state that exhibits a partial gapping of the Fermi-surface. The transition is marked by the formation of a gap of 7 meV which extends over 40% of the Fermi surface, a loss of 91% of the carriers and a lambda anomaly in the specific heat associated with an entropy of 0.3 kB ln(2) per uranium ion. The nature of the order parameter remains enigmatic despite over 30 years since the transition was first discovered. Inelastic neutron scattering and x-ray experiments have ruled out that the transition being due to either simple magnetic or charge/orbital density orderings. De Haas – van Alphen measurements have given indirect evidence that the transition is a type of density wave, involving nesting of the Fermi-surfaces through the wave vector Q=(1,0,0). In collaboration with an experimental group at Los Alamos, we have shown that the Fermi-surface develops hot-spots and reconstructs at the transition with wave vector Q. We developed a theoretical model which exhibits a phase transition to a novel type of density wave state that is of the form of a compensated orbital density wave state. Specifically, the state can be described as an orbital density wave for the spin up electrons which is out of phase with the orbital density for the spin down electrons. As such, the order parameter cannot be measured in measurements which are only sensitive to either the magnetization density or charge density. This mechanism also breaks spin-rotational invariance, but does not produce any static dipole moment. We have shown that below the transition the breaking of spin-rotational invariance produces an anisotropic magnetic susceptibility, similar to a symmetry breaking of the susceptibility in the a-b plane found in magnetic torque measurements. We have investigated the phase diagram of the model and have shown that although the application of a field reduces the transition temperature, the transition changes from second-order to first-order as found in the experiments performed at Los Alamos.

Electron Correlations in USb2

The f electron dispersion relation of USb2 has been measured by ARPES experiments. It has been found that the dispersion relation has a maximum just below the Fermi-surface and that there is a sharp kink which separates renormalized quasi-particles from quasi-particles with unrenormalized masses. We have shown theoretically that, even though the dispersion relation does not pass through the Fermi-energy so intra-band processes do not produce mass renormalizations, intraband processes can. Together with an experimental group at Los Alamos, we have developed a simplified model of interband processes that can be used to model experimental results.

Phonon Anomalies and ILMs

It has been reported that the acoustic phonon spectrum of alpha-uranium softens as the temperature is raised. Furthermore, measurements of the phonon spectrum indicate that new peaks evolve for a narrow temperature range around T=450 K. We developed a model for the anomaly in which the phonon softening is connected with a polaronic renormalization of the hybridization between the 5f and conduction states. Similar anomalies have been found in Pu compounds by inelastic x-ray scattering measurements and have been associated with a temperature dependent softening of the electronic density of states via Kondo-like correlations. The extra peaks in alpha-uranium have also been attributed to the formation of Intrinsically Localized Modes (ILMs). ILMs are persistent lattice vibrations of a homogeneous lattice that have finite spatial extents that are stabilized by anharmonic interactions. We have shown that quantized ILMs in one-dimensional materials are of the form of bound states, and that the presence of one-dimensional van-Hove singularities ensure the existence of ILMs for even small values of the anharmonicity. Furthermore, we have shown that ILMs may exist in three-dimensional systems for momentum transfers at high symmetry points in the Brillouin zone, where the van-Hove singularities in the two-phonon density of states coalesce. Such features have been observed in inelastic neutron scattering measurements on NaI.

Future Plans

The Uranium Monochalcogendes and Pnictides (Ferromagnetism and the Kondo Effect)

At high temperatures, the susceptibility of the uranium mono-chalcogenides show evidence of large local moments and the transport properties show logarithmic temperature dependencies associated with the Kondo effect, but order ferromagnetically. As contrasted with cerium compounds, the Curie temperatures are relatively high temperatures ~100K and have ordered moments of the order of 1 μB. Photoemission experiments carried out at Los Alamos show that the 5f electrons are itinerant but exhibit an increased tendency for localization adown the chalcogenide column of the periodic table. We investigate the possibility that these materials may be described by the underscreened Anderson lattice model, in which the screening of the local moment results in a non-zero net moment that then orders ferromagnetically. We shall also investigate the effect of the Hund's rule exchange interaction and the unusual magnetic anisotropy found in these cubic materials. In addition, we shall investigate the properties of the antiferromagnetically ordered uranium -pnictide compounds based on the underscreened Anderson lattice model. Te results will be compared with photoemission data.

Pseudo-gaps and Collective Fluctuations in URu2Si2

NMR and tunneling spectroscopy measurements indicate that a small gap already forms in the density of states at 23 K, which is significantly higher than the temperature of 17.5 K associated with the phase transition. It has been suggested by Haraldsen et al. that this precursor gap is due to the presence of pre-critical fluctuations that occur at temperatures just above the phase transition. It is usually expected that the pre-critical fluctuations will experimentally manifest themselves in a temperature range above the transition which is governed by the Ginzburg criterion. The wide temperature range appears to indicate that the fluctuations are unusually large. We shall investigate possible causes for large fluctuations, such as the coexistence of two distinct types of collective pre-critical fluctuations, such as the antiferromagnetic fluctuations and the Hidden Order fluctuations. These fluctuations appear to act on the same nested regions of the Fermi-surface and appear to have comparable strengths, since a small applied pressure can interchange the stability of the Hidden Order and Neel states. We shall investigate these two types of collective fluctuations above and below the transition and whether these and other fluctuations, such as orbital density fluctuations, can act cooperatively above the transition temperature giving rise to an anomalously large precursor gap. We shall also investigate whether the existence of various types of states with similar types of nearest neighbor correlations could either produce novel types of pseudo-gap phases without there being static long-ranged ordering or provide a new route to quantum critical behavior.

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Electric Field Tuning of the Rashba Effect in the Polar Perovskite Oxides

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Project Scope

The overall goal of this DOE-sponsored project is to understand and develop a theoretical description of the physics of the correlated oxides and their interfaces. One line of research we have carried out recently is the study of the Rashba effect at the oxide surfaces and interfaces. The Rashba effect describes the momentum-dependent spin splitting of the electron states and is the combined result of the spin-orbit interaction (SOI) and the inversion-symmetry breaking. Control of the Rashba effect by an applied electric field is at the heart of a class of proposed spintronics devices for manipulating the electron spin and as such the effect has been well studied for the semiconductor structures. The recently grown perovskite surfaces and interfaces are expected to have a much larger Rashba effect than their semiconductor counterparts owing to the presence of high Z elements and a strongly localized two-dimensional electron gas (2DEG) formed by the polar catastrophe. In this piece of work, we show that the Rashba effect at the polar perovskite structures can be tuned by manipulating the 2DEG by an applied electric field, using it to draw the 2DEG out to the surface or push it deeper into the bulk, thereby controlling the surface-sensitive phenomenon. These ideas were studied by a comprehensive density-functional study of the recently discovered polar $KTaO_3$ surface with and without an applied electric field and with full atomic relaxation. Analytical results obtained with a tight-binding model unravel the interplay between the various factors affecting the Rashba effect such as the strengths of the spin-orbit interaction and the surface-induced asymmetry. The work helps interpret the recent experiments on the $KTaO_3$ surface as well as the $SrTiO_3/LaAlO_3$ interface.

Recent Progress

1) Rashba Effect in the Perovskite Oxides: A Case Study of the $KTaO_3$ Surface with density-functional calculations

The Rashba effect describes the momentum dependent spin splitting of the electron states at surfaces or interfaces, commonly described by the Rashba Hamiltonian, $H_R = \alpha_R(\vec{\sigma} \times \vec{k}) \cdot \hat{z} = \alpha_R(k_y\sigma_x - k_x\sigma_y)$, where the Rashba coefficient α_R measures the strength of the effect. It is the combined result of spin-orbit coupling and broken inversion symmetry. Since both these effects are large at the perovskite surfaces and interfaces, a large Rashba effect is expected in these systems. In addition, in polar surfaces and interfaces such as the LAO/STO interface or KTO surface, the polar catastrophe results in a highly-localized 2DEG there, so that the Rashba effect is expected to be especially large. In fact, recently a strong Rashba effect was observed at the LAO/STO interface, which also showed an ill-understood asymmetric dependence on the sign of the electric field applied along the interface normal, while ordinarily one expects the magnitude of the Rashba effect to be independent of the field direction. In order to understand these effects, we performed density-functional theory (DFT) study on the prototypical KTO surface and developed a tight-binding model for the d electron systems to understand the DFT results. The KTO surface is an ideal

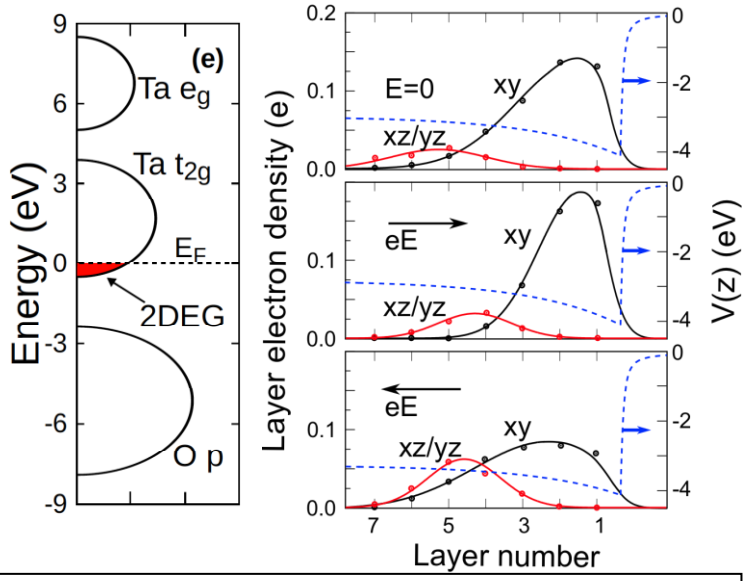

Fig. 1: The 2DEG at the KTO surface (left) localized at the surface due to polar catastrophe and the manipulation of the 2DEG density profile by an electric field (right) as obtained from DFT.

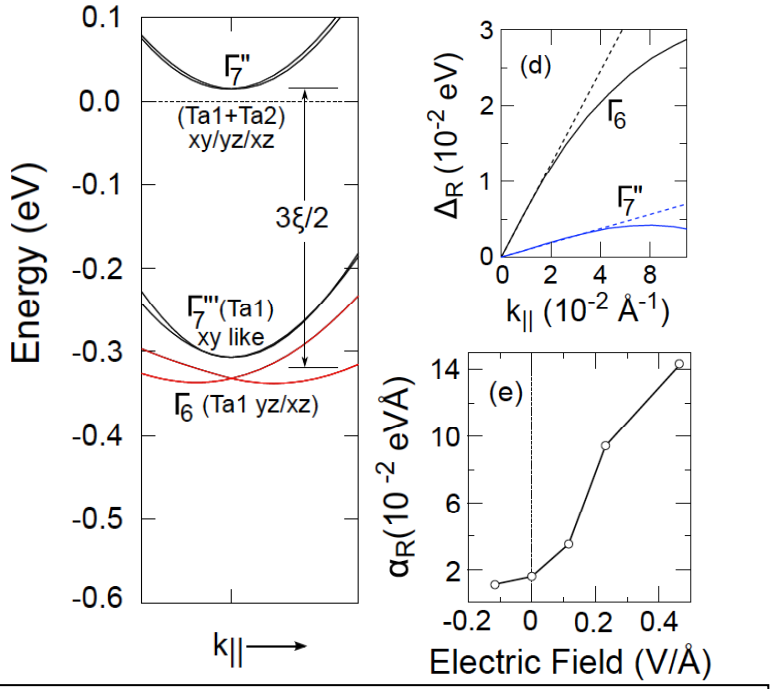

Fig. 2: Rashba splitting of the surface bands in KTO (left). The splitting is orbital dependent (a prominent splitting is shown in red) and is linear in momentum (top right). The bottom right panel shows the asymmetric Rashba coefficient as a function of the electric field.

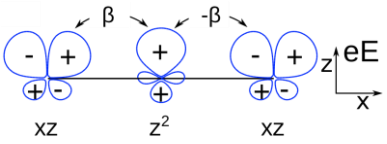

Fig. 4: New hopping matrix elements introduced by the electric field, producing orbital-dependent Rashba effect.

system for the study of the Rashba effect because Ta is a high Z element with strong SOI, a polar-catastrophe induced 2DEG has been observed there recently similar to the LAO/STO interface, and finally a surface rather than an interface is more easily amenable to external electric fields.

The DFT calculations establish the formation of the 2DEG at the KTO surface (Fig. 1) and furthermore demonstrate how the charge-density profile of the 2DEG can me moved away or towards the surface by the application of an external electric field. The subband structure, shown in Fig. 2, clearly shows a linear Rashba splitting as a function of the momentum. Furthermore, the asymmetric field dependence of the Rashba coefficient is understood to be due to the moving of the 2DEG away from the interface for the electric field of the appropriate sign, so that the Rashba effect is quenched as the surface layer component of the charge density of the 2DEG quickly diminishes. The surface layers are important because as shown by our DFT calculations (Fig. 3), the overwhelmimg contribution to the Rashba effect comes

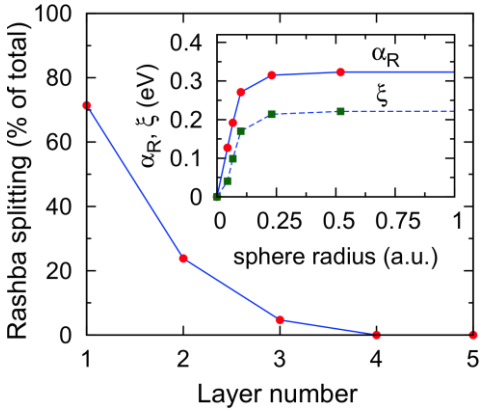

Fig. 3: The origin of the Rashba splitting from the first few surface layers (strong broken inversion symmetry) as obtained from the DFT results.

from the first few surface layers as beyond these layers and deeper in the bulk, there is no strong inversion symmetry present, which is necessary for the Rashba effect.

2) Tight-Binding model for the Rashba Effect in the d electron systems

We studied the Rashba effect in the d electron systems from a tight-binding model applicable to all d electron solids in general and showed that the effect depends strongly on the orbitals involved in a particular band (Ref. 2-3). The spin-orbit coupling produces spin-orbit entangled states, with each state having different Rashba coefficients. The symmetry breaking electric field introduces new matrix elements in two distinct ways, viz., via mixing of the atomic orbitals on the same site and by introducing new inter-site hopping terms within the tight-binding description (Fig. 4), both of which we examined in studying the Rashba effect. From the tight-binding model, we derived the expressions for the Rashba coefficients in both limits of weak and strong SOI by using the perturbative Löwdin downfolding of the full tight-binding Hamiltonian. The d electron systems offer a rich system for manipulating the Rashba effect, not only because the magnitude of the effect can be strong owing to the large atomic numbers Z as already mentioned, but also because the orbital characters and the their energies are sensitive to external forces such as strain, which can be used for tailoring the effect for potential applications in oxide electronics.

Planned Activities: 2014-2015

1) Spin-Orbit Entangled Mott Insulators in the 5d Oxides: In our study of the Rashba effect described above, we studied how the large SOI affects the one electron band structure producing a momentum-dependent spin splitting via spin-orbit entangled orbitals. In this research, we will study the consequences of the presence of both a strong spin-orbit coupling as well as a strong electronic correlation that exist in the perovskite oxides with 5d electrons. Recently this class of materials has garnered considerable attention due to the novel Mott-Hubbard physics, where the strong spin-orbit coupling plays an essential role in the formation of the insulating state. Examples are the Iridates such as Sr_2IrO_3, where the strong SOI splits the 5d-derived t_{2g} states into spin-orbit entangled J_{eff} = 3/2 and 1/2 states, with the Hubbard U Coulomb interaction further splitting the spin-orbit entangled doubly-degenerate J_{eff} = ½ state into a lower and an upper Hubbard band producing a Mott insulator. In this project, we will study the electronic structure of the iridates using the mean-field as well as density-functional methods. Of particular interest is the development of spin-rotational invariant methods for the simultaneous treatment of the SO and Coulomb interactions, similar to the rotationally invariant LDA+U method, which is necessary for a proper description of the spin-orbit entangled states present in these systems. The spin-rotational invariant methods will be first tested within the Hartree-Fock solution of model Hamiltonians before incorporating them into the DFT codes.

2) Phase Separation in Doped Mott Insulators: The doping of the Mott insulators has been actively studied by a variety of techniques, which however produce different results depending on the precise models considered. The problem is more relevant now since many perovskite oxides of current interest such as $LaMnO_3$, $LaTiO_3$, $YTiO_3$, etc. show phase separation between metallic and insulating phases as a function of carrier doping. Although metallic conduction is expected as soon as dopants are introduced in the half-filled Mott insulating state, experiments show otherwise, viz., that the insulating state continues until a critical amount of doping ($x_c \sim 0.05 – 0.25$) is introduced into the system and only beyond this value that the metallic state occurs. The underlying physics is controlled by doping of the Mott-Hubbard insulator

around the half-filling, with a significant role played by the electron-lattice (Jahn-Teller) coupling present in many of these compounds. We are currently studying the band-width controlled metal-insulator transition in $LaMnO_3$ using the Gutzwiller solution of a model Hamiltonian containing electron-electron as well as electron-lattice interaction terms. Our initial results (Ref. 8-9) indicate phase coexistence for a wide range of the band-width values, which are accessible in high pressure experiments. Our theory predicts a percolative transport consistent with the measured resistivity as a function of pressure and temperature, obtained by our experimental collaborator M. Baldini from the Argonne National Lab. We plan to study these issues in more detail using Hartee-Fock and Gutzwiller solutions of model Hamiltonians as well as from density-functional studies of realistic solids.

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4. K. V. Shanavas and S. Satpathy, Orbital ordering in $La_{0.5}$ $Sr_{1.5}$ MnO_4: Density functional and exact diagonalization studies, Phys. Rev. B 87, 235137 (2013)

5. M. Sherafati, S. Satpathy and D. Pettey, "Gutzwiller Variational Method for Intersite Coulomb Interactions: The Spinless Fermion Model in One Dimension," Phys. Rev. B 88, 035114 (2013)

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STRONGLY CORRELATED ELECTRONS

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Project Scope

The research in this program is on aspects of heavy fermions, quantum criticality and ultracold fermionic atoms confined to a 1D optical trap. Here I briefly report on three projects. (1) The low T phase diagram as a function of magnetic field and chemical potential of the 1D Fermi gas with attractive potential and arbitrary spin S. The system displays phase separation along the trap and instabilities to superfluid phases with FFLO signatures. (2) A renormalization group (RG) study of a two pocket model that opens the possibility to a superconducting dome around the QCP in quantum critical heavy fermion systems. (3) SmB_6 is a strong topological Kondo insulator. Recent studies confirmed this for the electrical conductivity below 5 K. There are however several open questions concerning the low T magnetization and the NMR relaxation.

Recent Progress

(1) Phase separation and FFLO signatures in ultracold Fermi gas of atoms

Confinement of ultracold atoms in 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 delta-function potential in space. The 1D gas of fermions of spin S with delta-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 properties investigated are similar to those studied in actual materials.

The Bethe solution yields N=2S+1 basic states, namely bound states of N, N-1, …, 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. 1 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 μ. Hence, these systems of fermions are only locally homogeneous and within the local density approximation display phase separation with the vari-

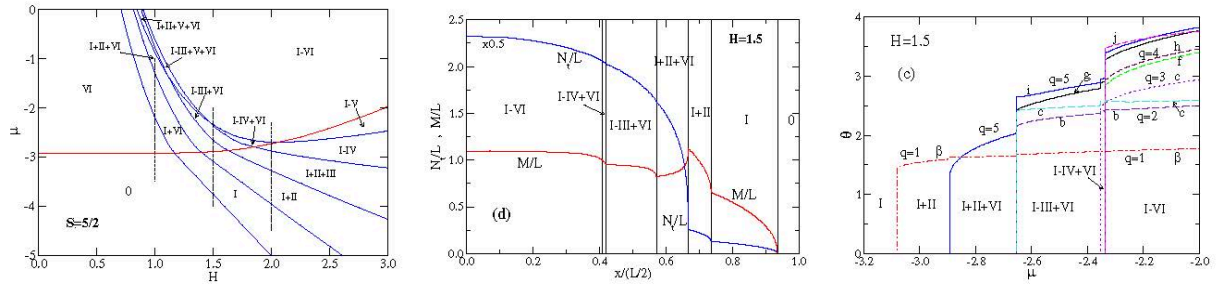

Fig.1 *Left panel:* Ground state phase diagram for a homogeneous fermion gas of spin S=5/2 with unit interaction strength. The phase denoted with 0 (lower left corner) has no particles. The Roman numbers indicate the number of particles in the bound state. Regions with more than one Roman number are 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.

ation of μ along the tube of length L (see middle panel in Fig. 1).

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. 1. The most favorable first phase is denoted with β, corresponding to pairing of particles with spin component S_z=5/2 and 3/2. The period of oscillations is determined by the spin imbalance and 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.

(2) Quantum criticality of heavy fermions

Properties of the QCP have been studied within the Hertz-Millis-Moriya theory, in which all the fermionic degrees of freedom are eliminated at the expense of bosonic fields (spinwaves). They can alternatively be treated within a renormalization group (RG) approach of the fermionic Hamiltonian. I had proposed a fermionic nested two-pocket model (Schlottmann, Phys. Rev. B **59**, 12379 (1999) and **68**, 125105 (2003)), that reproduces many of the NFL properties, namely, the mass enhancement, logarithmic dependence of the specific heat, T-linear dependence of the resistivity, the linewidth of the quasi-particles, the crossover from Fermi liquid to NFL as a function of T and a tuning parameter δ (mismatch of the Fermi surfaces), and the amplitude of the de Haas-van Alphen oscillation through a modified Lifshitz-Kosevich expression.

The above two-pocket model has been extended to include electronic Umklapp processes, i.e. two-electron transfers between pockets. This requires the nesting vector to be commensurate with the lattice. The RG analysis of the extended model opens the possibility to a superconducting dome without destroying the NFL properties in the specific heat and the linewidth of the qua-

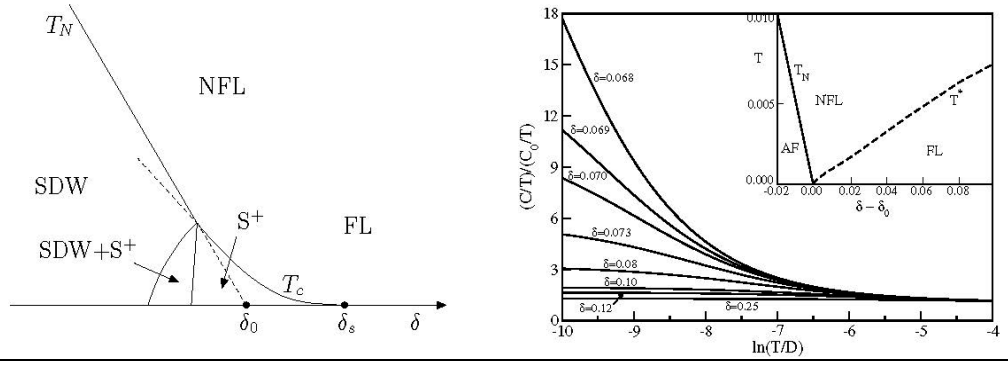

Fig.2 *Left panel:* Schematic phase diagram showing the SDW, the S^+ superconducting (starting at δ_s) and the possible coexistence of the phases. The dashed lines are the extrapolations of (a) the SDW boundary into the mixed phase (ending at δ_0 at T=0) and (b) the S^+ phase into the AF phase, respectively. The SDW and S^+ compete for the same portion of the Fermi surface. The NFL and FL regimes are also indicated. *Right panel:* C/T as a function of ln(T) for various values of δ and a Hubbard-like interaction with the S^+ phase suppressed. At intermediate T, C/T follows a logarithmic dependence and saturates at very low T. The crossover from NFL to FL as T is reduced depends on the value of $\delta > \delta_0$. The estimated crossover temperature is denoted T* and shown in the inset, together with the Néel temperature, T_N. The QCP is at $\delta = \delta_0$ for T=0.

si-particles, i.e. the electrical resistivity. Hence, the crossover from FL to NFL behavior with increasing temperature remains unchanged by the Umklapp processes. A schematic of the phase diagram and the T and δ dependence of the specific heat are shown in Fig. 2. The extended model is similar to the one studied by Chubukov (Physica C **469**, 640 (2009)) for a 2D Fermi surface in the context of the Fe pnictides.

(3) The strong topological Kondo insulator SmB_6

SmB_6 has been predicted to be a strong topological Kondo insulator (TKI) and experimentally it has been confirmed that at low temperatures the electrical conductivity only takes place at the surfaces of the crystal. I studied the temperature and magnetic field dependence of the NMR Knight shift and relaxation rate arising from the topological conduction states. For the clean surface the Landau quantization of the surface states gives rise to highly degenerate discrete levels for which the Knight shift is proportional to the magnetic field B and inversely proportional to the temperature T. The relaxation rate, $1/T_1$, is not Korringa-like. For the more realistic case of a surface with a low concentration of defects (dirty limit) the scattering of the electrons leads to a broadening of the Landau levels and hence to a finite density of states. The mildly dirty surface case leads to a T-independent Knight shift proportional to B and a Korringa-like $1/T_1$ at low T. The wave functions of the surface states are expected to fall off exponentially with distance from the surface giving rise to a superposition of relaxation times, i.e. a stretched exponential. It is questionable that the experimental ^{11}B Knight shift and relaxation rate arise from the surface states of the TKI. An alternative explanation is that the bulk susceptibility and the ^{11}B NMR properties are the consequence of the in-gap bulk states originating from magnetic exciton bound states proposed by Riseborough [Phys. Rev. B **68**, 235213 (2003)].

Future Plans

- To extend the study of pre-critical fluctuations to the quantum critical point in heavy fermion systems considering the Anderson lattice, i.e. two hybridized bands.
- Further study of the magnetic properties of the topological Kondo insulator SmB_6.

- To investigate the spontaneous breaking of the four-fold rotational symmetry of the tetragonal crystal URu_2Si_2 in the ``Hidden-Order'' phase as a Pomeranchuck instability for the spin-dependent l=2 Landau parameter with *xy* symmetry.
- Quantum criticality in ferromagnetic Kondo systems has recently been observed in Yb based compounds. I plan to investigate the quantum criticality of the Kondo lattice with *ferromagnetic* Heisenberg exchange using field-theoretical and RG techniques.
- To continue the study of spin-imbalanced ultracold gases of atoms of spin S confined to 1D traps with an attractive δ-function potential with *general* interaction amplitudes using a RG approach.
- A non-linear dispersion in the momentum in a Luttinger liquid yields an incorrect singularity threshold and critical exponent in a dynamical response function calculated using Conformal Field Theory. I propose to investigate this for gases of atoms using the Bethe *Ansatz*.
- To continue providing theoretical support to experimental groups through collaborations.

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3. **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).
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8. G. Cao, L.E. DeLong, and **P. Schlottmann**, The contradictory physical properties and extreme anisotropy of $Ca_3Ru_2O_7$, in *Frontiers of 4d- and 5d-Transition Metal Oxides*, eds. G. Cao and L.E. DeLong, World Scientific Publishing (Singapore, 2013), Chapter 6, p. 179.
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Theoretical Studies in Very Strongly Correlated Matter

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Project Start Date: September 1, 2013

Project Scope:

The proposal is concerned with developing new tools to solve the strongly correlated electron problem. The original inspiration comes from the cuprate materials, and more recently from sodium cobaltate and other high thermo-power materials. Several results center around a recently developed analytical approach by the PI- termed the extremely correlated Fermi liquid theory (ECFL). Detailed calculations of the ARPES (photoemission) line shapes, transport properties such as the Hall constant and thermo-power, and a description of the superconducting state are the current focus.

Recent Progress:

- **DMFT-ECFL studies:**

Recently we have completed a joint project Ref. [1] , with Professor Antoine Georges, where we provide a detailed comparison between the analytically rich ECFL theory and the numerically rich dynamical mean field theory DMFT. While the ECFL theory is not confined to any specific dimensions- it works equally well in 2, 3,...., ∞ dimensions, its present implementation is limited to low orders in a parameter λ. The parameter λ ($0 \leq \lambda \leq 1$) is a measure of double occupancy, with λ =1 representing complete elimination of double occupancy and λ =0 giving the free Fermi gas. One of the claims of the ECFL theory is that low order expansion in λ should capture important spectral features of strong correlations, e.g. the photoemission line shapes. It is now possible to check if this claim is realized in the case of high dimensions, where numerically exact results are available through the DMFT technique, and motivated this work. In Fig. 1, we show the results for the imaginary part of the (momentum independent) single particle self energy for various densities. The ECFL curves are obtained from a self consistent $O(\lambda^2)$ skeleton graph type calculation, and the DMFT curves use a state of art Numerical Renormalization Group (NRG) for the impurity solver. We have plotted the two curves after scaling the frequencies by the wave function renormalization Z. This scaling improves the fits, since the ECFL computation is not (yet) very accurate for this (single) number. We see that the scaled frequency dependence is very similar between the two theories at various densities considered, and exhibit a remarkable

asymmetry between particle (ω>0) and hole (ω<0) excitations that goes significantly beyond Landau's Fermi liquid theory (with a symmetric spectrum). This asymmetry is also responsible for the skewed ARPES line shapes in the theory.

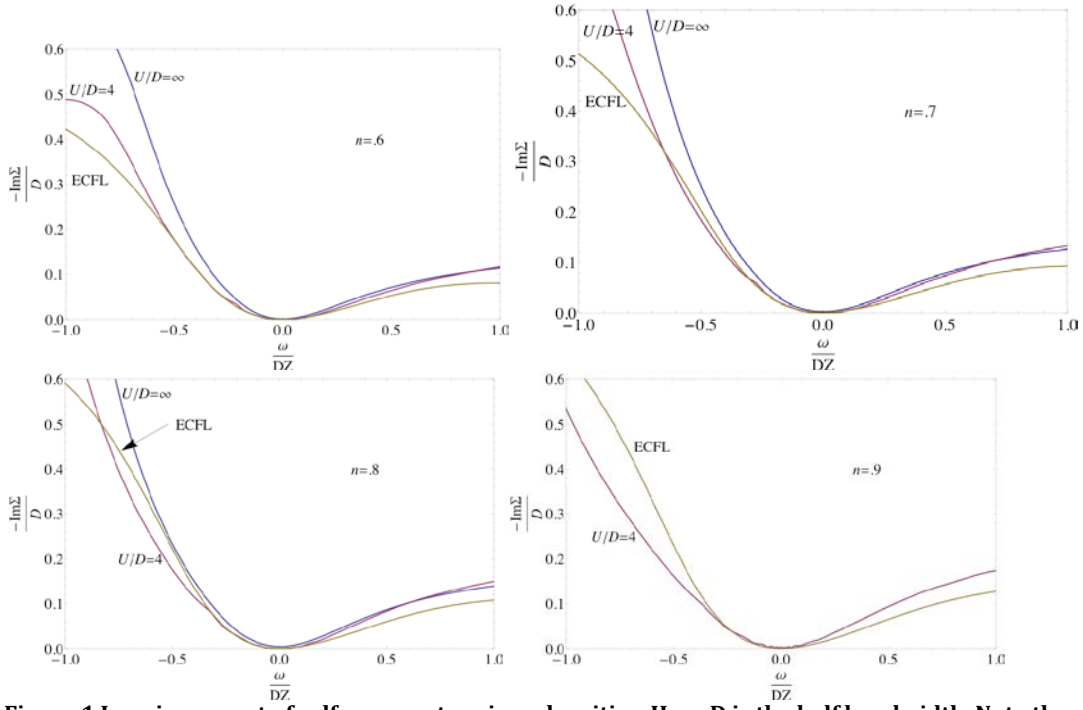
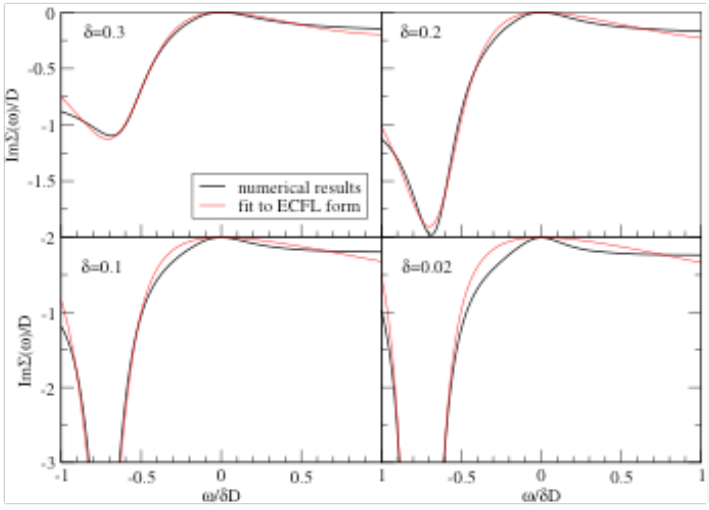


Figure 1 Imaginary part of self energy at various densities. Here D is the half bandwidth. Note the asymmetric behavior in ω, denoting the breakdown of particle hole symmetry of the Fermi liquid. This breakdown occurs at an (emergent) energy scale Δ, which shrinks as we approach the Mott insulating limit (n=1). Note that these O(λ^2) ECFL curves are closer to the case of U/D=4 than to U=∞.

One advantage of ECFL theory is that it provides (relatively) simple formulas, that capture the DMFT self energy quite closely, over a susbstantial energy range. Fig. 2 shows a comparison between the computations and a formula from ECFL,where



$$\mathrm{Im}\Sigma = -\frac{x^2}{\overline{\Omega}_1}\frac{1 - x/\overline{\Delta}_1}{(1 + x/\overline{\Delta}_2)^2 + x^4/\overline{\Omega}_2^2}.$$

Figure 2. Comparison of DMFT self energy over a substantial energy range with a simple formula from ECFL Note that the global features are quite similar. The low frequency comparison is improved by scaling the frequency with Z, as shown in Figure 1.

x= ω/δ and δ is the hole density, and the parameters Δj, Ωj are suitable energies.

- **ECFL-NRG studies for the asymmetric single impurity Anderson model at large U:**

Another benchmarking study, presented in Ref. [2], is closely related to the above work, and compares the results of the ECFL spectral functions with those obtained from the numerical renormalization group of Kenneth G. Wilson for the simpler impurity model. The well known Wilson NRG provides a numerical exact solution of the asymmetric Anderson impurity model. Here the dynamical information for spectral functions has been obtained only recently, in contrast to the static and thermodynamic information found originally by Wilson and co workers 30 years ago. The dynamics requires overcoming the demanding problem of analytic continuation, and hence the time lag. In collaboration with Professor Alex Hewson, we have compared the ECFL solution of this problem, again from a self consistent $O(\lambda^2)$ calculation, with the NRG results. From Fig.3 we see that the scaled impurity level spectral function compares well between the two theories. The impurity self energy again has a strongly particle hole asymmetric behavior.

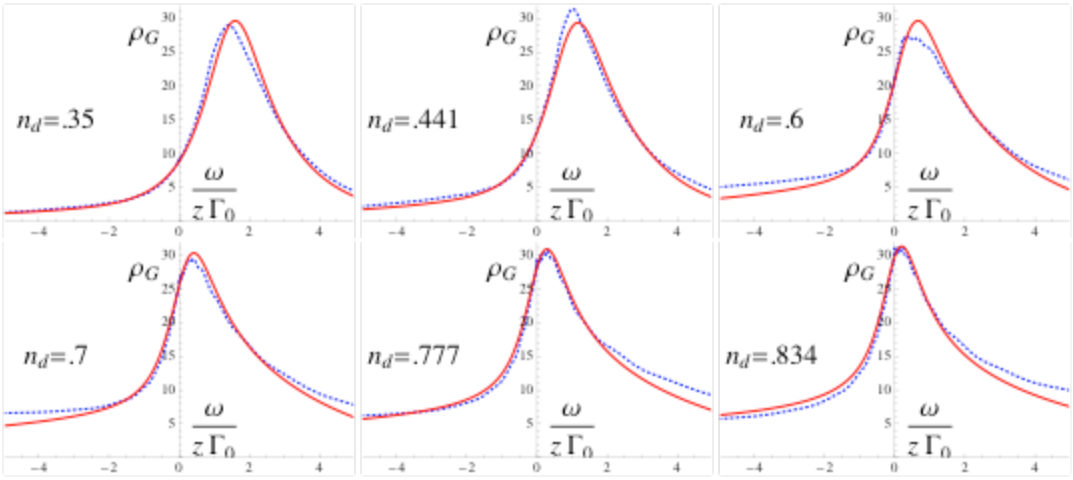


Figure 3. The asymmetric Anderson Impurity model NRG spectral function (i.e. A(k,w)) (dotted) compared to ECFL results (smooth lines) at various impurity level occupancies from Ref. [2]. The Friedel sum rule is exactly satisfied in ECFL, and the Kondo virtual bound state found just above the chemical potential. The asymmetric line shape is similar to that in the ECFL-DMFT study Ref. [1].

- **ECFL theory for Gutzwiller projection and analogy to the Dyson-Maleev theory for spin Boson mapping**

In Ref. [3], we have recently found a deep connection between the ECFL theory and techniques from quantum magnetism, originally due to Freeman Dyson. In a

seminal paper in 1956, Dyson found the non Hermitean representation for spin-S particles in terms of Bosons named after him and Maleev. His work on thermodynamics was extended to dynamics by Harris, Kumar, Halperin and Hohenberg (HKHH) in 1975, to obtain the decay rate of magnons in antiferromagnets.

In Ref. [3] we found that the ECFL theory equations for Gutzwiller projected electrons, originally obtained by us using the field theory method of Schwinger, have a very appealing re-interpretation. These can be understood as Fermionic analogs of the Dyson-Maleev theory mentioned above, and this mapping leads to a considerable pedagogical advantage. For example consider the ECFL theory finds

$$g(\vec{k}, i\omega) = \frac{1 - \frac{n}{2} + \Psi(\vec{k}, i\omega)}{g_0^{(-1)}(\vec{k}, i\omega) - \Phi(\vec{k}, i\omega)}$$

that the projected electron Greens function has a form (see equation above), that involves two self energies Φ and Ψ. This structure is identical to that in the HKHH work for the spin-Boson problem, who also found a twin self energy structure for the spin propagators.

To explain this connection, the fundamental idea in Ref. [3] is that Gutzwiller projected states continue to remain in the physical (i.e. projected) subspace, when acted upon by the bare (i.e. un projected) electron destruction operators. In contrast, the creation operators need to be modified by projectors. This leads to a fundamental asymmetry between creation and destruction operators, that is parallel to that in the spin-Boson problem. An exact formulation of the non Hermitean theory is provided, which requires Gutzwiller projection only at the most early time. Quite conveniently the equations of motion do not explicitly contain this projector at all. Most interestingly, the parameter λ alluded to above, is found to be the mathematical analog of the parameter $1/(2\,S)$, so that the semi classical limit of large spin $S \to \infty$ appears as the free Fermi limit $\lambda=0$. At the opposite end, the fully projected limit $\lambda=1$ appears as the extreme quantum limit $S=1/2$. This new and exact formulation appears to promise considerable advantage over other methods, it simplifies the various calculations and gives powerful new insights into the dynamics of systems with Gutzwiller projection.

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Novel Fractional Quantum Hall and Quantum Spin Hall Effects in Interacting Systems

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Project Scope

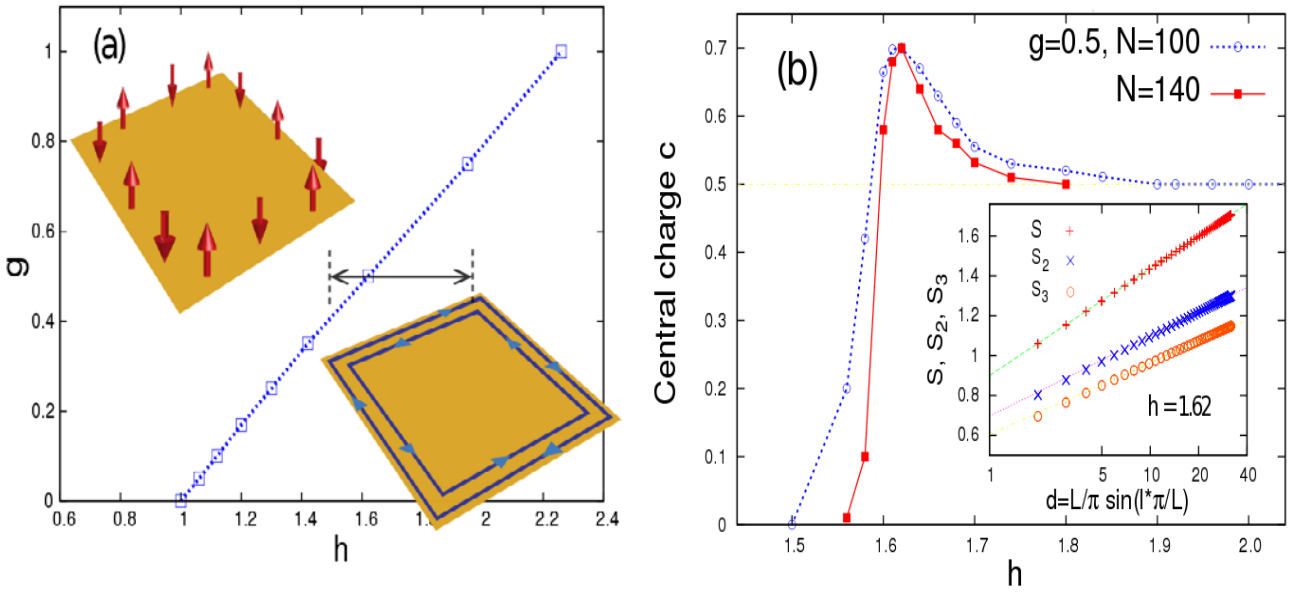
The research in this program involves theoretical (numerical) study of the correlated topological physics in strongly interacting systems. We study and determine the quantum phase diagram for such systems and the characteristic topological and transport nature of the new emerging quantum phases with topological order and fractionalized quasi-particles. In our computational approach, we develop novel numerical algorithm for detecting and characterizing new topological phase, entanglement spectrum, and the topological nature and statistics of the quasi-particles in these systems. We have focused on a few related topics in strongly correlated systems including: (a) The fractional quantum spin Hall effect (FQSHE) in topological bands without a magnetic field and quantum phase transition; (b) The space time emergent super-symmetry in the edge state of topological superconductor; (c) Extracting Modular matrix through minimum entangled states to identify different topological phases; (d) Theoretical discovery of the chiral spin liquid and quantum phase diagram for frustrated magnetic systems based on computational method developed in the past a few years.

Recent Progress

Fractional Topological Insulator and FQSHE: The fractional topological insulator is a remarkable new state of matter, where fractionalized quasi-particles emerge in the time-reversal invariant system. It is a very active field in condensed matter research to search for physics systems hosting such a fractionalized state without breaking time-reversal symmetry (TRS). We have recently identified and demonstrated the topological nature of a strong coupling fractional topological insulator phase on coupled topological bands with each carrying an opposite Chern number conserving TRS. By means of finite size exact diagonalization, we identify the topological nature of two quantum phases, with 9-fold and 3-fold degeneracies, respectively, with weak and strong spin dependent interactions. These states were identified before, however the topological nature of the 3-fold state was unclear. Numerical evidence from the evolution of low-lying energy spectra and Berry phase reveals that these two different ground states share the same topological spin Chern number. The counting rules of spin excitation spectra are demonstrated as the fingerprints of the FQSHE. Currently we are developing large scale

DMRG simulation to further investigate the nature (entanglement spectrum and modular matrix) of the strong coupling phase.

DMRG simulations of the nontrivial quantum phase transition and the space time supersymmetry (SUSY): We explore the novel feature of the quantum phase transition for topological superconductors in the presence of spontaneous breaking of the TRS. In contrast to ordinary symmetries, super-symmetry interchanges bosons and fermions. Specifically, the quantum phase transitions induced by the competition between the magnetic ordering and topological ordering at the boundary of topological superconductors in both two and three dimensions display super-symmetry when probed at long distances and times.



Shown in Fig(a): we illustrate the phase diagram for a system with Majorana edge of a two dimensional
time-reversal invariant topological superconductor coupled to
Ising magnetic fluctuations. The vertical axis g is the coupling between the Majorana fermions and the Ising order parameter. The transverse field induces a quantum phase transition between the state with ordered to disordered Ising spins with the gapless counter-
propagating Majorana modes. (b) Central charge c as a function
of h, for fixed g = 0.5. For h > hc (= 1.62), one finds c = 1/2,
consistent with gapless Majorana modes while for h < hc , one
finds c = 0 indicating the gapped phase. The critical point
separating the two phases is characterized by c = 7/10 which
corresponds to super-symmetric tri-critical Ising point.

The topological states themselves may be interpreted as arising from spontaneously broken super-symmetry, indicating a deep relation between topological phases and SUSY. We demonstrate the fractional central charge and scaling law of spin correlations to establish the super-symmetry numerically. We discuss prospects for experimental

realization of SUSY in films of superfluid He3-B.

Develop computational method to identify and characterize quantum states with topological order: Following theoretical proposal, we develop numerical methods of obtaining minimum entangled states (MES) and extracting the modular matrix to characterize the topological order of quantum systems. Using both Abelian FQH and non-Abelian Moore-Read/Read Rezayi states for bosons on the topological flat bands as examples, we identify multiple independent MESs based on exact diagonalization calculations. We extract the modular transformation matrices S(U) through calculating the overlap between different MESs, which contain the information of mutual (self) statistics, quantum dimensions, and the fusion rule of quasi-particles. We also demonstrate that these matrices are robust and universal in the whole topological phase against different perturbations until the quantum phase transition takes place. Very recently, we generalize such a method to larger scale simulation based on DMRG calculations. By studying two coupled FC insulators, we find a new route to realize non-abelian QHE state in strongly coupled bilayer systems.

Discovery of the chiral spin liquid in frustrated magnetic system: Based on numerical methods we developed in the past a few years, we have made significant progress in identifying novel topological phases in realistic materials. By studying an extended kagome Heisenberg model with up to the third neighboring couplings, we uncover a FQHE state emerging in the spin system known as the chiral spin liquid (CSL) through spontaneously breaking TRS. The CSL can naturally lead to the exotic superconductivity that originates from the condense of anyonic quasiparticles. Although CSL was highly sought after for more than twenty years after the initial theoretical proposal, it had never been found in a realistic Heisenberg model or related experimental materials. The kagome model we identified hosts a robust CSL, which will stimulate new theoretical and experimental researches in this field to resolve the nature of the quantum phases for different frustrated magnetic systems. An exciting next step will be identifying theoretical models and experimental materials which can host exotic topological superconductivity by doping different CSLs.

Future direction: We will further study the challenging issues related to FQSHE and symmetry protected topological phases in interacting systems. The instability of these states in the system with open edges have only been addressed based on field theory while the physical condition for the fractional topological states to be robust in microscopic systems remains unclear. We are developing simulation methods based on adiabatic DMRG to address this issue for these systems with competing interactions. The strong coupling FQSHE such as the one identified in our recent study [1] is

particularly interesting which cannot be described by a simple coupled Laughlin wavefunction. We will extract entanglement information and quasi-particle statistics based on modular matrix to fully characterize such a state in larger systems. Furthermore, we will explore new route for finding non-Abelian FQHE states by studying the coupled bilayer FQHE systems at different fillings with tunneling and different strength of inter-layer coupling. In such systems, non-Abelian states may be realized through gapping out the anti-symmetric states from ground state degenerating manifold. However, the possible non-
Abelian states are in general weak states due to competing effects from bilayer FQH states. Large scale DMRG simulation is expected to play an important role in such a direction. Beside the low energy spectrum, entanglement information studies, we are also developing inserting flux simulations to detect the quantum phase transition and to make prediction on quantum transport for experimental measurements. We will also study open issues about non-Abelian FQHE in 2D electron systems, graphene and its bilayers, as well as the surfaces of the topological insulators using our newly developed DMRG codes.

Publications

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2. Tarun Grover, *D. N. Sheng*, Ashvin Vishwanath, *Emergent Space-time Supersymmetry at the Boundary of a Topological Phase*, Science **344**, 280 (2014).
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Materials Theory

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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, electrical and thermal transport, 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, transparent conductors, van der Waals and hydrogen bonded energy materials, and materials with unusual characteristics, such as uncommon bonding patterns. The overarching goal behind this is materials discovery.

Recent Progress

One approach for addressing the challenge of using theory to accelerate materials discovery is the use of guided search strategies, illustrated in Figure 1. The central idea is develop microscopic understanding of properties in chemical and structural terms and to use this understanding to identify new or modified materials for study. The approach is therefore iterative and can incorporate both theoretical and experimental knowledge.

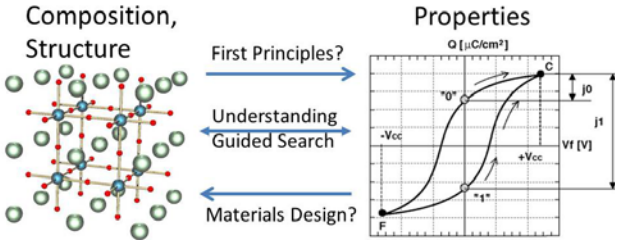

Figure 1. First principles calculations in materials discovery. For some properties, e.g. ferroelectricity, direct predictions can be made, while for others such as unconventional superconductivity this is not the case. Even in such cases theory can play a valuable role by providing microscopic understanding and in exploring trends. "Guided Search" is the use of understanding, trends and prediction for materials discovery.

We are using this approach for various materials classes including superconductors, magnets, ferroelectrics, and transparent conductors. In this work we have recently discovered new ways of obtaining very high magnetic coercivities in oxides through band effects, identified trends in magnetic properties that may help find new unconventional superconductors, elucidated the fact that certain types of disorder (A-site size

disorder), can strongly enhance ferroelectricity in many systems, and found a relationship between structure and the electronic and optical properties of GeTe-based phase change materials that can be simply understood in terms of local bonding.

In this abstract we focus on one part of our work, specifically, very recent work on transparent conductors, which is illustrative of the approaches that we are using.

Transparent Conductors:

Transparent conducting materials (TCM) are used as electrodes for displays, solar photo-voltaics and in smart windows. This is an active area of research with two main drivers: (1) n-type In_2O_3:Sn (ITO) replacement due to the limited supply of In and (2) identification of good p-type TCM to enable transparent electronics. Perovskite $BaSnO_3$ is a material that has been identified as a possible ITO replacement.

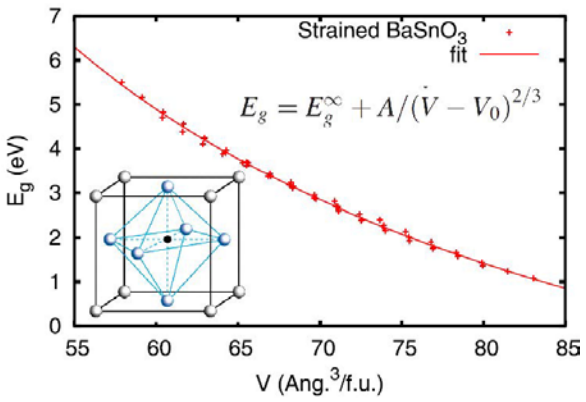

Figure 2. Band gap of $BaSnO_3$ for a wide variety of different strains, showing giant tunability and collapse onto a single volume dependent curve, well fit by a free electron form. The perovskite structure (inset) means that the Sn-Sn coupling must be via O, making the result that the gap is independent of octahedral rotation more remarkable.

The first question is how one can tune the properties of perovskite Sn (IV) oxides. We did hundreds of calculations of the electronic structure and optical properties of $BaSnO_3$ and its sister compound $SrSnO_3$ with different types of non-hydrostatic strain leading to typical perovskite distortion patterns, specifically different octahedral tilts and ion off-centerings as well as uniaxial and hydrostatic strains.

We found a most unexpected result. Specifically, the calculations showed that both the band gaps and the optical properties (refractive index, absorption spectra) are insensitive to octahedral rotation, opposite to well-studied perovskites like $SrTiO_3$, and that there is a much stronger sensitivity to volumetric strain (Figure 2). We found that the data fit a free electron model very well, which we explained in terms of the s-electron character of the conduction band and the bonding of the material.

In addition to providing an understanding of how the electronic structure can be tuned, it also suggests that an exceptionally wide range of electronic properties may be achievable in epitaxial heterostructures that include perovskite Sn(IV) compounds. We did detailed supercell calculations for heterostructures with $KNbO_3$ and $KTaO_3$ and indeed find that an exceptionally large range of properties may be achievable including 2DEGS on both the niobate and the stannate sides of the interfaces depending on the specific structure.

Another question has to do with how one can identify a good p-type TCM. We are using guided search based on microscopic understanding and trends. The challenge is that the materials

identified so far have poor hole mobility and typically also have poor stability in air. For example, Cu(I) based materials such as Cu_2O and delafossites have relatively heavy valence bands that give poor mobility and are readily oxidized in air. On the other hand, compounds that would be good transparent p-type conductors if only their band gaps were higher are known and the reasons are well understood in terms of band structure and chemistry. For example, ZnSe can be readily made p-type, has a much better p-type mobility than Cu(I) oxides, and is chemically stable in air, but its band gap is too low for a TCM.

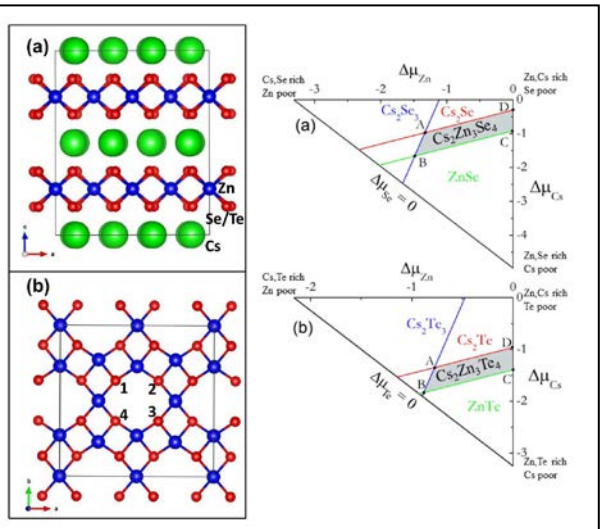

Figure 3. Structure and phase diagram showing conditions for synthesis of new compounds $Cs_2Zn_3Te_4$ and $Cs_2Zn_3Se_4$ proposed by theoretical calculations and subsequently successfully synthesized and initially characterized at ORNL. As predicted, these are air stable compounds in spite of the presence of a large amount of Cs in the formula.

We combined these facts with observations from Zintl chemistry and ideas related to stabilization of vacancies by Coulomb interactions and were led to study layered cation defect ternary compounds with large electropositive ions. Finally, we found stable previously unknown phases in our calculations that show promise as TCM, specifically $Cs_2Zn_3Se_4$ with an ideal band gap and also a lower band gap material $Cs_2Zn_3Te_4$. The structure and phase diagram are shown in Figure 3. Key features are the layering and ordered Zn vacancy structure, which leads to an increase in the band gap.

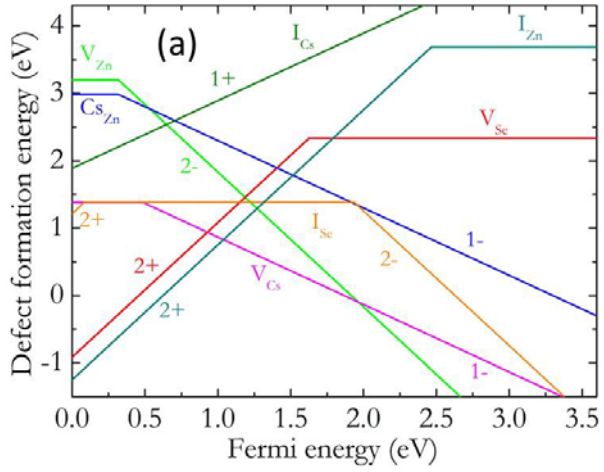

Figure 4. Calculated defect energies for $Cs_2Zn_3Te_4$ with the chemical potentials corresponding to point B in the phase diagram (Fig. 3), i.e. the chalcogen rich side. The results show that the material will form p-type, but that the p-type doping level will be limited by the formation of Zn interstitials at low Fermi energy.

Calculations of defect formation energies and optical properties were performed, confirming the anticipated p-type dopability and the favorable electronic properties, specifically as regards the valence band mass and other indications of good hole mobility.

Following these predictions, synthesis was attempted at ORNL (B. Saparov and co-workers, funded by DMSE) and both compounds were successfully made. Initial characterization shows that the phases are indeed stable in air and that they do have band gaps consistent with the predictions. $Cs_2Zn_3Se_4$ is predicted to dopable by Cs vacancies as shown in Figure 4, although the doping level may be limited.

Thus we have successfully designed new

previously unknown functional compounds using a guided search approach. These predicted compounds were experimentally synthesized following the predictions.

Future Plans

We plan to continue using guided search strategies to find interesting new materials and to develop microscopic understanding of the properties of materials in terms of their structure and bonding. Understanding of mechanisms and trends is particularly important for guided search. This is often very subtle. For example, the association of spin-fluctuations with the sign changing s-wave state commonly thought to occur in the Fe-based superconductors raises the question of what structural and chemical features underlie the specific type of magnetism in those compounds, and then what other compounds might show such behavior. Similarly, the predicted extremely high thermal conductivity in BAs, similar to chemically very different diamond structure C, raises the question about what are the bonding features that are important and are different from other lower conductivity materials. Our future plans center around developing and using this type of understanding with the goal of materials discovery.

Publications

The following is a partial list of recent publications:

J.L Feldman, D.J. Singh and N. Bernstein, "Lattice-dynamical model for the filled skutterudite $LaFe_4Sb_{12}$: Harmonic and anharmonic couplings", Phys. Rev. B **89**, 224304 (2014).

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D.J. Singh, "Superconductivity and magnetism in YFe_2Ge_2", Phys. Rev. B 89, 024505 (2014).

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Many-Body Theory of Energy Transport and Conversion at the Nanoscale

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1 Program Scope

This project addresses the fundamental challenge of understanding quantum systems far from equilibrium, while simultaneously exploring the potential of nanostructured materials for applications in energy-conversion technologies. The main focus of the project is *quantum thermoelectrics*. The enhancement of thermoelectricity due to electron wave interference in nanostructures will be investigated in both the linear and nonlinear regimes. The focus will be on increasing the power factor via electron-wave engineering. This approach can be combined with higher-order nanostructuring designed to minimize the thermal conductance to create revolutionary new types of thermoelectrics with exceptionally high figure of merit ZT. To elucidate the local quantum mechanisms responsible for enhanced thermoelectricity, the project will investigate *local probes of thermoelectricity* in quantum systems. The nonlinear Peltier effect will be studied, with the goal of increasing the efficiency of quantum heat pumps in the nonlinear regime through engineered junction asymmetry. Fundamental research on the *nonequilibrium many-body theory of nanostructures* will be conducted in parallel, to enable the applied research on nanoscale energy conversion. The local properties of interacting quantum systems far from equilibrium will be investigated using nonequilibrium Green's functions (NEGF), including the development of new nonperturbative approximations to describe local heat dissipation.

2 Recent Progress

Probing the local temperature of nonequilibrium quantum systems

Recent advances in thermal microscopy [1–5], where spatial and thermal resolutions of 10nm and 15mK, respectively, have been achieved [4], raise a fundamental question, "On how short a length scale can a statistical quantity like temperature be meaningfully defined?" We tackled this question theoretically [6] by first providing a physically motivated and mathematically rigorous definition of an electron thermometer as an open third terminal in a thermoelectric circuit. We then developed a realistic model of a scanning thermal microscope (SThM) with atomic resolution, including an analysis of the factors limiting both spatial and thermal resolution. With this model of a nanoscale thermometer, we investigated what happens when a temperature difference is applied across a single molecule. We found that individual atoms (or bonds) within a molecule can be hot or cold relative to their neighbors due to quantum thermal oscillations; quantum interference mimics the actions of a Maxwell Demon, allowing electrons from the hot electrode to tunnel onto the temperature probe when it is at certain locations near the molecule, and blocking electrons from the cold electrode, or vice versa.

In collaboration with Justin Bergfield, Mark Ratner, and Massimiliano Di Ventra, we investigated [7] the local electron temperature distribution in graphene and carbon-nanoribbon (CNR) based junctions subject to an applied thermal gradient, including the effects of phonon thermal transport. We predict quantum thermal oscillations whose wavelength is related to that of the Friedel oscillations. Experimentally, this wavelength can be tuned over several orders of magnitude by gating/doping, bringing quantum temperature oscillations within reach of the spatial

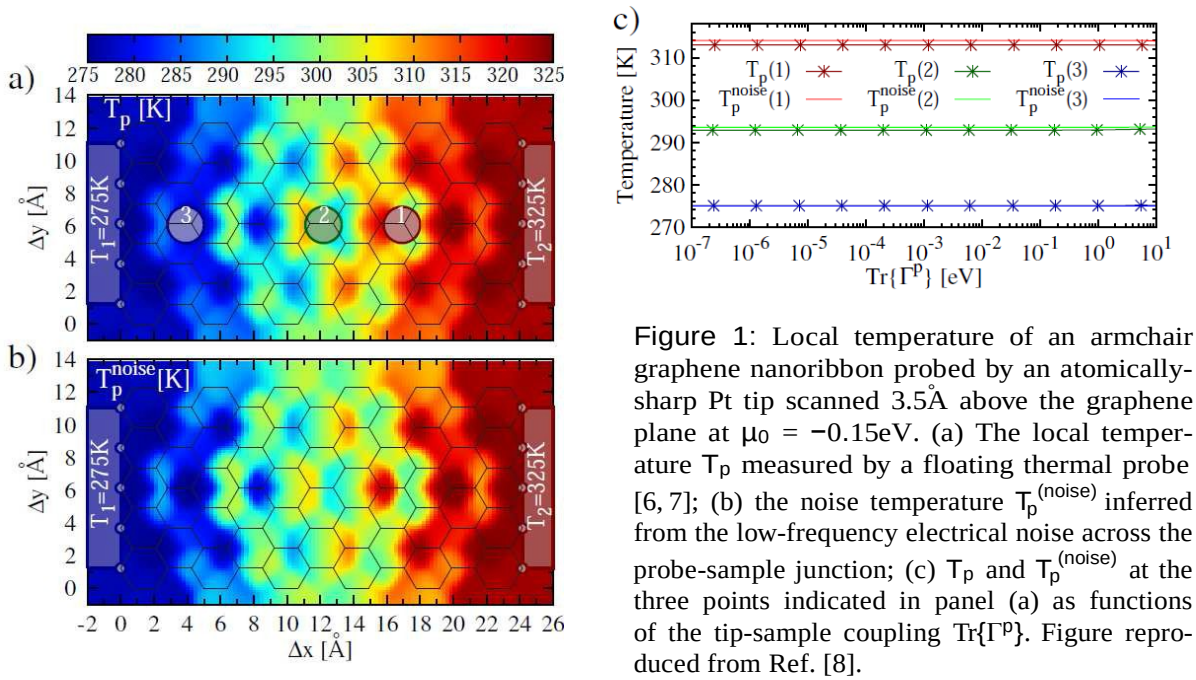

Figure 1: Local temperature of an armchair graphene nanoribbon probed by an atomically-sharp Pt tip scanned 3.5Å above the graphene plane at $\mu_0 = -0.15$eV. (a) The local temperature T_p measured by a floating thermal probe [6, 7]; (b) the noise temperature $T_p^{(noise)}$ inferred from the low-frequency electrical noise across the probe-sample junction; (c) T_p and $T_p^{(noise)}$ at the three points indicated in panel (a) as functions of the tip-sample coupling $\mathrm{Tr}\{\Gamma^p\}$. Figure reproduced from Ref. [8].

resolution of existing measurement techniques. Moreover, we show that only modest advances in thermal resolution beyond current SThM technology are required to observe these predicted quantum effects for the first time.

An interesting question raised by the ability to measure the local temperature of a quantum system out of equilibrium is to what extent such a local temperature satisfies the conditions obeyed by a bona fide equilibrium temperature. Our analysis [8] indicates that, within linear response, the local electron temperature measured by a thermoelectric probe satisfies both the zeroth (transitive property of equilibrium) and second (relation of efficiency to absolute temperature) laws of thermodynamics under reasonable assumptions, such as the validity of a Sommerfeld expansion. Moreover, we showed that the temperature so defined agrees with that inferred from an independent calculation of the low-frequency electrical noise across the probe-sample junction (see Fig. 1), thus establishing the validity of a local *fluctuation-dissipation relation* in this weakly-driven nonequilibrium quantum system. These results were obtained for noninteracting systems within linear response and to leading order in the Sommerfeld expansion. In addition to the case of DC bias investigated by the PI and collaborators [8], the validity of such a fluctuation-dissipation relation was also established under certain conditions for AC bias [9, 10].

3 Future Plans

Local thermodynamics of an interacting quantum system far from equilibrium

NEGF provides a systematic method to study the statistical mechanics of nonequilibrium systems; however, a corresponding thermodynamic description has generally been lacking. The project will investigate under what conditions a *fluctuation-dissipation theorem* also applies to the far-from-equilibrium case, and to what extent the local temperature and chemical potential so defined are consistent with the laws of thermodynamics. The ability to consistently define local thermodynamic variables points to the possibility of constructing a thermodynamic description—if only a partial one—of far-from-equilibrium quantum systems. The effect of coarse graining (or measurement resolution) will also be investigated. Interestingly, how far a system is from local

equilibrium may depend upon how closely one looks.

The analysis of Ref. [8] will be extended to *interacting quantum systems* under steady-state conditions *arbitrarily far from equilibrium*. In addition to the zeroth and second laws, we also propose to investigate the conditions under which local thermodynamic variables can be assigned consistent with the first and third laws of thermodynamics. Furthermore, the project will investigate under what conditions a fluctuation-dissipation relation applies to the far-from-equilibrium case. The later project will be carried out (at least initially) in the elastic transport regime (e.g., for noninteracting electrons), where the current-current correlation function can be explicitly calculated far from equilibrium.

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5 Publications 2012–2013

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Non-equilibrium Relaxation and Aging Scaling of Magnetic Flux Lines in Disordered Type-II Superconductors

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Project Scope

Considerable progress has been achieved in our understanding and characterization of the phases in thermal equilibrium of vortex matter lines subject to thermal fluctuations and point-like or extended disorder. A large body of work has addressed the non-equilibrium steady states of current-driven vortices in disordered superconductors. However, a satisfactory description of the fluctuation phenomena associated with the relaxation kinetics towards equilibrium or non-equilibrium steady states has not yet been achieved. Our research projects aim for a thorough numerical investigation and theoretical characterization of the random fluctuations and out-of-equilibrium relaxation processes of interacting magnetic flux lines in type-II superconductors subject to various defect types. Previous support through DOE-BES has advanced our understanding of physical aging phenomena in superconductors with uncorrelated point disorder, and revealed distinct intriguing temporal regimes that could be addressed separately in different defect geometries. We now investigate in detail the dynamical relaxation features starting from experimentally realizable initial conditions, encompassing sudden changes of external parameters such as temperature, magnetic field, and driving current, and explore universal and material-specific characteristics in the physical aging as well as glassy relaxation regimes. Thereby we hope to identify unique dynamical signatures that distinguish between systems with point pins and extended correlated defects centers (columnar or planar defects). It is our goal to propose specific experimental setups that will allow probing the different dynamical regimes, and stimulate the development of novel tools for material characterization and optimization.

Recent Progress

Characteristic length scales in non-equilibrium vortex systems

Our previous work on disordered magnetic systems showed that a detailed understanding of a coarsening process can be achieved through the identification and investigation of the characteristic length scales associated with it. In recent months we have applied this approach to non-equilibrium vortex systems, for which the relevant growth scale is given by the correlation length that governs the decay of the spatial height-height correlations along the vortex lines. In a first step, we have utilized Monte Carlo simulations to extract this correlation length for a range of different situations (with and without repulsive vortex interactions, with either point or columnar defects). Figure 1 summarizes our results for the case of attractive point-like pinning sites with varying strength p. The information contained in the correlation length L(t) allows us to better understand and analyze the scaling properties during relaxation toward the steady state.

More crucially, this quantity also provides us with new insights into the origin of the observed deviations from scaling as reported in our previous work. A paper presenting our determination of the correlation length and its temporal growth is currently in preparation.

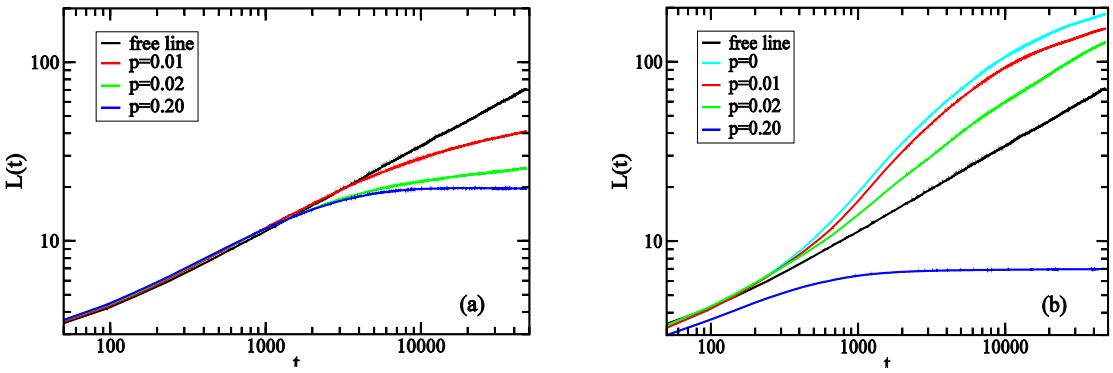

Fig. 1: *Time-dependent correlation length obtained from the height correlation function of the fluctuating flux lines.* (a) *Random point pins with strength p and non-interacting flux lines;* (b) *random point pins and vortices with repulsive interactions. Different growth regimes are readily observed that allow us to gain a complete understanding of the relaxation processes encountered during the coarsening of vortex systems. The flux lines extend over a length of 2560 lattice constants which is large enough to exclude the appearance of finite-size effects during the run time of the Monte Carlo simulations.*

Non-equilibrium relaxation and aging scaling in the Bose glass

In the presence of extended, linear defects, our Langevin dynamics simulations can probe the relaxation of vortex line fluctuations as they become localized at the pins. However, we cannot access the structural relaxation of the flux lines at much later times as they move between defects to optimize their pinning energy and minimize their mutual repulsive interactions. In order to focus on this aging regime for the vortex density correlations, we have resumed our investigations of an effective two-dimensional Bose glass model by means of Monte Carlo simulations. Figure 2 (a) shows the soft gap in the density of states or distribution of pinning energies that develops due to the essentially logarithmic repulsive forces. These energetic anti-correlations induce very slow relaxation kinetics in the vortex density, which is governed by simple aging scaling, as depicted in Fig. 2 (b): The associated scaling exponents are not universal, depending on temperature and filling fraction, i.e., external magnetic field; their values

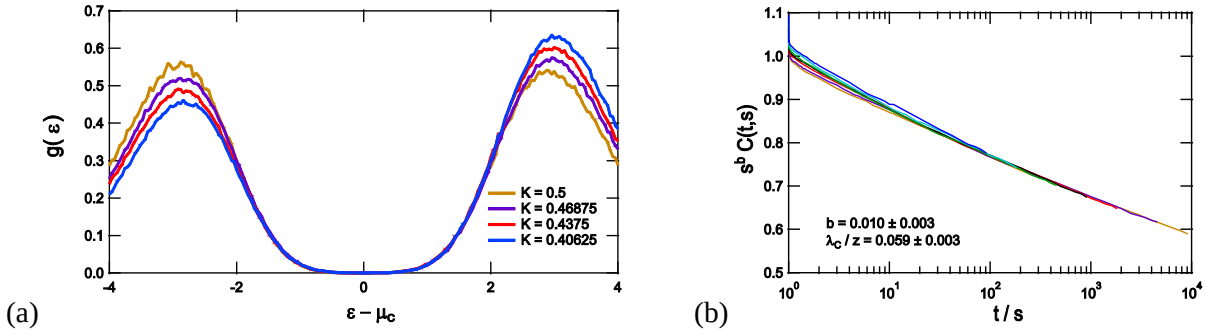

Fig. 2 (a): *Density of states for the two-dimensional Bose glass at low temperature for various filling fractions K;* (b): *aging scaling collapse for the density autocorrelation function at half filling.*

are close to zero, indicating almost logarithmic aging. We have recently submitted a manuscript that details this work and compares the Bose glass relaxation scaling to related Coulomb glass features in two- and three-dimensional disordered semiconductors to *The Physical Review E*.

Distribution of pinning times of fluctuating vortex lines

At the *DOE Theoretical Condensed Matter Physics Principal Investigators' Meeting* in August 2012, Valerii Vinokur proposed that we should extract the histograms of pinning times for vortex line elements to defect sites from our simulation data, and compare our results to theoretical predictions in the literature. We modified our Langevin dynamics code accordingly, and have since carefully studied this problem for uncorrelated point disorder with various distributions of pinning potential strengths. The results differ drastically when the defects are purely attractive, in contrast to when the pinning strength distribution is centered at zero. In the latter case, we observe clear evidence of sharp transitions indicating the characteristic Larkin length or energy scale that separates short-range from collective pinning behavior, see Fig. 3 (a). Furthermore, the temporal extension of the crossover region before the asymptotic scaling regime is reached strongly depends on how the pinning potential is implemented; for example, if the pinning centers are modeled as isolated localized defects, or described by a continuous energy landscape. In the pinned state, we measure a power law decay for the distribution of pinning times, similar to earlier predictions, with a temperature-dependent decay exponent α(T), see Fig. 3 (b). We have recently submitted these novel results for publication in *EPL (Europhysics Letters).*

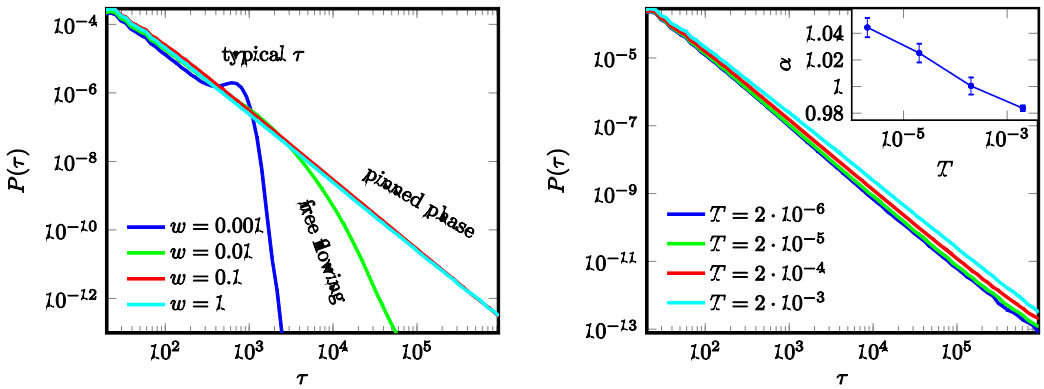

Fig. 3 (a): *Pinning time distribution P(τ) for discrete pinning sites for varying standard deviation w of the pin strength, both in the pinned and moving phases. The local maximum of P(τ) deep in the freely flowing phase indicates a characteristic pinning time.* (b) *Pinning time distribution P(τ) for discrete pinning sites at different temperatures T in the pinned state; the inset depicts the algebraic decay exponent α(T).*

Future Plans

Non-equilibrium vortex relaxation with different quench scenarios

We have begun to systematically explore the effects of sudden field quenches, i.e., instantaneous removal or addition of magnetic flux lines on the relaxation dynamics of interacting vortices in disordered type-II superconductors subject to either point or columnar pinning centers, by means of our Langevin molecular dynamics simulations. The following complementary investigations should lead to important new insights: (1) Extracting the growing correlation length L(t), we will

attempt to rescale two-time observables in the aging relaxation regime as functions of the ratio L(t) / L(s) rather than a fixed power of t / s. (2) We intend to study these different vortex systems' responses to fast temperature resetting. (3) We will assess which of these aging relaxation scenarios may be realized experimentally, and what observables can probe predicted features.

Non-equilibrium relaxation of driven vortices to new steady states

We are currently in the process of extending our analysis of the relaxation kinetics of interacting flux lines in disordered superconductors towards thermal equilibrium to analogous investigations of driven vortex matter that approaches a new non-equilibrium stationary state after initial preparation in a distinct steady-state configuration. Various intriguing possibilities for such novel studies include: (1) instantaneous temperature quenches within the non-equilibrium stationary state of driven vortices subject to point or extended defects; (2) sudden magnetic field, i.e., vortex density quenches in the driven state, which we expect to be followed by fast relaxation dynamics that likely prevents any detectable aging scenario; (3) fast changes in the driving force (applied current) should similarly lead to fast relaxation, provided the system remains in flowing steady state. However, when the drive switch extends into the pinned region below the critical current, and thus to a frustrated glassy phase, the accompanying relaxation processes are probably very slow, which in turn may open sufficiently large time windows for intriguing aging behavior. Furthermore, (4) in our simulations we hope to mimic aging features that have been experimentally observed in the induced voltage by applying current pulses of varying duration; and finally, (5) one would anticipate a host of complex relaxation scenarios when the driving force quench would be directly onto the critical depinning current (at low temperatures), whereupon genuine critical aging scaling should be observable, governed by the diverging correlation length of the continuous zero-temperature depinning phase transition.

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  Nonequilibrium relaxation and critical aging for driven Ising lattice gases,
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  Eur. Phys. J. B **86**, 228 -- 1-15 (2013) [e-print arXiv: 1211.6929].

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  submitted to Phys. Rev. E (2014) [e-print arXiv: 1403.6615].

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  submitted to EPL (Europhys. Lett.) (2014) [arXiv: 1405.7261].

Unconventional Metals in Strongly Correlated Systems

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Project scope:

A growing number of metals display phenomena that defy textbook paradigms for metallic behavior in electronic systems. These arise due to either strong electron correlations, reduced dimensionality, or disorder effects (or a combination of more than one of these effects). One class of metals (famously in the cuprates) do not fit the Landau fermi liquid paradigm. In many cases the non-fermi liquid state seems optimal for superconductivity to develop on cooling. Our theoretical understanding of such unconventional metals and their superconducting instability is rather primitive.Though many basic questions about such non-Fermi liquid metals are open, there has been slow but steady progress over the years. A major component of the project seeks to develop methods capable of dealing with non-fermi liquid physics and its relation with superconductivity. A different class of unconventional metal arises at the surface of a three dimensional topological insulator. This kind of metal is prohibited from existing in any two dimensional material. Another goal of the project is to understand strong correlation effects on this class of metals. Finally many correlated metals also exhibit tendencies toward charge or spin density waves. These kinds of broken symmetries are typically very sensitive to disorder, and a part of the project aims to elucidate these effects.

Recent progress:

1. **Superconductivity and non-fermi liquid metals:**

Quantum criticality is often implicated for both the breakdown of Fermi liquid theory and the superconductivity seen in many correlated metals. In a recent paper[1] we described progress in studying these issues theoretically in two dimensional metals pushed close to the onset of nematic order which breaks crystal rotation but not translation symmetries. A theoretical framework for such a quantum critical point was developed earlier in my group (D. Mross, J. McGreevy, H. Liu, and T. Senthil, Phys. Rev. B 82, 045121 (2010)) but that work

did not address possible instabilities toward superconductivity. Controlled calculations within this framework were reported in our recent paper[1] and showed that superconductivity is strongly enhanced near such quantum critical points.
This is one of the few, and hence valuable, examples where the idea that quantum criticality can enhance superconductivity can be theoretically analyzed reliably and given firm foundation.

The methods developed also enabled solving a different class of problems - namely the quantum phase transition between the composite Fermi liquid state in the half-filled Landau level and the Moore-Read non-abelian quantum Hall state. Closely related is the phase transition between two different kinds of popular quantum spin liquids (the spinon Fermi surface state and a different `paired' version).

2. **Strongly correlated three dimensional electronic topological insulators**

A fundamental open problem in condensed matter physics is how the dichotomy between conventional and topological band insulators is modified in the presence of strong electron interactions. In a paper[2] (published in Science) I, together with my student C. Wang and former MIT student A. Potter showed that there are 6 new electronic topological insulators that have no non-interacting counterpart. Combined with the previously known band-insulators, these produce a total of 8 topologically distinct phases. Two of the new topological insulators have a simple physical description as Mott insulators in which the electron spins form spin analogs of the familiar topological band-insulator. The remaining are obtained as combinations of these two `topological paramagnets' and the topological band insulator. We proved that these 8 phases form a complete list of all possible interacting topological insulators. We discussed the experimental signatures for these phases. A key prediction is that in some of these interacting topological insulators proximity coupling to a gapped s-wave superconductor will drive their surface gapless.

A related but distinct project we made progress on is the effects of strong correlation on the surface of the conventional electronic topological insulator. It is well known that the 3D electronic topological insulator (TI) with charge-conservation and time-reversal symmetry cannot have a trivial insulating surface that preserves symmetry. It is often implicitly assumed that if the TI surface preserves both symmetries

then it must be gapless. In a paper[3] (published in Phys Rev B), I (again with students Chong Wang and A. Potter) showed that it is possible for the TI surface to be both gapped and symmetry-preserving, at the expense of having surface-topological order. In contrast to analogous bosonic topological insulators, this symmetric surface topological order is intrinsically non-Abelian. We showed that the surface-topological order provides a complete non-perturbative definition of the electron TI that transcends a free-particle band-structure picture, and could provide a useful perspective for studying strongly correlated topological Mott insulators.

3. Spin and pair density wave glasses

Despite many decades of study the effect of impurities on density wave ordered metals continues to be poorly understood. The PI's efforts have been toward the effects of non-magnetic impurities on spin density wave metals. This is of importance for a number of correlated metals (iron arsenides, cuprates as well as classic spin density wave metals like Chromium). Related questions also arise in the context of `pair density wave' superconductors that involve finite momentum Cooper pairing. These have been proposed to occur in some cuprates and in some have fermion superconductors. The PIs ongoing work (with former student D. Mross) reveals a number of novel phenomena in such systems. In the spin density wave case a new kind of spin glass which preserves long range spin quadrupolar order is shown to arise. In the `pair density wave' case there is the interesting possibility that half-quantum vortices may be nucleated around impurities, and is currently being studied through numerical simulation and analytic arguments.

Planned activities:

I plan to study the question of quasiparticle mass and pairing gap renormalization in a strongly correlated superconductor. The motivation is recent Angle Resolved Photoemission Spectroscopy measurements of the Fermi velocity and pairing gap (near the node) in cuprate superconductors by my colleague I. Vishik and co-workers. These measurements find a systematic decrease of the nodal quasiiparticle Fermi velocity as the doping is decreased while the near nodal pairing gap remains constant. A similar behavior has also been found in high field quantum oscillation measurements. We plan to explore an explanation of this surprising result within the framework of the `incoherent Fermi liquid' normal state introduced by P. Lee and me a few years back. The effect of superconductivity

on that model has not been explored thus far and may enable us to explain the experiments.

I also plan to continue the study of quantum criticality associated with electronic nematicity and other lattice symmetry breaking orders in a metal.
In particular I plan to study the effect of nematic fluctuations on the anisotropic gap structure of d-wave superconductors. A related project which I wish to pursue is an explanation of striking recent experiments demonstrating a sharp cusp in the penetration depth as a function of isovalent substitution in an iron-based superconductor.

Publications supported by DOE (since Aug 2012):

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http://arxiv.org/abs/1403.3694 (submitted to Phys Rev B).

2. Classification of interacting electronic topological insulators in three dimensions, Chong Wang, Andrew C. Potter, T. Senthil, Science 343, 6171 (2014).

3. Gapped Symmetry Preserving Surface-State for the Electron Topological Insulator, Chong Wang, Andrew C. Potter, T. Senthil, Phys. Rev. B 88, 115137 (2013).

ORBITAL-FREE QUANTUM SIMULATION METHODS FOR APPLICATIONS TO WARM DENSE MATTER

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K. Runge (Materials Science and Eng., Univ. Arizona, and BWD Assoc.)
14 July 2014

Project Scope

Matter at extreme temperatures (T) and pressures (P) is the physical context. Rapidly growing interest in warm dense matter (WDM), ranging from giant planet interiors to ICF capsule compression, is the driver. Limited experimental accessibility to the WDM regime heightens the importance of theory and simulations. The simulation context is *ab initio* molecular dynamics (AIMD): classical motion thermodynamics of ions under forces from quantum electrons within the Born-Oppenheimer approximation. Typically the quantum part is minimal implementation of Mermin free-energy density functional theory (DFT). At each AIMD step, the Kohn-Sham (KS) equations are solved with ground-state exchange-correlation (XC) functionals evaluated on densities with T-dependence from Fermi-Dirac occupations. The computational cost scales as the number of thermally occupied KS orbitals cubed. Irrespective of computer-power progress, that limits the maximum system size and T compared to ordinary MD. Currently a few hundred ions for a few thousand steps up to several tens of kK is the limit for all but national-scale computers.

The challenge we address is to make significant advancements in methodological accuracy and computational speed for thousands to millions of ions over an almost arbitrarily large T range. Thus, we develop reliable, soundly based, *orbital-free approximations for the KS kinetic energy and entropy* to escape KS scaling via orbital-free DFT (OFDFT), we develop *true free-energy XC functionals* non-empirically, and we develop *open-source software* specifically for finite-T AIMD. These thrusts are undergirded by analysis of *free energy DFT* analogous with ground state scaling, asymptotics, etc. We have made substantial progress on all four as well as on key supporting work (e.g. pseudo-potentials, PAWs, analysis of T-dependent exchange via thermal Hartree-Fock, orbital-free XC functionals). After progress summaries on the four, we outline the most important parts of research presently underway or in prospect.

Recent Progress

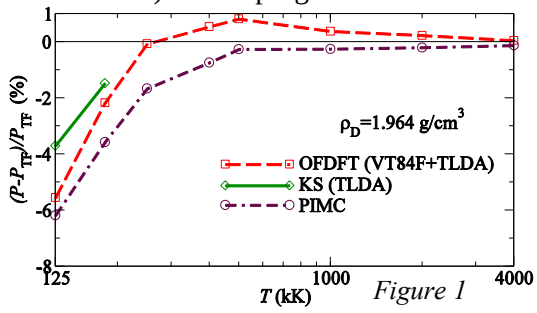

Figure 1

Orbital-free KS kinetic energy and entropy functionals – As in ground state DFT, a large fraction of the free energy is the non-interacting KE and entropy (i.e., the KS KE and entropy). Publications [8] and [16] present first-principles generalized gradient approximation (GGA) functionals for the KS KE and entropy that yield T=0 K binding of simple crystals and good behavior at large T. Ref. [8] removed the mildly empirical parametrization in [16] via a novel functional form and a new constraint to provide the first successful fully non-empirical GGA for the KS free energy. Figure 1 shows percentage pressure shift relative to Thomas-Fermi for our new functional, VT84F + TLDA XC

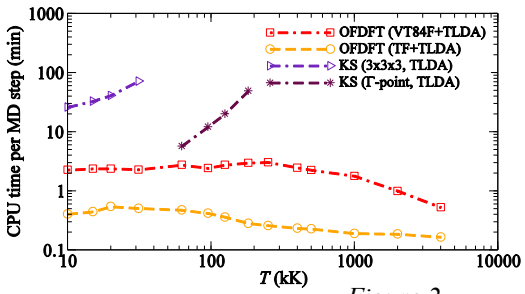

Figure 2

(see next item for our TLDA) compared with ordinary KS and with path integral MC (PIMC) results. Note the inadequacy of Thomas-Fermi below 750,000 K. Figure 2 shows the flat cost per MD step for OFDFT-AIMD vs. KS-AIMD bottleneck scaling. KS-AIMD values stop because of computational cost.

True Free-energy XC functionals – Though the non-interacting (KS) free energy magnitude is much larger than the XC magnitude, the materials physics is sensitive to the XC part. The color map in Fig. 3 shows the important T-dependence of the XC free energy as $\log_{10}\{|f_{xc}(r_s, T) - \varepsilon_{xc}(r_s)\ | / |f_s(r_s, T)|\}$, with f_{xc} = XC free energy per particle, ε_{xc}= XC energy per particle at T=0, and f_s = non-interacting free energy (KE and entropy), all for the homogeneous electron gas (HEG). The axes are T (vertical) and r_s (horizontal). Since solid density (ambient or compressed) WDM lies in the middle of the plot, the fractional shift *relative to the large non-interacting piece* easily can be 15% or more. For this our Ref. [2] provides a major step forward. It gives the local-spin density approximation (LSDA) for the XC free energy solely from quantum Monte Carlo HEG data, a first more than 40 years after the Perdew-Zunger and Vosko-Wilk-Nussair LSDAs from the Ceperley-Alder MC data at T=0 K. Our LSDA includes a new T-dependent spin-polarization interpolation and proper low and high density limits. Related work is in [9], [17], and [19].

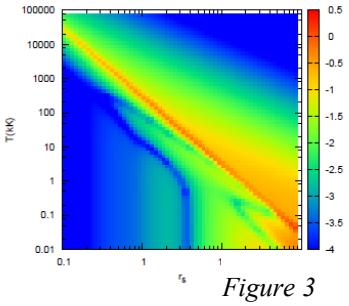

Figure 3

Open-source Software – Ref. [1] presents libraries and source code for "PROFESS@QuantumEspresso". It is our software to couple our modifications of Carter et al.'s PROFESS OFDFT code to drive AIMD simulations in modified QuantumEspresso on the same technical footing (MD algorithms, thermostats, parameters, etc.) as for KS DFT. PROFESS modifications include our functionals just discussed [2,8,9,16]. The software is downloadable from www.qtp.ufl.edu/ofdft under GNU GPL.

Free-energy functional properties – Publications [8]-[12] (and earlier work summarized in [3]) develop properties of free-energy density functionals and use them as constraints. In [9], the compressibility sum rule was enforced to improve the Vashishta-Singwi formulation of the HEG free energy. Ref. [8] used positivity, matching of the gradient expansion at low *s* (dimensionless density gradient), and recovery of von Weizsäcker KE at large *s* as constraints for successful parametrization.

Related and Supporting Work – [i] Downloadable pseudopotentials and PAW data sets valid for H, Li, and Al to very high compression; [ii] better orbital-free, constraint-based ground-state XC functionals [6,13, 20-22]; [iii] new self-interaction-free XC functional at high magnetic fields (high confinement) [5]; [iv] DFT fundamentals [14, 23]; [v] T-dependence in well-defined models [17,19]; [vi] relevant techniques for either AIMD or for extracting calibration data [7,15,18]; [vii] two reviews [3,4]; and [viii] Workshop on Ab Initio Simulations at Extreme Conditions at the 54th Sanibel Symposium (16-21 Feb. 2014).

Investigations Underway and Planned

Predicting material behavior at extreme conditions requires at least the equation of state (EOS), the shock Hugoniot, and the liquid-vapor coexistence curve. Though in principle the Hugoniot comes from the EOS, in practice Hugoniot measurements are used to probe the EOS for pressures beyond reach of diamond anvil cells. Hugoniot measurements have large error bars however. That ambiguity should be resolvable (or at least reducible) by simulations. But the last decade has seen notoriously conflicting results for H and D from calculations by almost all imaginable methods. An advantage of the OFDFT methods we are developing is the ability to do extensive calculations on large systems at high T. We are calculating the H Hugoniot directly (by searching the locus of points that satisfy the Rankine-Hugoniot condition) as well by computing the EOS to determine the effects of the T-dependent LSDA and to explore the reliability of the orbital-free non-interacting functionals by direct comparison with KS calculations.

The liquid-vapor critical point is so tedious computationally that, to our knowledge, only two calculations have been done with KS-AIMD [*Atomic Processes in Plasmas*, CP-1161, K.B. Fournier ed. (Amer. Inst.

Phys. NY, 2009) p. 32 for Al; J. Phys.: Condens. Matter **18**, 5597 (2006) for Rb and Cs]. The challenge is that well-converged thermodynamic variables are required to identify the diverging isothermal compressibility. We are poised to exploit the speed advantage of reliable OFDFT functionals to attack this problem. In addition to addressing the computational challenge of stable numerical treatment of low material density regimes, we will be considering ways to use classical and/or classical-mapped gas-phase approximations as routes to both better accuracy and to better speed.

For insight beyond thermodynamics there is transport. Another challenging application which we are poised to pursue is to compute conductivities in the OF-AIMD framework via the widely used Kubo-Greenwood (K-G) expressions. Those require a set of one-electron states at a subset of ionic configurations ("snapshots") from an AIMD run. In KS-AIMD, a K-G conductivity is calculated via the KS orbitals and eigenvalues for each configuration. Those conductivities then are averaged over the snapshot set. For OF-AIMD, the snapshotting will involve building a KS potential from the density at each selected configuration. A single diagonalization of the corresponding KS Hamiltonian then will yield non-self-consistent orbitals and eigenvalues for use in the K-G expression. Methodological questions are, first, whether such non-self-consistent orbitals are adequate in the K-G expressions, and second, whether our orbital-free GGAs for the non-interacting KE and entropy are good enough to make this procedure viable. If so, we will have a comparatively fast route to transport coefficients.

Beyond the Born-Oppenheimer approximation, quantum nuclear effects (QNEs) are a chronic concern for light nuclei, e.g. H and D, in the WDM regime. We have underway a set of path-integral molecular dynamics calculations for H motion driven by OF-DFT electrons using the functionals described above. Initial investigations show that QNEs do not substantially alter calculated P at T = a few tens of kK and moderate densities. Exploration of Trotter decomposition detail remains to be done. Investigations are underway for two cases in which QNEs are more likely to affect calculated P values, namely, when nuclear temperatures are relatively low compared to electron temperatures and for higher material densities.

For further advances in the orbital-free functionals, recently we have recognized that a given XC approximation intrinsically is paired with a specific non-interacting KE and entropy functional. The key result is a cascade of gradient dependences. In general, the non-interacting functionals are two orders higher in gradient dependence than the assumed XC functional. This relationship provides a new way to select among the many possible non-singular high-order reduced density derivatives available for non-interacting KE and entropy approximations [Phys. Rev. B **80,** 245120 (2009)]. It also provides a possible novel route to two-point non-interacting functionals. Both are under exploration. Also on the theory side, we are about to publish a renormalized Thomas-Fermi theory that gives densities which are properly non-singular at nuclear sites systematically rather than by repair (as with earlier schemes) and a new analysis of scaling for the components of the Mermin functional.

Finally, on the software front, we have two pending initiatives. Because of the ubiquitous use of VASP for KS-AIMD simulations, especially in the national labs, we have been urged to develop and publish a counterpart to Profess@QE for VASP. Within personnel resource limitations we hope to embark on that development soon. Secondly, with J.J. Rehr (U. Washington) we are exploring introduction of our XC free-energy functionals into his FEFF code, so that FEFF GW and Bethe-Salpeter calculations of excited system properties will be properly T-dependent.

In sum, we have moved OFDFT well beyond the state of Thomas-Fermi plus some *ad hoc* fraction of von Weizsäcker with fully constraint-based GGA functionals. We have pushed free-energy DFT into the refinement level of a model-independent LSDA for the XC free energy. We have made our methods freely available in usable code. Applications to key problems of matter at extreme conditions and critical refinements for greater accuracy at the same speed are in prospect.

Publications (2012 – present)

[*Note all publications and software are at http://www.qtp.ufl.edu/ofdft*]

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Strongly Correlated Systems: further away from the beaten path.

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Project Scope

In recent years the activity of our FWP has been focused in a number of different areas. The common features of these activities is that they all point away from traditional well understood physics. In pursuing these activities we have been greatly assisted by the new numerical methods developed in our group and by the past expertise in nonperturbative techniques our group possesses. Our theory group is working in close contact with experimentalists. Out of 32 papers published since 2011, nine were published in collaboration with experimentalists.

Recent Progress

Topological Kondo effect: The topological Kondo effect takes place when fermionic excitations of the bulk are scattered on a composite quantum "spin" nonlocally encoded by Majorana zero modes located at spatially different points. We have found examples of systems displaying such a Kondo effect. We predict that some will also display quantum critical behavior. This means that the topological spin is not completely screened at T=0 and the system displays non-Fermi liquid behavior. Refs. 8, 14, 16, 17.

Particles with non-Abelian statistics: Parafermion zero energy modes are a vital element of fault-tolerant topological quantum computation. Although it is believed that such modes form on the border between topological and normal phases, this has been demonstrated only for Z_2 (Majorana) and Z_3 parafermions. In Ref. 19 we have considered an integrable model of one-dimensional fermions where such demonstration is possible for Z_N parafermions with any N. The procedure is easely generalizable for more complicated symmetry groups. See also Ref. 5.

Deviations from Landau Fermi liquid theory in Hund's metals: Ref. 9 We have described and successfully solved a Kondo-type Hamiltonian representing an analytically tractable version of the model used by Yin *et.al.*, Phys. Rev. B **86**, 2399 (2012) to explain the non-Fermi liquid behavior of iron chalcogenides and ruthenates in an intermediate energy range. We consider a regime where a complete screening of the local degrees of freedom proceeds in two stages described by two characteristic energy scales – the orbital Kondo temperature T_K^{orb} and much smaller scale E_0 . The first scale marks a screening of the orbital degrees of freedom and the second one marks a crossover to the regime with coherent propagation of quasiparticles. Non-Fermi liquid effects take place at the crossover region between the two scales and are explained by the proximity of the RG trajectory to the quantum critical point of the orbital Kondo model.

New mechanism of order parameter formation. In Ref. 18. A. Tsvelik and A. Chubukov considered a new mechanism of order parameter (OP) formation when the OP is formed as a bound state between two charge density waves (CDW). As a result CDW never order, but the four-fermion OP does.

Out-of-equilibrium dynamics
As part of our work on renormalization group techniques for strongly correlated systems, we have developed the ability to study quench dynamics in one dimensional cold atomic gases (Refs. 21 and 27). We have exploited this ability to study the consequences of a quench where the gas is prepared in a parabolic trap and released into a cosine potential. The one dimensional Bose gas is described by Lieb-Liniger model and so absent a potential is integrable. The cosine potential breaks the integrability however. However we have argued that provided this integrability breaking is weak, the exotic conserved charges that would be present absent the cosine survive in the low energy Hilbert space. We believe this provides a quantum analog to the classical KAM theorem.

Future research:

Pnictides and DMFT:

In collaboration with Prof. Kotliar who has agreed to spend regular periods of time at BNL to facilitate a closer collaboration, we plan to continue our research on Hund's metals. This research is likely to be coupled with the efforts to understand the complicated behavior of the strongly correlated system FeTe. This project will involve a collaboration with J. Tranquada and I. Zaliznyak from BNL's Neutron Scattering Group.

Heavy Fermion Physics:

An interesting collaboration is proceeding with the group of Prof. M. Aronson at BNL. This group has made studies of a non-Fermi liquid quantum critical point in a layered metal YFe_2Al_{10} and discovered a robust scaling of its thermodynamic properties. The magnetization, specific heat, and electrical resistivity display $T/B^{0.59}$ scaling which does not fit any existing theory. One paper with participation of A. Tsvelik is already prepared for submission. We plan to continue to work on this problem.

Parafermions:

The problem of parafermions is likely to continue to occupy our attention. Parafermions are particles with non-Abelian statistics. There are numerous suggestions for realizations of such particles which are one of the cornerstones for realizing quantum computing. We have already published some work in this direction and plan to continue to develop these ideas.

Ultrafast:

In the past three years we have developed unique capabilities in studying quantum quenches in low dimensional strongly correlated systems. Heretofore our focus in this area has been on fundamental questions in statistical mechanics of non-equilibrium systems (Refs. 21 and 27) with applications to cold atomic systems . In the near future we intend to bootstrap this expertise to study time dependent phenomena in solid state materials. This is becoming particularly relevant to experimental efforts at BNL. BNL's electron spectroscopy group, already active in this area in collaboration with scientists at the Universität Duisburg-Essen, is on the verge of having an operational laser ARPES lab capable of performing time dependent ARPES measurements. And BNL's x-ray scattering group has an established record in pump-probe studies of strong correlated systems.

Unlike cold atomic gases, where the phenomenology can be understood in the context of simple model Hamiltonians, solid state systems are much more complex, and high-energy phenomena requires a careful consideration of optical transitions between different electronic bands. This implies a great need for theoretical frameworks and computational methods able to aid BNL's experimentalists in the modeling and interpretation of their data.

One key that this framework necessarily must provide in order to understand phenomena taking place in the femtosecond time-scale will be a sensible account of the many-body effects of electron-electron interactions. There are only a few techniques that can help to understand these phenomena at a fundamental level, including time-dependent DMRG and NRG, DMFT+Keldysh, diagrammatic Monte Carlo, and the time-dependent Gutzwiller approximation. They all have their strengths but they all suffer from limitations. We thus intend to leverage our previously developed expertise in numerical renormalization group techniques as well as our unique approach to DMRG in two dimensions to complement these already available approaches. In particular we plan to actively develop our DMRG codes so that they are able to describe time dependent phenomena in two dimensions. This is work that will be done with Andrew James, a former post-doc in the group, who has won a fellowship in London to pursue exactly this problem.

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X-ray Spectroscopy as a Probe of Intersystem Crossings, Coherence, and Collaborative Effects in Nonequilibrium Dynamics

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Project Scope

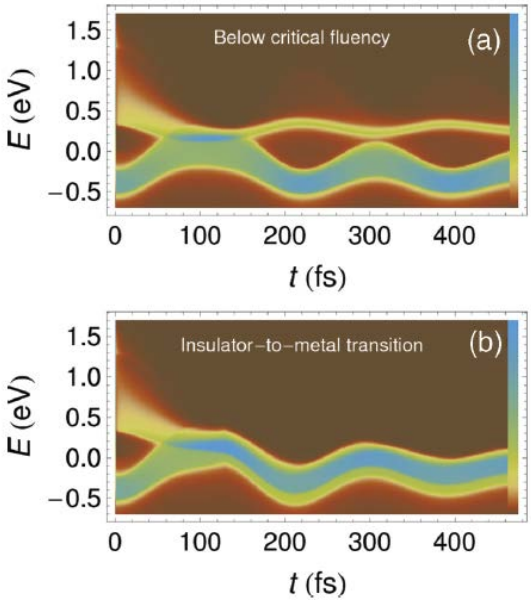
The focus of this grant is on the development of an understanding of new spectroscopies and the information they can provide on the materials under investigation. Recently, significant attention has been paid to optical pump/X-ray probe experiments as performed at X-ray free-electron lasers, such as LCLS. Intriguing problems in this direction are the observation of the melting of charge, orbital, and magnetic excitations on a femtosecond timescale. The interpretation of these experiments requires a deeper understanding of X-ray spectroscopy on nonequilibrium systems. These problems have been approached from different angles, for example, the effects of intersystem crossings on X-ray spectroscopy, phenomenological approaches to photo-induced metal-insulator transitions and the study of the nonequilibrium dynamics of strongly correlated systems coupled to phonons via exact diagonalization. In addition, the project focuses on related spectroscopies, such as (resonant) inelastic X-ray scattering and X-ray absorption with a strong recent emphasis on pressure effects and spin-orbit coupling dominated materials such as iridates.

Recent Progress

Ultrafast dynamics

The beginning of the 21st century has seen an exciting increase in our ability to control materials at the quantum level, which could have an enormous impact on a wide array of critical technologies. Many phenomena related to quantum control, such as catalysis, photochemistry, photosynthesis, photoinduced effects, and device physics, require an understanding of the nonequilibrium dynamics underlying these physical processes. In order to characterize the dynamics in quantum systems, scientists are developing a wide array of experimental tools that have as goal the measurement of the response of the structural and electronic properties of a material to an external stimulus, often an optical or terahertz pulse. Typical examples of photoinduced phenomena are insulator-to-metal transitions, magnetization and demagnetization, spin-crossover transitions, and melting of charge and orbital order. The typical timescale of the dynamics is of the order of picoseconds down to femtoseconds. The goal of the program is to lay a fundamental basis for the use of x-ray spectroscopy to study dynamics and nonequilibrium effects. This program theoretically investigates the use of time-dependent x-ray absorption and scattering in the study of dynamics and nonequilibrium phenomena, in particular, on strongly-correlated systems, such as transition-metal compounds.

This project focuses on the theoretical understanding of nonequilibrium systems and, in particular, how pulsed X-rays can aid in unraveling these complex phenomena. In earlier work, we studied the effects of intersystem crossings in spin crossover systems, such as the low- to high-spin transition in trivalent iron complexes and the singlet-to-triplet transition in ruthenium complexes [Phys. Rev. Lett. **104**, 067401 (2010), Phys. Rev B. **82**, 075124 (2010), Chem. Phys. **407**, 65 (2012)]. The recent work tries to obtain a deeper understanding how excitation by optical pulses can affect long-range order effects.



Total electron densities in photoexcited VO_2 as a function of energy and time. (a) The total electron density as a function of energy and time for a different photoinjected electron below (a) and above (b) the critical fluency needed for a insulator-to-metal transition.

For transition-metal oxides, well known for their often unusual properties, a wide variety of phenomena have been observed after excitation with a sub-100-fs pulse. Insulator-to-metal transitions have been observed in VO_2, V_2O_3, magnanites, etc. The physics underlying insulator-metal transitions is one of the most intriguing questions in materials science. Ultrafast science allows the study of the physical pathways between the different structural and electronic phases and the competition between the various interactions. A prototypical example is vanadium dioxide, a compound that has been studied extensively. The $3d^1$ compound VO_2 undergoes a transition from a high-temperature metallic rutile phase to a low-temperature insulating monoclinic phase. Using model calculations, an explanation is given for the ultrafast insulator-to-metal transition in VO_2 following photoexcitation. The photoinduced orbital imbalance induces a coherent motion of the V-V dimers affecting the electronic structure. After the closing of the gap, Boltzmann scattering equilibrates the electron densities. If the electron density exceeds a critical value, a phase transition occurs to the metallic state. The model explains several key features, such as a structural bottleneck, coherent structural motion combined with phase shifts in the oscillation, the absence of ultrafast metal-to-insulator transitions, and the need for a critical fluency.

The interplay between the electrons and the lattice in the nonequilibrium dynamics has also been approached using exact diagonalization of small many-body clusters. The competition of the Coulomb repulsion of electrons and effective attraction generated by the electron-phonon coupling is believed to be significant in understanding many condensed matter. The presence of both interactions causes a competition between spin-density-waves and charge density-waves. The equilibrium properties of these systems have attracted significant interest recently. We examined using exact diagonalization the one-dimensional Hubbard-Holstein model at half-filling where the electrons are coupled to bond phonons. We have considered both quantum phonons and classical phonons, the latter including damping. The phase diagram shows a separation of Mott and Peierls insulator phases and an intermediate metallic phase, in agreement with previous studies on the Hubbard-Holstein model. The time-domain study of charge and spin

order after a uniform particle-removal excitation from the Peierls insulator indicates the dynamics of a phase transition, the competition of different orders, and the possibility of the disappearance of long-range order. The dominant energy scale in this dynamics is demonstrated to be phonon frequency renormalized by electrons.

(Resonant) inelastic X-ray scattering

In the past decade, Resonant Inelastic X-ray Scattering (RIXS) has made remarkable progress as a spectroscopic technique. In collaboration with Ken Ahn from New Jersey Institute of Technology and experimentalist from Brookhaven and Argonne National Laboratories, a study was made of resonant inelastic x-ray scattering on single-layered charge, orbital and spin ordered manganites $La_{0.5}Sr_{1.5}MnO_4$. A formula for K-edge RIXS with completely localized 1s core hole was developed. A good agreement has been found between the theory and experiment, which demonstrates the potential of K-edge RIXS as a probe for the screening dynamics in materials. A better understanding on the periodicity of the K-edge spectrum in reciprocal space has been achieved for solids with a basis of multiple core-hole sites. The results were related to the screening dynamics in manganites.

Additional research was done on valence excitations measured with nonresonant inelastic x-ray. Relative few low-energy experiments have been done using this technique. The comparison between the measured angular distributions of scattering and those from theoretical indicates that, in terms of a hole picture, the lowest-energy dd excitation is the orbital transition $x^2-y^2 \rightarrow xy$. In addition, the transition $x^2-y^2 \rightarrow 3z^2-r^2$ has an energy higher than $x^2-y^2 \rightarrow yz/zx$, in contrast to a previous interpretation. The combined theoretical and experimental work demonstrates that IXS can provide important information for modeling of the electronic structure of d ions embedded in a complicated crystal field.

Future Plans

This year progress was made in the description of systems away from equilibrium. A basis was laid for understanding phase transitions in photoexcited systems. Initial work demonstrated the possibility of inducing a metal-insulator transition in a material by taking into account electron relaxation, lattice dynamics, and dynamical changes in the electronic structure. So far, the work has been restricted to a limited number of systems. We plan to extend the work by including orbital degrees of freedom, looking at different fillings, and considering multiple phonon modes. In addition, we intend to demonstrate the effects on the time-dependence of the X-ray absorption and resonant elastic and inelastic spectral line shapes.

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Computational studies of hydrogen interactions with materials

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Project Scope

We are conducting computational studies with the goal of developing new insights for hydrogen interactions with materials. For hydrogen storage materials our results provide direct insight into the processes of hydrogen uptake and release, and help in developing guidelines for designing storage media with improved storage capacity and kinetics. Our recent work has focused on borohydrides, LiH, layered compounds such as MoS_2 and MoO_3, and perovskite-structure oxides. In addition to the hydrogen storage aspect, we view our results from the perspective of other applications, including electrochromism and photochromism, as well as proton conduction.

Recent Progress

Role of native defects in the decomposition of $Li_4BN_3H_{10}$

Complex hydrides such as $Li_4BN_3H_{10}$ have been considered for hydrogen storage because of their high theoretical hydrogen density. $Li_4BN_3H_{10}$, which is synthesized from mixtures of $LiBH_4$ and $LiNH_2$, releases greater than 10 wt% hydrogen when heated. Still, its practical application is limited due to the cogeneration of ammonia (NH_3) and the irreversibility of the decomposition reaction. Metal additives such as Ni, Pd, and Pt can suppress the release of NH_3 and lower the dehydrogenation temperature. However, the decomposition process and the role of these additives is still poorly understood.

The decomposition and dehydrogenation of $Li_4BN_3H_{10}$, like those of other complex hydrides, involves the breaking and forming of chemical bonds and mass transport inside the material. We have performed first-principles density functional theory (DFT) calculations of point defects and defect complexes in $Li_4BN_3H_{10}$. An important finding is that Li interstitials and vacancies are highly mobile and can be created in the interior of the material via a Frenkel-pair mechanism (**Figure 1**). Based on our results we have proposed an atomistic mechanism for the material's decomposition that involves mass transport mediated by native defects.

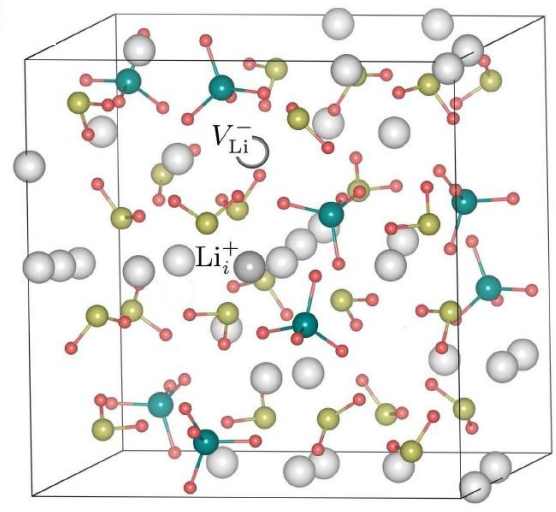

Figure 1: Ball-and-stick model, showing the structure of $Li_4BN_3H_{10}$, as well as a Li Frenkel defect pair, (Li_i^+ ,V_{Li}^-). Large (gray) spheres are Li, medium (blue) spheres B, small (yellow) spheres N, and smaller (red) spheres H. Vacancies are represented by empty spheres.

In light of this specific mechanism, we argue that the release of NH_3 is associated with the formation and migration of negatively charged hydrogen vacancies inside the material, and it can be manipulated by the incorporation of electrically active impurities. Our study provides explanations for a number of experimental observations and contains guidelines for improving the hydrogen storage performance. A paper describing these results has been submitted for publication [1].

Lithium hydride as a Li^+ and H^- ion provider

Lithium hydride (LiH) is in principle of interest for hydrogen storage because of its very large hydrogen content. However, with a decomposition temperature of 720 °C, it is not very useful for practical applications. The use of LiH in combination with other complex metal hydrides, on the other hand, has been shown to lower the dehydrogenation temperature and improve hydrogen kinetics. LiH is also present in lithium-ion battery electrodes that are based on conversion reactions. In both cases, the hydrogen storage or electrochemical performance ultimately depends on the reaction kinetics, which is controlled by mass transport mediated by native defects in the reactant materials. Other experimental observations include the production of H^- ions by heating LiH in vacuum, and loss of hydrogen from LiH surfaces, causing the formation of a lithium metal phase. LiH is also known as an ionic conductor.

We have applied first-principles techniques in a comprehensive study of native defects in LiH. We have found that the negatively charged lithium vacancy and the positively charged hydrogen vacancy are the dominant defects in LiH. The relatively low formation energy of these defects implies that LiH can easily provide Li^+ and/or H^- ions for reactions between LiH and another reactant. Ionic conduction in LiH occurs via a vacancy mechanism with an activation energy of about 1.30 eV. The results have been published in *Solid State Ionics* [2].

Van der Waals interactions in DFT calculations

Layered materials are intensively investigated because of the many potential device applications based on their two-dimensional (2D) character: while there are strong covalent bonds in the plane, the layers are weakly bound by van der Waals (vdW) interactions; a surface of these materials therefore does not exhibit dangling bonds. This is attractive for electronic devices, but other applications include lubrication, catalysis, and intercalation (e.g., for hydrogen storage or batteries).

Here we focus on MoS_2 and MoO_3. While both are molybdenum-based, they have very different structures and properties (**Figure 2**). Both MoS_2 and MoO_3 exhibit strong chemical bonds within each layer, but the layers themselves interact through vdW interactions. Providing a good description of the vdW interaction is essential for a reliable first-principles modeling of this class of materials—particularly if the goal is to study defect formation or

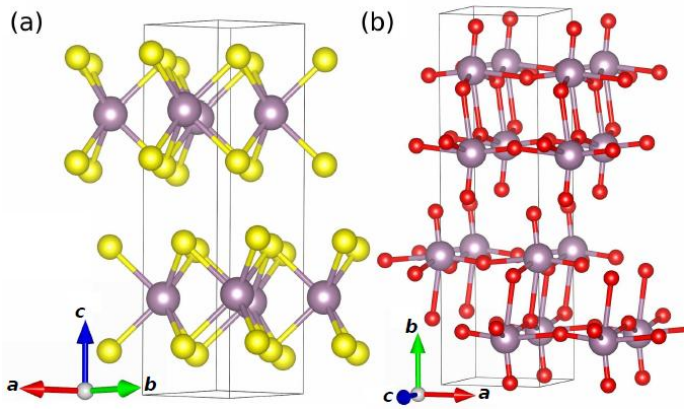

Figure 2: Ball-and-stick model of (a) MoS_2 and (b) MoO_3. Unit cell and unit vectors are indicated.

intercalation, processes which may strongly affect the interlayer distance and are in turn sensitive to this distance. However, vdW interactions are not included in regular density functional theory (DFT) calculations, leading to inaccuracies in the calculated interlayer distance.

A number of methods have been proposed to include vdW interactions within DFT. None of them is fully general or universal. We have compared the performance of several of these functionals specifically for describing the structural and electronic properties of MoS_2 and MoO_3, the materials at the focus of our study. Our conclusion is that the combination of the semiempirical Grimme D2 method with the hybrid functional Heyd-Scuseria-Ernzerhof (which we refer to as HSE06-D2) leads to a very good description of structural and electronic properties. The results were published in *J. Phys. Condens. Matter* [3].

We have applied this DFT+vdW methodology for calculating specific properties that are essential for applications but still unknown or controversial. For instance, we have used the HSE06-D2 functional to trace the evolution of the band structure as a function of the number of layers in MoS_2, starting from a monolayer, which has a direct gap, to the bulk material, which has an indirect gap. We can trace the position of the band extrema with respect to the vacuum level, finding that the valence-band (VB) maximum increases rapidly with the number of layers, while the conduction-band (CB) minimum remains almost constant on an absolute energy scale. These findings are analyzed in terms of the orbital composition of the valence- and conduction-band edges at the various high-symmetry points in the Brillouin zone (**Figure 3)**. Our results produce unexpected insights; e.g., we demonstrate that the common belief that the change in band gap of MoS_2 as a function of the number of layers is due to quantum confinement is unfounded [4].

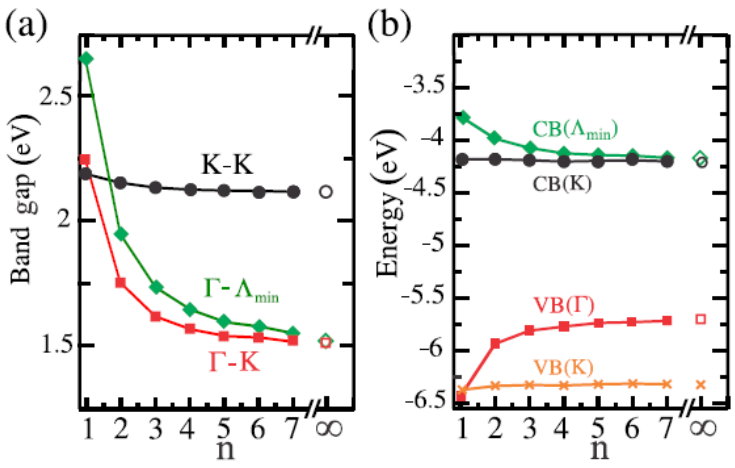

Figure 3: (a) Evolution of band gaps as a function of the number of layers (n) in MoS_2. Hollow symbols indicate the bulk band gaps. (b) Position of the band edge with respect to the vacuum level for the VBs and Γ, and the CBs at K and Λ_{min}.

Another example centers on elastic constants. These play an important role in describing lubrication properties and intercalation, but the reported experimental and theoretical values display significant inconsistencies. We have performed hybrid functional calculations of the elastic constants in bulk MoS_2 with vdW interactions explicitly included, using the HSE06-D2 functional. We have also investigated the effects of hydrostatic pressure, shedding light on experiments. We consider our values to be the most reliable that are currently available. A paper has been published in the *Journal of Phyical Chemistry C* [5].

Future Plans

Hydrogen intercalation and conductivity in MoO_3

We have started studies of hydrogen in MoO_3. Hydrogen is often unintentionally present in MoO_3, and it is important to study how it affects the material properties.

Hydrogen doping and electrochromism in oxides

The understanding we are building of MoO_3 establishes the foundation for investigating the effect of doping, defects, and impurities in various phases, with the goal of elucidating the mechanism(s) of electrochromism.

Hydrogen in perovskites

We are calculating properties of acceptors and hydrogen in zirconates and cerates to investigate effects of oxygen vacancies on proton mobility.

Recent publications

[1] "Role of native defects in the decomposition of $Li_4BN_3H_{10}$", K. Hoang A. Janotti, and C. G. Van de Walle, submitted to Phys. Chem. Chem. Phys.

[2] "LiH as a Li^+ and H^- ion provider", K. Hoang and C. G. Van de Walle, Solid State Ionics **253**, 53 (2013).

[3] "First-principles study of van der Waals interactions in MoS_2 and MoO_3", H. Peelaers and C.G. Van de Walle, J. Phys. Condens. Matter **26**, 305502 (2014).

[4] "Nature and evolution of the band-edge states in MoS_2: from monolayer to bulk", J. E. Padilha, H. Peelaers, A. Janotti, and C. G. Van de Walle, submitted to Phys. Rev. B Rapid Communications.

[5] "Elastic Constants and Pressure-Induced Effects in MoS_2", H. Peelaers and C.G. Van de Walle, J. Phys. Chem. C **118**, 12073 (2014).

SELF-HEALING NANOMATERIALS: MULTIMILLION-ATOM REACTIVE MOLECULAR DYNAMICS SIMULATIONS

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Project Scope

This project focuses on self-healing nanomaterials capable of sensing and repairing damage in harsh chemical environments and in high temperature/high pressure operating conditions. This will drastically increase the lifetime and lower the maintenance cost of material systems used in broad energy technologies. We perform petascale reactive molecular dynamics (RMD) and quantum molecular dynamics (QMD) simulations to study self-healing processes in anticorrosion coatings for metals and in ceramic nanocomposites.

Recent Progress

1. QMD Simulations of Self-Healing Ceramic Composites

A major focus of this project is self-healing of cracks during fracture in Al_2O_3 matrix embedded with SiC nanoparticles (n-SiC). For this purpose, it is essential to understand the structure and strength of SiC/Al_2O_3 interfaces. We have performed QMD simulations to study the effect of thermal annealing on the structure of SiC/Al_2O_3 interfaces (Fig. 1).[1] Thermal annealing produces strong interfaces consisting solely of cation-anion bonds and their consequence on interfacial structures. The 'purification' of the interfacial bonds (*i.e.* elimination of cation-cation and anion-anion bonds) is summarized in Fig. 2 using the Mulliken bond overlap population (BOP) analysis. The figure compares the total BOP summed over all interfacial bonds per surface unit cell between the relaxed initial and thermally annealed configurations at both C- and Si-terminated interfaces. Interfacial bond purification is reflected by the disappearance of BOP contributions arising from C-O (red) and Si-Al (green) bonds at the C- and Si-interfaces, respectively, after annealing. Also, the total BOP increases, signifying the strengthening of interfacial bonding, due to annealing at both interfaces. We also note that the Si-interface has a larger BOP density than the C-interface, showing that the Si-terminated 3C SiC (111) surface forms a stronger bonding with Al_2O_3 than the C-terminated surface. Namely, the BOP density per interfacial unit cell is 8.08 and 3.27 at the Si- and C-interfaces in the relaxed initial configuration, respectively, whereas they are 8.58 and 4.55 in the annealed configuration.

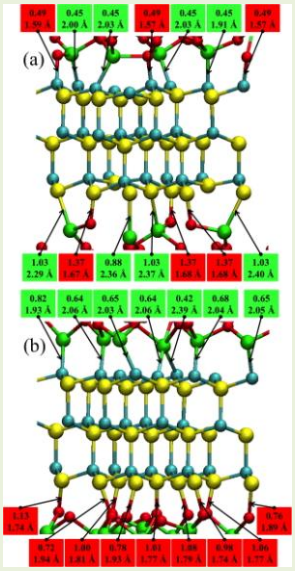

Fig. 1: Snapshots of the relaxed (a) and annealed (b) interfacial structures seen along the $\langle 12\ \bar{3}\ 0\rangle$ crystallographic direction of the SiC 3C crystal. The top and bottom numerals for each bond are the bond overlap population and bond length.

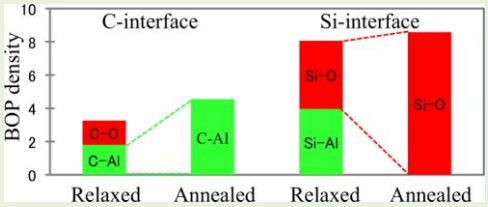

Fig. 2: Purification and strengthening of interfacial bonds by annealing. Total bond overlap populations (per interfacial unit cell) of the C- and Si-interfaces are shown for both relaxed and annealed configurations. Red and green colors denote bonds containing O and Al, respectively.

We also found that the interfacial bond strengthening is accompanied by the formation of an Al_2O_3 interphase with a thickness of 2-8 Å, which is distinct from the bulk phase.

The interphase structure is determined by the tradeoff between the energy lowering by strengthened interfacial bonding and the energy increase due to the associated interphase structural deformation.

2. QMD SIMULATIONS OF HIGH-RATE, HIGH-YIELD AND SCALABLE HYDROGEN-ON-DEMAND

We have enabled an unprecedented scale of QMD simulations through algorithmic innovations.[2, 3] Our new lean divide-and-conquer density functional theory (LDC-DFT) algorithm significantly reduces the prefactor of the $O(N)$ computational cost for an N-electron problem based on complexity and error analyses. In LDC-DFT, the total system is a union of overlapping domains, and global properties are expressed as linear combinations of domain properties. A global-local self-consistent-field (SCF) iteration calculates the global electron density and local electronic wave functions. LDC minimizes the $O(N)$ prefactor through a density-adaptive boundary condition at domain peripheries. In addition, a globally scalable and locally fast solver hybridizes a global real-space multigrid with local plane-wave bases.

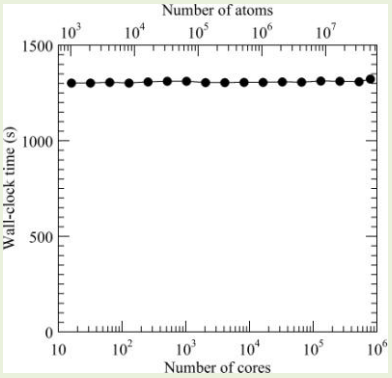

Fig. 3: Wall-clock time per QMD simulation step of the parallel LDC-DFT algorithm, with scaled workloads — 64P-atom SiC system on P cores (P = 16, ..., 786,432) of Blue Gene/Q.

The resulting weak-scaling parallel efficiency was 0.984 on 786,432 IBM Blue Gene/Q cores for a 50.3 million-atom (or 39.8 trillion degrees-of-freedom) system (Fig. 3). The time-to-solution was 60-times less than the previous state-of-the-art, owing to enhanced strong scaling by hierarchical band-space-domain decomposition and high floating-point performance (50.5% of the peak).

The LDC-DFT algorithm has allowed us to perform production QMD simulation involving 16,661 atoms for 21,140 time steps (or 129,208 SCF iterations), which revealed a novel nanostructural design for on-demand hydrogen production from water, advancing renewable energy technologies.[4]

Hydrogen production from water using Al particles could provide a renewable energy cycle. However, its practical application is hampered by the low reaction rate and poor yield. Using large QMD simulations on 786,432 Blue Gene/Q cores, we have shown that orders-of-magnitude faster reactions with higher yields can be achieved by alloying Al particles with Li (Fig. 4).[4] The 16,661-atom simulation involved $Li_{441}Al_{441}$ in water. To study the size effect, we have also simulated smaller particles, $Li_{135}Al_{135}$ and $Li_{30}Al_{30}$, in water, involving a total of 4,836 and 606 atoms, respectively. We have validated the LDC-DFT algorithm against a conventional $O(N^3)$ DFT code for the 606-atom system.

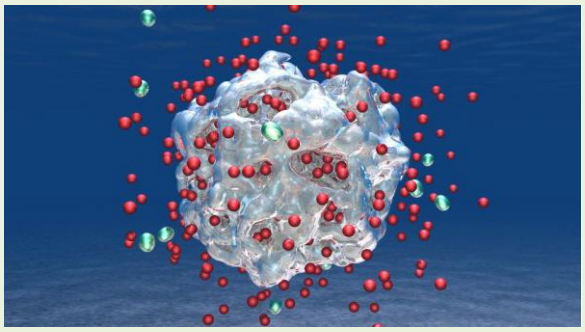

Fig. 4: H_2 production from water using a $Li_{441}Al_{441}$ particle in 16,661-atom QMD simulation. The valence electron density (silver isosurface) is centered around Al atoms, whereas some of the Li atoms (red sphere) are dissolved into water. Green ellipsoids represent the electron charge density around produced H_2 molecules. Water molecules are not shown for clarity.

Through detailed analyses of the simulation data, a key nanostructural design has been identified as the abundance of neighboring Lewis acid (Li)-base (Al) pairs in the Zintl crystal, where water-dissociation and hydrogen-production require very small activation energies. Among various H_2 production reactions is

$$Li\text{-}OH_2 + Al\text{-}H \rightarrow Li\text{-}OH + Al + H_2.$$

Figure 5(a) shows snapshots of one of these reactions. Figure 5(b) shows the time evolution of Mulliken BOPs for key atomic pairs involved in this reaction. We see the decrease of $O_{H2\text{-}Al2}$ around 0.12 ps, indicating the breakage of the Al-H bond. This is accompanied by the increase of $O_{H2\text{-}H3}$ due to the formation of the H_2 product. To estimate the energy barrier for the H_2 production reaction, we performed a nudged elastic band (NEB) calculation for the reaction represented in a simpler system shown in Fig. 5(c) without surrounding water molecules. Here, the left, center and right images are the reactant, saddle-point and product states, respectively. Figure 5(d) shows the calculated energy profile along the reaction coordinate, which is the distance between the two H atoms that form the H_2 product. The calculated activation barrier (0.04 eV) in Fig. 5(d) is much lower than that (0.1 eV) for the H_2-production reaction on Al_n surface. The stronger Lewis acid (Li)-base (Al) pairs may explain the faster H_2 production from water using Li_nAl_n instead of Al_n. This mechanism explains the experimentally observed alloy composition-dependence of the reaction speed for H_2 production from water using Li_xAl_{1-x} alloy particles. Namely, the observed reaction speed is an increasing function of x up to x = 0.5. This is consistent with the increased number of Lewis acid-base pairs as a function of x in the range [0, 0.5].

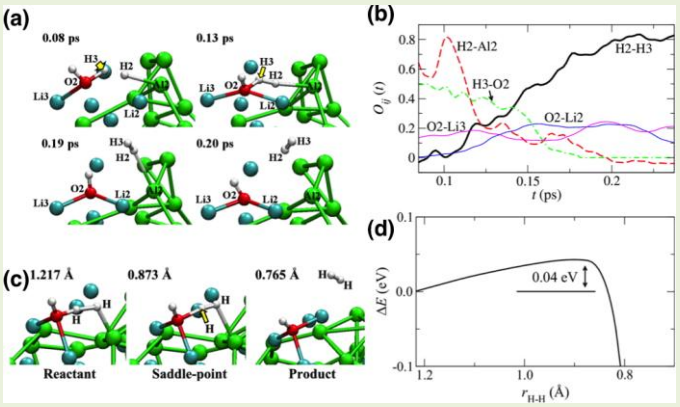

Fig. 5: Atomistic mechanisms of rapid H_2 production on a LiAl-particle surface. (a) H_2 production at a Lewis acid (labeled Li2) and base (Al2) pair. (b) Time evolution of bond-overlap populations for key atom pairs involved in the reaction. (c) Initial (or reactant), saddle-point and final (or product) states for a H_2 production reaction. The numerals denote the distance between the two H atoms that form the H_2 product. (d) Energy as a function of the reaction coordinate (H-H distance) of the H_2 production reaction.

These reactions are facilitated by wide charge pathways across Al atoms that collectively act as a "superanion". Furthermore, dissolution of Li atoms into water produces a corrosive basic solution that effectively inhibits the formation of a reaction-stopping oxide layer on the particle surface, thereby increasing the yield significantly. We have also found a surprising autocatalytic behavior of bridging oxygen atoms that connect Li and Al. Namely, Li-O-Al is not merely an inert reaction product but instead plays an unexpectedly active role in the oxidation process by assisting the breakage of O-H and formation of Al-O bonds.

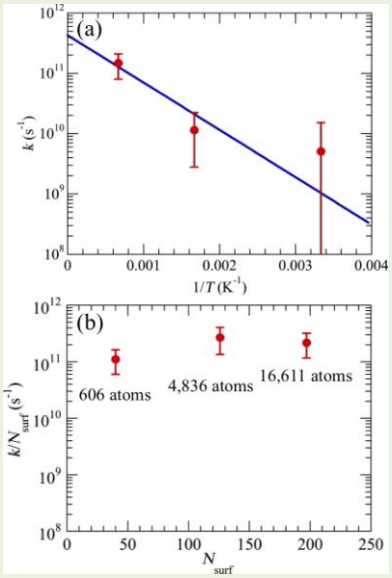

Fig. 6: Rapid and scalable hydrogen-on-demand. (a) H_2 production rate as a function of inverse temperature (red circles with error bars), where the blue line is the best fit to the Arrhenius equation. (b) Hydrogen production rate normalized by the number of surface atoms, N_{surf}, as a function of N_{surf}.

Figure 6(a) shows the calculated hydrogen production rate as a function of inverse temperature. By the Arrhenius fit, the activation barrier was estimated to be 0.068 eV. The corresponding hydrogen production rate is 1.04×10^9 s^{-1} at 300 K per LiAl pair, which is orders-of-magnitude higher than that for pure Al [F. Shimojo, S. Ohmura, R. K. Kalia, A. Nakano and P. Vashishta, *Phys Rev Lett* **104** (12), 126102 (2010)].

A major problem of H_2 production from water using Al particles is the lack of scalability. Namely, the high reactivity of Al nanoparticles cannot be sustained for larger particles that are commercially mass-produced. To investigate the scalability of the high reactivity

of Li_nAl_n with water, we have compared the $Li_{30}Al_{30}$, $Li_{135}Al_{135}$ and $Li_{441}Al_{441}$ systems. Figure 6(b) plots the H_2 production rate normalized by the number of surface atoms, N_{surf}, as a function of N_{surf} for the three systems. The normalized H_2 production rate is constant as a function of N_{surf} within error bars. The size effect is thus negligible, indicating that the Li_nAl_n surface is equally reactive regardless of the surface curvature. Thus, the nanostructural design proposed here is expected to scale up to industrially relevant particle sizes.

Though experimental validation of the hydrogen production rate is beyond the reach of current experimental technologies, our calculation does explain recent experimental observations:[4] (1) Hydrogen-production rate peaks at the alloy composition of equal Li and Al contents; and (2) hydrogen production is accompanied by increased pH of surrounding water.

Future Plans: RMD Simulations of Self-Healing Ceramic Composites

We are currently performing RMD simulations to study the self-healing of cracks during fracture in Al_2O_3 matrix embedded with n-SiC. Figure 7(a) shows a preliminary RMD simulation of fracture of a notched Al_2O_3/n-SiC composite under uniaxial tension. Near the cracked region, SiC gets oxidized in the high-temperature oxygen environment, resulting in the formation of amorphous silica (SiO_2); see Fig. 7(b). Silica has a much lower melting temperature than those of SiC and Al_2O_3, and thus it flows into the damage zone, heals the crack, and restores the thermomechanical behavior of the composites (Fig. 7(c)).

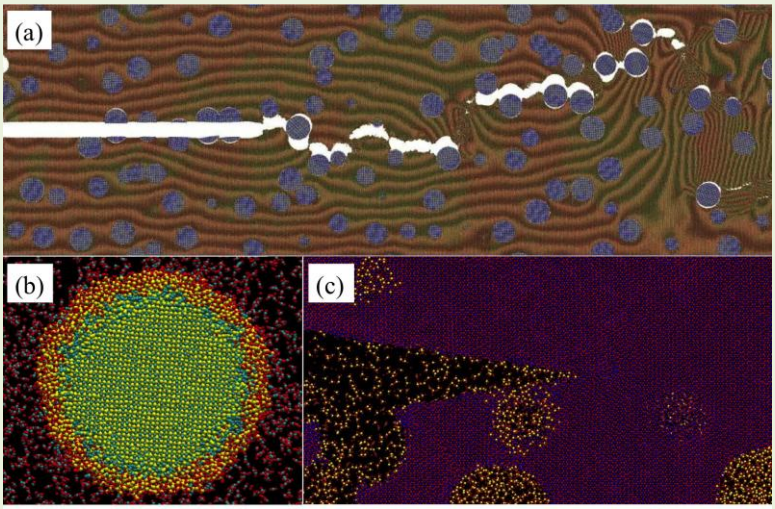

Fig. 7: (a) Fractured Al_2O_3 matrix embedded with SiC nanoparticles (n-SiC). (b) Oxidation of n-SiC. (c) Molten silica filling a crack.

We will investigate atomistic mechanisms underlying:

- Oxidation of n-SiC and the structure of its interfaces with Al_2O_3.
- Residual stresses at interfaces between oxidized n-SiC and Al_2O_3.
- Self-healing of cracks by flow of molten silica from n-SiC.
- Fracture toughness, oxidation and creep resistances of the nanocomposites.

Publications (2013-2014)

1. K. Shimamura, F. Shimojo, R. K. Kalia, A. Nakano and P. Vashishta, *Physical Review Letters* **111** (6), 066103 (2013).
2. F. Shimojo, R. K. Kalia, M. Kunaseth, A. Nakano, K. Nomura, S. Ohmura, K. Shimamura and P. Vashishta, *Journal of Chemical Physics (Special Issue on "Advances in Density Functional Theory")* **140** (18), 18A529 (2014).
3. K. Nomura, R. K. Kalia, A. Nakano, P. Vashishta, K. Shimamura, F. Shimojo, M. Kunaseth, P. C. Messina and N. A. Romero, *Proceedings of IEEE/ACM Supercomputing, SC14* (2014).
4. K. Shimamura, F. Shimojo, R. K. Kalia, A. Nakano, K. Nomura and P. Vashishta, *Nano Letters*, published online, DOI = http://dx.doi.org/10.1021/nl501612v (2014).

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

GRANTS DE-FG02-05ER46203, DE-FG02-05ER46204

Principal Investigators:
Giovanni Vignale, Department of Physics, University of Missouri, Columbia
Massimiliano Di Ventra, Department of Physics, University of California, San Diego

Project scope

The focus of this research program is on developing 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. Part of this work is done in collaboration with Max Di Ventra at UCSD. In the following I concentrate on the work we have recently done on extending the time-dependent density functional theory to thermoelectric transport phenomena, by introducing the (time-dependent) energy density as a new basic variable, and the Luttinger "gravitational" field as its conjugate driving field. We have shown that this approach generalizes the standard Landauer-Büttiker formalism and offers a relatively simple way to include electron-electron interaction effects. We have also completed a many-body theoretical calculation of the thermal conductivity of an interacting electron liquid in graphene, showing the existence of a simple relation between the thermal transport time and the quasiparticle lifetime, and a strong violation of the conventional Wiedemann-Franz law.

Recent progress

1. Density Functional Theory of Thermoelectric Phenomena

The problem of calculating the thermal and electrical transport properties of nanoscale conductors has recently attracted great interest in the context of growing efforts to achieve efficient conversion of heat into electricity, and vice-versa. On the theoretical side, the field is riddled with conceptual difficulties that can be traced back to the very foundations of statistical physics. Concepts like temperature, heat current, and thermal conductivity were originally defined at the macroscopic level, or in quasi-equilibrium situations in which they vary slowly in space and time. One of the main theoretical questions is how to convert the temperature, originally defined as a statistical parameter governing the equilibrium of energy exchanges between different parts of a macroscopic system, into a dynamical field coupling to mechanical degrees of freedom, which can be driven strongly out of equilibrium. The recent development of scanning thermal microscopy, allowing for measurements of a local effective temperature on the

atomic scale, provides additional strong motivation for seeking a sharp answer to the above questions. Many years ago Luttinger took an important step in this direction by proposing that the thermoelectric transport properties of a macroscopic electron liquid could be calculated by subjecting the system to a space- and time-varying field $\psi(\mathbf{r},t)$. The ψ field was to be linearly coupled to the energy density, for which Luttinger chose one of several possible definitions – all equivalent in the long-wavelength limit. Luttinger's idea was that the dynamical response of the system to the varying ψ field would be equivalent to the response to a temperature gradient in situations in which the latter is slowly varying, but would extend the concept of thermal response to situations in which the traditional notion of temperature is no longer meaningful. Noting the similarity to Einstein's theory of gravity – a field coupling to the energy density – Luttinger dubbed his ψ field a "gravitational field" – in a purely formal sense of course. The gradient of this field drives the thermal current, just as the gradient of the electric potential drives the electric current.

In a recent paper **[1]** we have developed Luttinger's idea into a full-fledged time-dependent density functional theory of local temperature and associated energy density variations, which should be useful for the ab-initio study of thermoelectric phenomena in electronic systems. We have identified the excess-energy density – i.e., the difference between the actual energy density and the energy that would be in equilibrium with the instantaneous particle density – as a second basic variable of the theory, in addition to the particle density. Both the particle density and the excess energy density are reproduced – exactly, in principle – in an effective non-interacting Kohn-Sham system. The time evolution of this effective system is driven by a new kind of Kohn-Sham equation, featuring a time-dependent and spatially varying mass which represents local temperature variations. This is precisely how the Luttinger ψ–field enters the Schrödinger equation of a noninteracting system. We have also examined the two basic approximation strategies for the effective potentials that enter the Kohn-Sham equation. In the adiabatic approximation the interaction contribution to the Kohn-Sham effective potential is related to the entropy, the latter viewed as a functional of the particle and energy density of the homogeneous electron gas. In the first step beyond the adiabatic approximation – the first step that includes dissipative effects – the time derivatives of the density and energy density make their appearance as arguments of the potential functional. These quantities are related to the longitudinal parts of the particle and energy currents. In a homogeneous electron gas, the currents are related to their conjugate fields by a well known matrix of thermoelectric transport coefficients. Based on this observation, we have been able to show that the leading dissipative contributions to the Kohn-Sham potential can be expressed in terms of the particle and thermal currents and of the thermoelectric linear transport coefficients of the homogeneous electron gas.

2. Luttinger-field approach to thermoelectric transport in nanoscale conductors

In the half century elapsed since the publication of the original paper, Luttinger's idea has found several applications in the calculation of the linear response of macroscopic systems. However, we found no reported applications of these ideas to nanoscale conductors. One of the most successful models of transport at the nanoscale, the Landauer-Büttiker formalism (LB) assumes the nanoscale system to be connected, via ideal leads, to several reservoirs independently in equilibrium at different chemical

potentials and temperatures. The electric and thermal currents are expressed in terms of the quantum mechanical transmission probabilities from each lead into the others, and the equilibrium distribution functions of the reservoirs. This approach leaves no room for dynamical effects arising from time-dependent fluctuations of the effective field in which the electrons propagate.

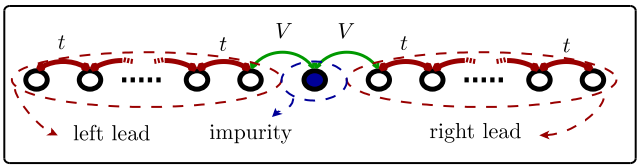

Fig. 1: Sketch of the model studied in Ref. [2]

In our recent paper **[2]** we have worked out a first application of Luttinger's ψ–field idea to the calculation of thermal transport through a nanoscale junction. This means that we completely replace the different temperatures in the reservoirs by ψ fields. The conventional statistical temperature remains constant throughout the system. To calculate the currents we closely follow the formulation of the non-equilibrium Green's function theory introduced by Cini et al., in which the leads and the nanoscale system are initially in equilibrium with a unique reservoir at a single chemical potential and temperature. At the initial time different electric potentials and Luttinger fields are applied to the leads. The resulting electric and thermal currents are calculated in the long-time limit. Our main result is that, for a non-interacting system, in the linear response regime, the current calculated in this manner coincides with the current calculated in the LB approach. Furthermore we demonstrate that the LB result can be fully recovered in the non-linear regime, if the TM fields are applied during the initial preparation of the system, and turned off at the initial time. This is good news, which builds confidence in the general applicability of Luttinger's approach to nanoscale conductors. Many-body effects were not included in these calculations, but we expect to be able to handle them through the density-functional formalism of Ref. [1]. In practice, we have done our calculation for the simple model described in Fig. 1, describing a single impurity site coupled to semi-infinite leads, and we have carefully compared the results of the ψ–field approach with those of the conventional LB approach, in both the linear and nonlinear regimes. Fig. 2 presents representative results for the thermal currents that flow in response to applied voltages and temperature gradients.

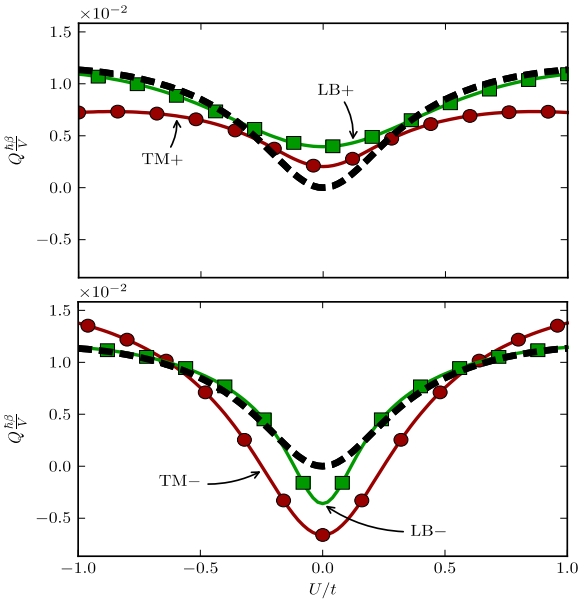

Fig. 2 Comparison of the steady-state heat current Q in the ψ–field approach and in the LB approach. The currents are plotted against the potential bias U in units of the hopping t. The upper panel depicts the currents when the temperature in the left lead is raised to twice its initial value and the lower panel shows the heat current when the temperature in the left lead is reduced to half its initial value. The dashed, black curve is the heat current at zero relative temperature variation. The circles (red curve, labeled TM) correspond to the current in the ψ–field approach and the squares (green curve, labeled LB) to the LB approach.

Planned activities

An obvious next step will be the application of the Luttinger field theory to interacting models, for example the model of Fig. 1, with electron-electron repulsion on the impurity site. This model can be studied by many-body theoretical methods and also by the newly developed density functional method of [1]. The results of the different approaches will be compared. In this context, we will also begin to work toward the construction of approximate effective potentials in the adiabatic approximation and in the leading correction to the adiabatic approximation - along the lines discussed in [1]. Our recent study of the thermal conductivity of the electron gas in graphene [3] equips us with the tools for carrying out the necessary calculations of thermal transport coefficients in the uniform electron gas. Lastly, we will investigate the reason for the differences between the ψ–field approach and the LB approach in the nonlinear regime. The issue at stake here is whether the ψ–field is just a formal device to do linear response, or carries a deeper physical information, at least in certain experimentally realizable situations.

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QUANTUM MESOSCOPIC MATERIALS: THE PHYSICS OF QUANTUM COHERENT STATES

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Project Scope

The research in this program involves theoretical investigations of phenomena of quantum coherence and entanglement on the mesoscale in low-dimensional disordered systems such as disordered superconducting films and wires, nanopatterned structures, Josephson junction and proximity arrays, and hybrid structures. The main lines of research are development of predictive theory capable to resolve the fundamentally important and difficult questions of formation of coherent states in mesoscopic systems and emergence of decoherence in closed quantum systems using exemplary context of superconductor-insulator transition and, at the same time, create a platform for design and technological applications of quantum coherent materials. Our current research focus is on understanding the superconductor-insulator transition (SIT) as transition between two quantum coherent states with the emphasis on the role of Coulomb interactions and disorder; on identifying the role of quantum entanglement of electrons as one of the fundamental mechanisms of preserving quantum coherence and formation of irreversibility and glassiness on mesoscale; and on quantitative description of quantum coherent transport in the vicinity of SIT in terms of duality between vortices and Cooper pairs in disordered films, quantum wires and hybrid structures.

Recent Progress

Divergence of activation energy with the sample size

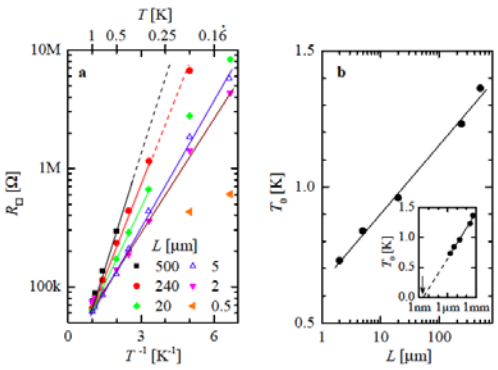

Fig. 1. Activated resistance and logarithmic dependence of the activation energy on the TiN film lateral size.

One of the definitive components of superinsulation, the phase-coherent state at the insulating side of SIT, is a 2D logarithmic charge interactions in the disordered film. This should result, in its turn, in logarithmic divergence of the characteristic energy controlling tunneling conductance. The low-temperature measurements and data analysis carried out in collaboration with the Regensburg University yielded logarithmic scaling of activation energy with the sample size as shown in Fig. 1. We found that the characteristic scale normalizing the logarithmic dependence coincides with the film thickness. A crosscheck based on our theory of fluctuation conductivity confirmed that the characteristic energy scale from transport measurements coincides with the independently obtained Berezinskii-Kosterlitz-Thouless (BKT) transition temperature. We found a transition from Cooper-pair insulator into a quantum metal in high magnetic field

by saturation of the resistance to a quantum value at lowest temperatures. These results provided an experimental ground for our planned numerical study of the role of Coulomb interactions in conductivity of insulators and of formation of the bad metal, see below.

Quantum fluctuation contribution to conductivity

We derived full fluctuation conductivity in disordered 2D superconductors and developed a high-precision procedure for determining T_c in thin superconducting films based on the complete accounting of quantum contributions, enabling us to infer microscopic and macroscopic material parameters like electron decoherence time, superconducting critical temperature T_c, and upper critical field H_{c2} with unprecedented precision and to describe non-monotonic temperature behavior of the film resistance. We showed that superconducting fluctuations give rise to an appreciable decrease in the resistance even at temperatures well exceeding the superconducting transition temperature, T_c. This approach was used to determine BKT transition temperature of TiN films above.

Vortex and phase slips dynamics in nanostructures

We made a major breakthrough towards resolving vortex pinning problem that impedes technological applications of superconductivity. The strategy is that instead the designing sophisticated combinations of pinning sites we change the nature of the vortex state itself via the clever patterning of a superconductor. We showed that in a narrow wire or in a film carved into an array of holes so that only few vortices could fit into the inter-hole areas, the high magnetic fields heal superconductivity instead of destroying it since vortices get tightly squeezed and form immobile clusters. As a result the resistance drops over 6–7 orders of magnitude at applied field of the order of 1 T see Fig. 2. This work, published in Nature Communications, is highlighted at the DOE Office of Science website and in the MSE Research Accomplishments 2013 report.

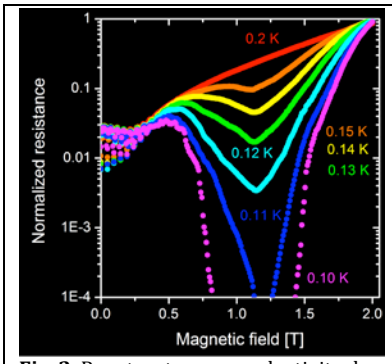

Fig. 2. Reentrant superconductivity due to formation of vortex clusters in nanoperforated film.

Future Research Plans

Our focus lines intended to answer the question of how quantum coherent states form and persist in low-dimensional disordered mesoscopic systems are summarized as follows:

- **2D Coulomb interactions and tunneling conductance of a 2D insulator –**

We will model an insulating state that forms at the insulating side of SIT by random array of capacitors and carry out Monte Carlo procedure in order to study in depth its density of states and activated hopping conductivity. Our preliminary results indeed show logarithmic scaling of the activation energy with the sample size, see Fig. 3.

- **Formation of a bad metal at SIT –**

We will study formation of quantum metallic state (bad metal) that possesses high temperature-independent resistance comparable to that of insulators and does not have neither superconducting nor insulating gap and referred. To this end we will explore 1D and 2D arrays of small superconducting granules coupled by weak links. Adequate approaches are Keldysh technique, time-dependent Ginzburg-Landau equations, different kinds of Monte-Carlo methods, and diagonalization of the reduced Hamiltonian in a Hilbert space with subsequent statistical analysis of the level spectrum.

- **Investigation of dissipative modes at SIT –**

A conventional second order phase transition is accompanied by low energy soft modes. This, however, may not be so for SIT where the long range Coulomb interaction prevents long wave oscillations of the Cooper pairs density. Furthermore, low energy modes in a disordered system do not imply dissipation if these modes are localized. The question we will address is whether the disorder-driven SIT is accompanied by formation of the low energy *delocalized* modes at the insulating side. To answer it we will perform numerical study of energy spectra of model quantum systems: in a localized phase energy levels obey Poisson distribution, while the delocalized modes imply level repulsion hence Wigner-Dyson distribution.

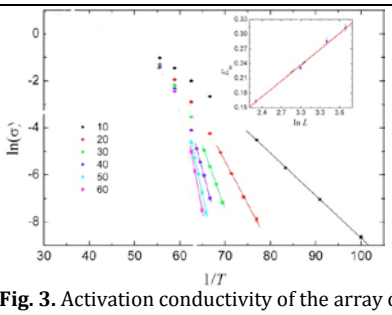

Fig. 3. Activation conductivity of the array of capacitors for different system sizes. Inset: activation energy governing conductivity as function of log *L*.

- **Vortex Mott insulator and dynamic vortex Mott transition –**

Our preliminary results revealed remarkable realization of the vortex-Cooper pair duality: the vortex Mott insulator that forms in the proximity arrays at commensurate magnetic fields and its critical dynamic behavior driven by applied current rather than by temperature near the Mott critical point. We will outline a straightforward quantum mechanical picture to describe tunneling dynamics both in the deep Mott insulating state and in the vicinity of the critical point, to explain the observed scaling behavior. The experimental discovery of the new tunable Mott state holds high potential for constructing unifying picture of duality between the equilibrium-nonequilibrium phase transitions and between quantum and classical approaches in the physics of many-body systems.

- **Critical superconductivity –**

Bogomolnyi critical point (BCP) that originally appeared in Abelian-Higgs model, which is an adaptation of the Ginzburg-Landau theory to particle physics, marks the boundary between ideally diamagnetic bulk type-I and type-II superconductors hosting vortices. At Bogomolny critical point the vortex state is infinitely degenerate with respect to arbitrary vortex configurations. We plan to investigate in depth the situations in finite weak type I- and multi-band superconductors where BCP broadens into a finite domain and the notion of new kind of superconductivity, *critical superconductivity*, can be introduced.

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Accelerated Molecular Dynamics Methods

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BES Program Summary, July 2014

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, 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 systems, on applying them to materials problems of relevance to DOE/BES.

Recent Progress

Accelerated simulations of diffusive deposition: AMD methods are designed to accelerate systems that evolve through rare events, which, in practice, often means systems that vibrate for long periods of time in the same configuration before rapidly making a transition to a new state, where they would again be trapped. In contrast, systems that evolve diffusively, i.e., through a continuous but slow motion, were thought not to be amenable to AMD, leaving an important class of systems out of reach. Using

the recently developed formal understanding of the Parallel Replica Dynamics method, we showed that certain diffusive problems can in fact be accelerated if reformulated adequately. As proof of concept, we demonstrated an accelerated simulation of the growth of a silver crystal through deposition of atoms from a solution. This was made possible by the key insight that, while diffusive motion itself does not proceed through rare events, absorption of solutes on the surface is a proper rare event in quasi-equilibrium between the surface and solution. Using an efficient multiscale representation, our simulation achieved hundred-fold acceleration over standard methods. This advance demonstrates that the range of validity of AMD methods is much wider than previously thought.

Scalable rate calculations: In the study of the long time evolution of materials, it is often crucial to be able to predict the rate at which a certain transition will occur. For example, one might discover an important process with an AMD simulation and ask how it would vary with stress or strain. Rate theories, such as transition state theory (TST), are in principle ideally suited to answer these questions. However, these methods can be very expensive, especially for large systems. For example, even the simplest approximation of TST --- harmonic TST --- incurs a computational cost that scales with the cube of the number of atoms. While this might be acceptable for very localized transition, it is prohibitive for delocalized transitions, such as processes that couple to a long-range strain field. To address this challenge, we developed a new approach based on an iterative moment expansion of the vibrational density of states. The cost of the method scales linearly with the number of atoms, it is embarrassingly parallel, and can provide rough approximations very cheaply. It allows for routine calculations on systems containing hundreds of thousands of atoms, an heroic feat using standard methods.

The performance of ideal hyperdynamics: Hyperdynamics is an elegant and powerful method to accelerate activated dynamics through the modification of the potential energy landscape of the system. Indeed, if one can design a bias potential that is strictly zero at the dividing surface between states, hyperdynamics provides a uniform acceleration of all the possible transitions. The downside however is that one needs to be able to design a valid bias potential without knowing about the dividing surface ahead of time. To motivate and guide the development of better bias potentials, it is useful to ask about the limiting performance of this approach. We answered this question by constructing an ideal bias based on the *a priori* knowledge of all the pathways out of a given state. Using this bias, we demonstrated that one could very accurately escape out of any state in a matter of about ten picoseconds, a time that is very close to the ultimate acceleration limit set by the need to locally equilibrate within a state on transition timescales. While this bias is not practical for AMD simulations, it demonstrates the huge potential of hyperdynamics and motivates further development of high-performance bias potentials. This same functional form can also be used to very efficiently and accurately compute the transition rate of a specific process using direct simulations.

Applications of AMD methods: We have applied the AMD methods to a wide range of problems of interest to DOE. For example, we investigated the influence of point defects on grain boundary mobility in tungsten and its possible role in radiation-damage healing under condition typical of fusion reactor operation. In the same vein, we are investigating the effect of the incorporation of He in tungsten for fusion applications by using Parallel

Replica Dynamics at the petascale. We also used AMD methods to study friction at nanoscale contacts, bridging some of the timescale gap between simulations and experiments.

Other developments: We recently proposed improvements on several other long timescale methods. For example, we developed a local version of hyperdynamics that overcomes the poor scalability of hyperdynamics in terms of system size. The new method enable massively parallel AMD simulations on systems containing millions of atoms, instead of thousands using the conventional method. We also proposed a computationally efficient way to account for the effect of strain on transition rates in Kinetic Monte Carlo simulations, which enables efficient simulations even in cases where long-range elastic couplings are present, e.g., to account for the elastic interaction of point defects with dislocations, a mechanism of importance to the radiation-induced growth of materials.

Future Plans

Our future work will be articulated around three pillars: extending the range of applicability of the AMD method, developing variants of the methods that can exploit extreme scale computers, and applying the methods to problems of relevance to DOE. One avenue for development is the extension of AMD method from classical to quantum dynamics. Indeed, even when using *ab initio* methods to compute the interatomic forces, the trajectories of the nuclei themselves are still classical. In order to account for quantum effects such as zero-point energy or tunneling, we will extend Parallel Replica Dynamics using ring-polymer molecular dynamics (RPMD). While very powerful, RPMD suffers from an even more severe timescale problem as trajectories are generated not on a single system, but on a ring polymer where each bead is a complete replica of the system. Coupling RPMD with Parallel Replica Dynamics will allow for the direct long-timescale simulation of systems containing light atoms at low-temperatures, where quantum effects can dramatically affect not only the transition rates but also the very nature of the transition pathways. We will also further pursue the development of a local variant of hyperdynamics where the target acceleration adjusts itself on the fly in order to insure the fidelity of the dynamics.

Based on our recent work as part of a LANL/LDRD computational co-design project, we will explore the concept of speculation as a tool to improve the scalability of the temperature accelerated dynamics method. The key idea of this approach is that one can speculatively begin work on a trajectory out of a putative final state even before the transition to that state is fully certified as legitimate. This way, work can proceed in parallel in many states at the time, thereby greatly improving performance and scalability of the method, turning an essentially sequential method into a massively parallel one. If a prediction turns out to be wrong, the speculative branch is terminated and the generated work stored for future reuse. We will develop management strategies that optimize the expected value of the speculative simulations and optimally manage the available computing resources.

Finally, we will apply the AMD methods to a range of systems of interest to DOE/BES. We will pursue our investigation of the behavior of He atoms in the tungsten wall of a

fusion reactor. Using Parallel Replica Dynamics, we will investigate He bubbles at different microstructural features and elucidate the processes by which they grow and burst, and characterizing the damage it inflicts on the material. By using petascale simulations, we expect to be able to closely match the experimentally relevant conditions. We will also closely interact with BES programs at LANL, using AMD methods to study the transport properties of complex oxide ceramics, the interaction of dislocations with grain boundaries and interfaces in metals and ceramics, and the nucleation and propagation of twins in hcp metals.

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Development of Methods for Crystal Structure Prediction and Material Discovery

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Project Scope

The scope of this project is to develop efficient computational algorithms and methods for crystal structure prediction that can help experimental efforts in new materials discovery. The urgent demand for new energy technologies has greatly exceeded the capabilities of today's materials and chemical processes. Accurate and fast theoretical structure/property determinations will complement the traditional experimental efforts in material design and accelerating the pace of technological advances. At present, computers and algorithms are at the tipping point where large parallel computers can effectively serve as the screening phase for finding material compositions and structures with promising "sweet spots" for property optimization and guide discoveries, especially when coupled with a strong synthesis effort to work in partnership to supply immediate feedback. Our method development is closely linked with the experimental synthesis and characterization efforts in EERE-VT project *"Development of Improved Powder for Bonded Permanent Magnets"* and BES project *"Structure and Dynamics of Condensed Systems"* at Ames Laboratory.

Recent Progress

We have developed a fast and efficient adaptive genetic algorithm (AGA) for crystal structure prediction [1]. Our method performs genetic algorithm (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. Therefore, the adaptive GA method can combine 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.

Unraveling the structural mystery of Zr_2Co_{11} polymorphs

It has been shown by experiments that Zr-Co alloys could be promising materials for high performance permanent magnet without rare-earth due to their high magnetic anisotropy. However, the crystal structure of these alloys remains elusive even after 30 years of experimental studies. Different experiments suggest different crystal structures and the number of atoms in the unit cell proposed by experiment is also controversial, ranging from 16 to about 120 atoms. The uncertainty in the crystal structure and exact stoichiometry of the high-performance magnetic phase greatly hinders further investigation and optimization of the material for high quality permanent magnets.

Using the AGA method developed from this project and computer time allocation on NERSC through the DOE-BES NISE program, we performed a systematic search to determine the low-energy atomistic structures for Zr_2Co_{11-x} alloys (with x=0.0, 0.5, 0.6, 0.8 respectively) with the

number of atoms in the unit cell ranging from 16 to 150. We predicted the lowest-energy structures for Zr_2Co_{11-x} up to 150 atoms per unit cell [2]. We show that the complex atomic structures of the orthorhombic, rhombohedral, and hexagonal polymorphs of Zr_2Co_{11} intermetallic compound can be resolved from our computational structure prediction using the novel adaptive genetic algorithm. As one can see from Fig. 1 below, the calculated X-ray diffraction spectra from our structure model with 150 atoms per unit cell for orthorhombic phase of Zr_2Co_{11} are in excellent agreement with available experimental data. The knowledge of the crystal structures at the atomic level allows us to identify the origin of the hard magnetic phase in Zr_2Co_{11} and provide useful insights for developing high performance permanent magnets without rare earth elements.

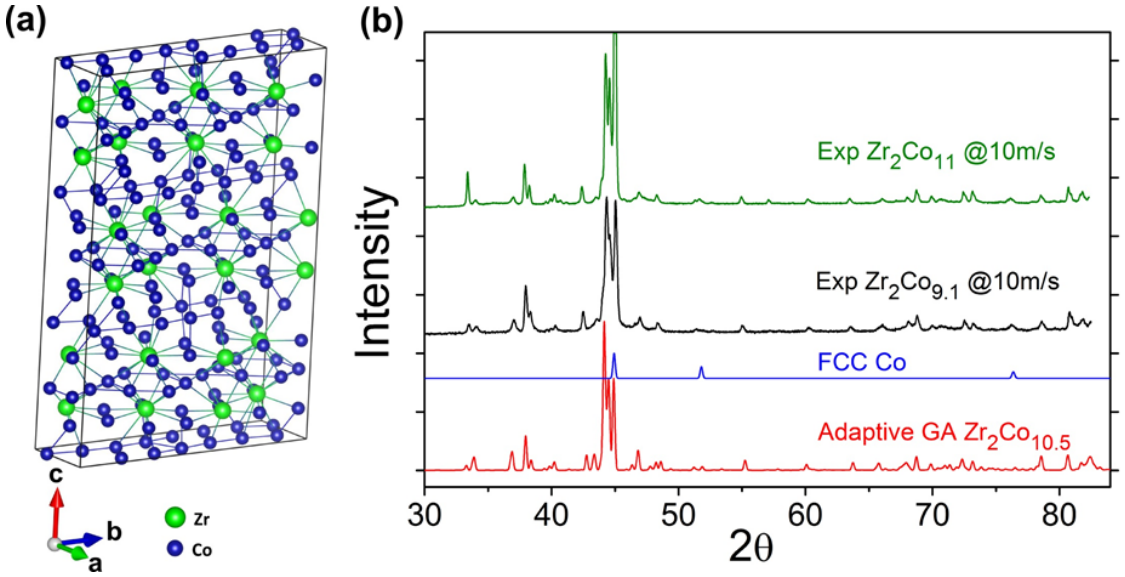

Fig. 1 Structure of the orthorhombic phase. **(a)** Atomic structure of the "orthorhombic" phase predicted from our adaptive GA search. This structure consists of 150 atoms in the unit cell. **(b)** Comparison of simulated XRD spectrum from the predicted "orthorhombic" structure model (red) with experiments (black and green, 10m/s indicates the wheel speed). The blue line shows the XRD spectrum from fcc-Co structure. Cu Kα line and a broadening factor $B(2\theta) = 3.1 \times 10^{-3}/cos\theta$ were used in the simulation. The experimental sample preparation and measurement are discussed in the methods section.

Interface Structure Prediction from First-principles

Information about the atomic structures at solid-solid interfaces is crucial for understanding and predicting the performance of materials. Due to the complexity of the interfaces, it is very challenging to resolve their atomic structures using either experimental techniques or computer simulations. We have developed an efficient first-principles computational method for interface structure prediction based on an adaptive genetic algorithm [3]. This approach significantly reduces the computational cost, while retaining the accuracy of first-principles prediction. The method is applied to the investigation of both stoichiometric and non-stoichiometric $SrTiO_3$ $\Sigma3(112)[\bar{1}10]$ grain boundaries with unit cell containing up to 200 atoms. Several novel low-energy structures are discovered, which provide fresh insights into the structure and stability of the grain boundaries.

An integrated approach to study the formation of metastable crystalline phases from amorphous metallic systems

Rapid quenching and thin film sputtering followed by thermal processing are commonly used techniques in the development of novel materials. Many metastable phases produced by such procedures exhibit interesting properties but are complicated by their transient nature, small grain sizes, and the fact they often contain disordered defects. To address the challenges we develop an approach that combines an efficient genetic algorithm and experimental diffraction data to solve complex crystal structures in far-from equilibrium transformations [4]. We demonstrate this approach by examining a polymorphic phase transformation from amorphous state to a metastable cubic phase with a ~ 14 Å in an Al-10%Sm alloy. Molecular dynamic simulations of the solid-liquid interface of the alloy validate the predicted disordered defects and provide a description of the transformation pathway. The metastable phase shares the same Sm-centered motif as the undercooled Al-10%Sm liquid, indicating a topological connection between the undercooled liquid and crystal structures.

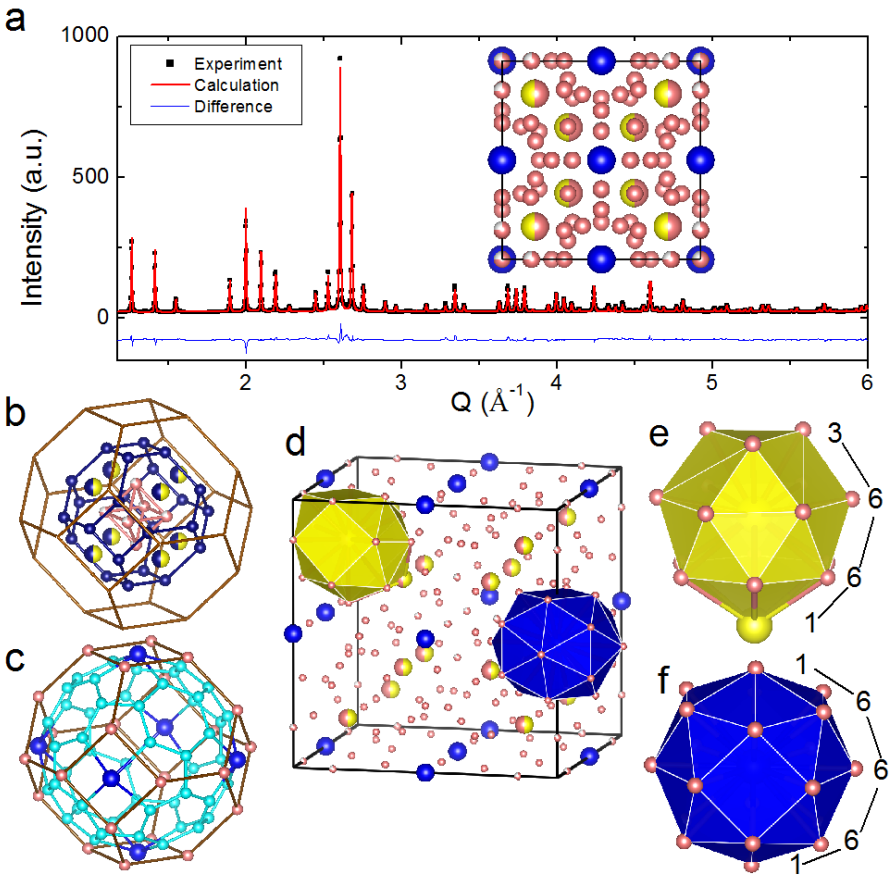

Figure 2 | Structure of refined $Al_{125}Sm_{14}$ and its XRD pattern. a, Fitted XRD pattern of $Al_{125}Sm_{14}$. Inset: structure of refined $Al_{125}Sm_{14}$. Blue/yellow and pink represent Sm and Al atoms, respectively. b and c, Detailed structure of refined $Al_{125}Sm_{14}$ in the Wigner-Seitz cell. d, Refined $Al_{125}Sm_{14}$ is made up of 2 Sm-centered motifs: e, the 3-6-6-1 motif, and f, the 1-6-6-6-1 motif. The 3-6-6-1 motif is the dominating motif in the undercooled liquid.

Future Plans

There is still need to improve the AGA method for more accurate and efficient prediction of larger and complex systems, such as battery materials and other oxide materials. We will further develop the algorithms for the method to better treat more complex materials, particularly when defects are take into consideration. 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.

Stable and metastable structures at finite temperature are important from the material processing and design perspectives. Knowledge about structures at finite temperatures is crucial for understanding and controlling phase selection and transformation pathway in material synthesis and processing. 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.

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Gutzwiller Density Functional Theory for First-Principles Calculation of Strongly Correlated Electron Systems

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Project Scope

"The *f*-electron challenge" in rare earth and actinide-bearing materials is one of the current scientific grand challenges in physics, chemistry, and materials science. While density functional theory (DFT) and computational codes, based on the Kohn-Sham approach, are highly effective and have been applied successfully to the prediction of the structures and properties of many materials, it fails for materials with strongly-correlated electrons such as the *f*-electron problem. The scope of this project is to pursue the development of first-principles theory, algorithms and computational codes that are different from the approaches currently available for strongly correlated electron systems. We will develop a unified density functional theory and computational approach that can incorporate strong correlation effects in a truly first-principles, self-consistent manner without empirical Hubbard U and Hund's J parameters. Computationally efficient and tractable algorithms and approaches for treating strong correlation, spin-orbit coupling, as well as additional relativistic effects under the new density functional formalism will also be developed and implemented to quantitatively describe the electronic properties and energetics of strongly correlated electron materials. Such a computational algorithm and code is highly desirable and would be widely applicable to many systems. This development is new and therefore should be considered as high risk, but it also has the potential for high payoff.

Recent Progress

Our development of first-principles theory and method for correlated electron systems is based on the Gutzwiller density functional theory (G-DFT) developed by Ho, Schmalian and Wang in 2008 (Phys. Rev. B, **77**, 073101). In contrast to the Kohn-Sham approach where the kinetic energy functional is introduced in reference to a non-interacting electron system, the G-DFT introduces a new kinetic energy functional in reference to an interacting electron system with exact treatment of the onsite kinetic energy and the 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. Two calculation methods based on the G-DFT have been developed.

LDA+Gutzwiller method and application to Ce and Pu

As an intermediate step towards the development of fully self-consistent G-DFT and computational code, we have developed a general efficient method to solve the equations

associated with the local electronic configuration occupation probabilities $\{P_\Gamma\}$derived from the G-DFT. The direct search for solutions of $\{P_\Gamma\}$ is mapped to an efficient simple steepest descent minimization problem. By combining the efficient Gutzwiller solver with the density functional theory, we have developed an efficient LDA+Gutzwiller (LDA+G) method for calculating the electronic structure and total energy of strongly correlated electron systems [1].

The LDA+G method has been applied to the investigation of the γ-α isostructural transition in Ce [2], in collaboration with J. Schmalian (Karlsruhe, Germany) and G. Kotliar (Rutgers University). The γ-α transition in Ce under pressure is due to strong electron-electron correlations, which were very difficult to describe correctly by previous DFT calculations. Our LDA+G calculation predicted correctly the γ-α transition within paramagnetic states, in close agreement with experiment as shown in Fig. 1. The predictive power of the LDA+G allows us to look into the mechanism of the phase transition in great details. We demonstrated that the γ-α transition is driven by a fascinating interplay between the Kondo effect and the spin-orbit interaction. The spin-orbit coupling acts as a catalyst of the γ-α transition by inducing the rapid change of *f* local moment between the two phases. The crossover behavior of the *f* local space affects drastically the conduction electrons because of Kondo effect, and consequently induces the γ-α transition according to the Kondo volume collapse mechanism.

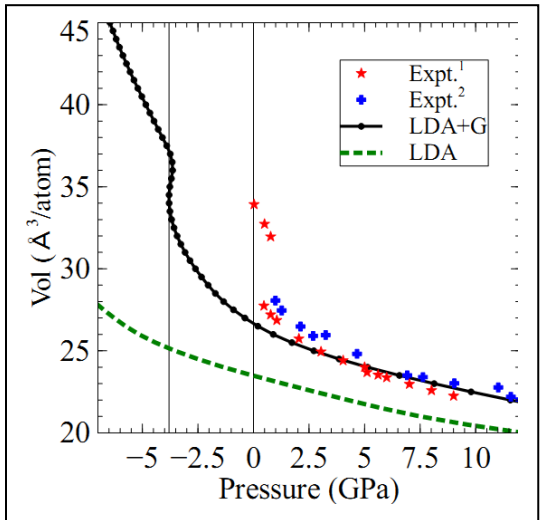

Fig. 1: The γ - α isostructural transition in Ce is well described by LDA+G calculations

The LDA+G method has also been applied to the study of the energetics and electronic structure of Plutonium, in collaboration with G. Kotliar group at Rutgers University [3]. Pu is the most exotic and mysterious element in the periodic table. It has 6 metallic phases and peculiar physical properties not yet understood. Using LDA+G, we have calculated the zero-temperature energies of various phases of Pu as the function of volume from first-principles. The results of relative phase stability compare well with experimental measurements. Our calculations also clarify how the electron correlations determine the unusual behavior of Pu solid. We also extend the LDA+G method to finite temperatures and calculate the pressure-temperature phase diagram for Ce [4]. The calculations allow us to clarify the entropic effects in the γ-α isostructural transition in Ce.

Correlation matrix renormalization (CMR) method

In order to develop a unified density functional theory and computational approach that can incorporate strong correlation effects in a truly first-principles, self-consistent manner without empirical Hubbard U and Hund's J parameters, we have developed a new general approach to remove a large part of the arbitrariness in determining the exchange-correlation functional in our G-DFT. In this general approach, the commonly-adopted Gutzwiller approximation for evaluation of the one particle density matrix is extended to treat the evaluation of the two-particle correlation matrix of the system. This approximation, which we call the correlation matrix renormalization (CMR) approximation [5], allows the expectation value of the many-

electron Hamiltonian with a variational many-body wave function of the Gutzwiller form to be evaluated with reduced computational complexity. In the CMR approach, both one-particle density and two-particle correlation matrices from the Hartree-Fock (HF) results are renormalized according to the local electron correlation effects.

The CMR method has been tested by studying the dissociation behavior of small hydrogen clusters, where correlation changes from the weak to strong regime, as the bond length increases between the hydrogen atoms [6]. We found the dissociation behavior of the hydrogen clusters calculated from the CMR method agrees well with the results from the high-level quantum chemistry CI or MCSCF calculations [6]. We also show that the CMR method can satisfactorily tackle great challenging problems faced by the density functional theory recently discussed in the literature [6]. For example, for a H_8 cubic cluster with varying electron filling, exact solution predicts a relatively big energy gap for the system at large bond length and half-filling N_e=8, while all the DFT calculations fail to reproduce this result because of the incapability to treat the strong electron correlation effects. Remarkably, the results from our CMR calculations agree with the highly accurate MCSCF results very well for all the bond separations and electron fillings as one can see from Fig. 2. These results demonstrate that the key many-body correlation physics in these systems has been well captured by the CMR method. Moreover, the CMR method does not need adjustable parameters and it does not have the double counting problems commonly encountered in many previous many-body approaches. The computational workload of our CMR method is similar to the Hartree-Fock approach while the results are comparable to high-level quantum chemistry calculations.

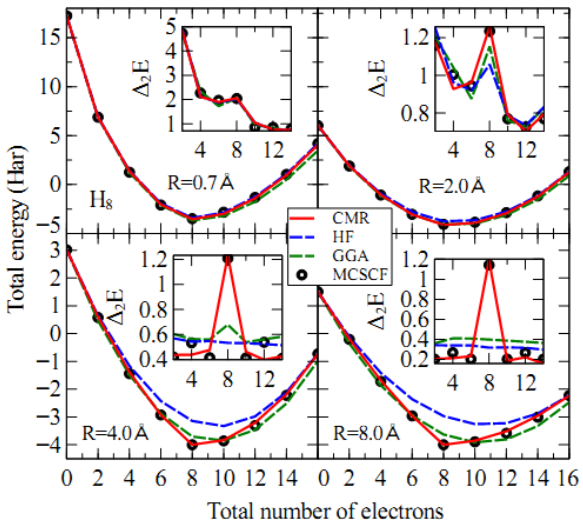

Fig. 2: The total energy E as a function of total number of electrons N_e obtained from the CMR, HF, GGA and MCSCF calculations for the H_8 cube with increasing bond length R from 0.4Å to 8.0 Å. Insets: the corresponding second order energy difference Δ^2E

The CMR method for studying the correlations in solids has also been being developed. Application of the CMR method to the studies of solid phases of hydrogen indicates that the approach is also promising for treating the electron correlations in periodic bulk systems.

Future Plans

In the next two years, we will approach the problem in two parallel routes: (1) further develop and apply LDA+G method, and (2) further develop correlation matrix renormalization (CMR) method to treat systems containing *f* and *d* electrons. The first route, while still needs U and J parameters, will serve as a ``short-cut'' for us to learn more about the physics of strongly correlated electron systems by systematically scanning U/J parameters. Such experience and

knowledge will provide physical insight and guidance for the CMR method development. The second route, CMR approximation, follows the rigorous derivation of DFT and is free of adjustable U/J parameters and double counting issues. The following topics will be investigated:

- Study the structures and electronic properties of various Pu phases as the function of temperature and pressure.
- Further develop the CMR method for multi-orbital systems. The knowledge learned from the development of the LDA+G method will be utilized as guidance for the development. We will use multi-orbital small molecules (e.g., N_2, O_2, Cr_3, Ce_2 molecules) as the benchmark systems, where a detailed analysis can also be performed using the accurate quantum chemistry calculations to provide useful insight and guidance for the CMR method development.
- We will further develop the algorithm and code to extend the CMR calculation for periodic bulk systems containing correlated *f* and *d* electrons.
- We will also extend the LDA+G and CMR to treat spin-unrestricted (magnetic) systems. Preliminary studies suggest the LDA+G and CMR methods are applicable to such systems.

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Strong Correlation in Density Functional Theory with Comparisons to Density Matrix Renormalization Group

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Project Scope

Density Functional Theory (DFT) requires approximation for the exchange-correlation functional since there is no first principles framework for its construction; only an existence proof that it must exist and is unique. Many approximations for this small piece of the total ground state energy exist and are useful for a variety of situations. We wish to determine the properties of the one universal functional as both a benchmark for approximations and to determine proofs of principle. In order to obtain the qualities of the universal functional, we conduct our investigation on one dimension where DFT performs structurally the same to the three dimensional case (*i.e.* the local density approximation will still not give the correct answer). In one dimension, a comparison with the numerically exact density matrix renormalization group (DMRG) and provides the opportunity to extract exact DFT quantities such as the Kohn-Sham potential and more. Further, computational feats that would require Herculean effort in three dimensions are often more manageable in one dimension allowing us to explore aspects of the theory more easily. Such a comparison between DFT and DMRG allows us to see where DFT fails and how it must be improved.

Recent Progress

Even if the universal functional is available, can one show that the ground state density be determined from it through some procedure? We showed that at each step of the Kohn-Sham convergence algorithm the energy can be lowered or (if and only if converged) remain the same. Consequentially, we have proven that for finite systems in three dimensions that the algorithm can be guaranteed to converge. This proof guarantees that the Kohn-Sham algorithm is a viable way to ensure exact DFT will generate the ground state even if computation time is large if the system considered has strong correlation, for example.

To qualify the possible difficulties in convergence, we conducted a proof of principle investigation in situations where convergence is difficult such as in the case of strong correlation and if the density is not *v*-representable. While these hurdles are present, our proof guarantees that the ground state may be found (or in the case of *v*-representability, approximated well on the grid) regardless. We also investigated the Kohn-Sham algorithm for efficiency in the number of steps to explore how to make the Kohn-Sham calculations converge faster. This investigation has direct consequences for real system DFT calculations and serves as an overview of possible hurdles.

Future Plans

The comparison between DFT and the leading solver of one dimensional systems, DMRG (particularly on the Hubbard model), has generated an interest in the comparison of many body physical properties solved in the Hubbard model and similar quantities in DFT. Specifically, we remark that the term 'exchange' is used to in both many body physics and DFT, but their meanings are not always the same. We are investigating one of the simplest models of strong correlation, the two site asymmetric Hubbard model. Using this stripped down model we are able to translate the many-body theory approach into DFT language, and vice versa. This model provides us simple parameters that we can adjust to better understand the effects of strong correlation in DFT. Exemplary, we can clearly see how the kinetic correlation effects the total correlation energy as we go from the weakly correlated to the strongly correlated regime.

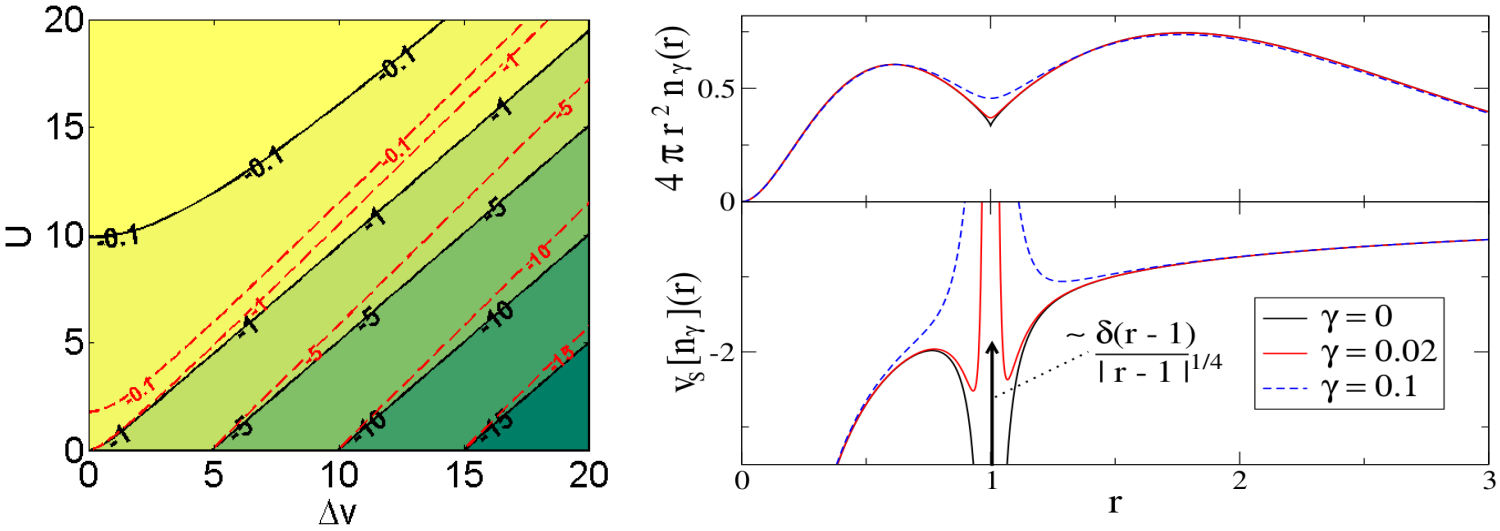

FIG 1. Left: Contour plot of the exact ground-state, *E* (labeled by contours with the restricted Mean Field energy overlaid in red), and restricted Mean Field solution for the asymmetric Hubbard dimer with t=1/2 (hopping) as a function of U (onsite repulsion) and Δv (potential difference between sites). Right: A non-*v*-representable density may be smoothed to give a *v*-representable one. Shown are the radial density (top) and Kohn-Sham

potential (bottom). A smoothing factor, γ, acts a lattice where all operators are bound and densities are reasonable. This density approaches the continuum value as γ goes to zero showing the density may be approximated on arbitrarily small grid sizes.

Our direct investigations with DMRG involve seemingly limitless applications for both well established approximations and proofs of principle. It is hoped that many of the structural aspects of DFT can be investigated with our comparisons to DMRG to bring lessons back to realistic systems. To continue our efforts, we are nearing completion on the generation of a whole new class of functionals to more easily allow for the study of localization effects. A suggested method for this is to use a short ranged exponential interaction over the commonly used soft-Coulomb interaction which is long ranged. We note that this modified exponential interaction contains a cusp analogous to the three dimensional Coulomb interaction and allows for the study of smaller systems with localization due to the fast decay of the interaction. Some topics of interest with this modified interaction are benchmarking the GW method and Fermi-weighted Kohn-Sham scheme, exploring the band gap problem, fixing time dependent DFT, surface states and energies, defects, Green's functions, and more.

Acknowledgements

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Thermodynamics and Kinetics of Phase Transformations in Energy Materials

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PROJECT SCOPE

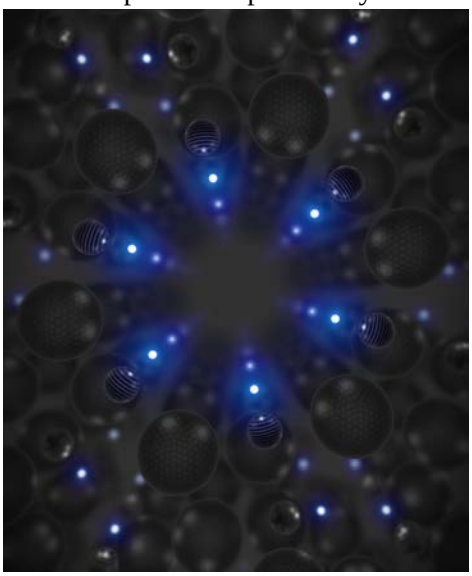
The previous project period involved work on developing a systematic, quantitative approach to designing novel materials with fast (de)hydrogenation kinetics using state-of-the-art first-principles density functional theory calculations based on microscopic models of nucleation, mass transport, and diffusion. The successful prediction of novel materials and reactions requires more broadly applicable computational tools, which we have developed, and will describe here: (i) computational solution of crystal structures of new materials, (ii) high-throughput computational (DFT) databases for screening new materials, and (iii) the use of high-throughput computation and data mining tools to elucidate descriptors for materials properties. In the future project period (just starting), our materials focus extends from hydrogen storage materials to include materials with applications in thermochemical water splitting reactions and other energy materials problems (see Future Plans).

RECENT PROGRESS

A Hybrid Computational-Experimental Approach for Crystal Structure Solution: First-Principles-Assisted Structure Solution (FPASS)

Crystal structure solution from diffraction experiments is one of the most fundamental tasks in materials science, chemistry, physics and geology. Unfortunately, numerous factors render this process labor intensive and error prone. Experimental conditions, such as high pressure or structural metastability, often complicate characterization. Furthermore, many materials of great modern interest, such as batteries and hydrogen storage media, contain light elements such as Li and H that only weakly scatter X-rays. Finally, structural refinements generally require significant human input and intuition, as they rely on good initial guesses for the target structure. To address these many challenges, we demonstrate a new hybrid approach, first-principles-assisted structure solution (FPASS), which combines first-principles-based algorithmic optimization, experimental diffraction data, and statistical symmetry information to automatically solve crystal structures. FPASS thus consists of three major elements: a computational structure optimization engine, which is a genetic algorithm acting on density functional total energies; the target crystal's

experimental candidate space group(s) and diffraction pattern; and mined information on Wyckoff site occupancies in different space groups from the Inorganic Crystal Structure Database. With these components, FPASS can solve—with no human intervention—crystals that defy both purely computational and purely experimental attempts at solution (see, e.g., Fig. 1). FPASS represents a potentially invaluable complement to experimental structural refinement.



We are currently working on solving a large set of unsolved structures within the Powder Diffraction File. This set of compounds have all been experimentally synthesized, have measured diffraction patterns, but the crystal structures have not been completely solved. This large set of structures has required us to "automate" the code in many ways. It is our intention to make the code freely available in the near future.

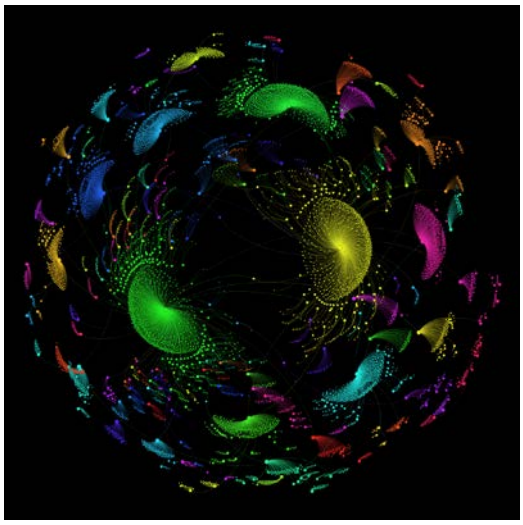
Figure 1: With traditional crystal structure solution techniques, light atoms such as the hydrogen present in MgNH (shown) often remain largely invisible, their positions unknown. Our FPASS method illuminates such elusive atoms with first-principles-based structural optimization. (*Art credit Robert Hodgin*)

Reference: B. Meredig and C. Wolverton, "*A Hybrid Computational-Experimental Approach for Automated Crystal Structure Solutions*" Nature Materials, 12, 123 (2013).

The Open Quantum Materials Database (OQMD)

High-throughput density functional theory (HT DFT) is fast becoming a powerful tool for accelerating materials design and discovery by the amassing tens and even hundreds of thousands of DFT calculations in large databases. Complex materials problems can be approached much more efficiently and broadly through the sheer quantity of structures and chemistries available in such databases. The Open Quantum Materials Database (OQMD) is a high-throughput database currently consisting of over 290,000 density functional theory (DFT) total energy calculations of compounds from the Inorganic Crystal Structure Database (ICSD) and decorations of commonly occurring crystal structures. To maximize the impact of this data, the entire database is being made available, without restrictions, at oqmd.org/download. In our group, we have found OQMD to be extremely helpful in screening materials for a wide range of applications and materials types: (I) Li-air battery combination catalyst/ electrodes, (II) Li-ion battery anodes, (III) Li-ion battery cathode coatings reactive with HF, (IV) Mg-alloy long-period stacking ordered (LPSO) strengthening precipitates, and (V) training a machine learning model to predict new stable ternary compounds.

We have also used this large database to evaluate the accuracy of the calculations therein by comparing DFT predictions with experimental measurements for: (i) stability of elemental ground state structures, and (ii) over 1,000 experimental formation energies of compounds. For formation energies, the apparent mean average error between experimental measurements and our DFT calculations is 0.099 eV/atom. In order to estimate how much error to attribute to the DFT calculations, we also examine deviation between different experimental measurements themselves where multiple sources are available, and find a surprisingly large mean absolute error of 0.082 eV/atom. *Hence, we suggest that a significant fraction of the error between DFT and experimental formation energies may be attributed to experimental uncertainties.* Finally, the



calculations of stability within the OQMD allows us to uncover interesting trends in materials discovery, based on historical data available within the ICSD.

Fig. 2. This image is a network graph—called a "minimum spanning tree"—showing the 7,410 DFT-predicted stable compounds from the Open Quantum Materials Database (OQMD) at the time the *JOM* article was completed. Since then, the number of stable compounds predicted in OQMD has risen to about 18,000 (out of 300,000 total compounds in the database). The tie lines connect compounds that are in stable equilibrium with one another. The plot was generated with the open source Gephi program (http://gephi.org).

Reference: J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton "*Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Mechanical Database (OQMD)*", JOM 65, 1501 (2013).

Combinatorial screening for new materials in unconstrained composition space with machine learning

Typically, computational screens for new materials sharply constrain the compositional search space, structural search space, or both, for the sake of tractability. To lift these constraints, we construct a machine learning model from the OQMD database of thousands of DFT calculations. The resulting model can predict the thermodynamic stability of arbitrary compositions *without any other input (i.e., without knowing the crystal structure of the compound)* and with six orders of magnitude less computer time than DFT. We use this model to scan roughly 1.6 million candidate compositions for novel ternary compounds ($A_xB_yC_z$), and predict 4500 new stable materials. We have used crystal structure prediction tools to validate ~8 of these predictions, and find compounds lower in energy than the currently-known T=0 convex hull. Our method can be readily applied to other descriptors of interest to accelerate domain-specific materials discovery.

Reference: B. Meredig, A. Agrawal, S. Kirklin, J. E. Saal, J. W. Doak, A. Thompson, K. Zhang, A. Choudhary, and C. Wolverton, "*Combinatorial screening for new materials in unconstrained composition space with machine learning*", Phys. Rev. B **89**, 094104 (2014).

FUTURE PLANS

In the coming project period, we will focus on developing a systematic, quantitatively accurate first-principles methods to address two important problems: (i) predict and optimize the thermodynamics of phase transformations over a large composition and structure space, and (ii) model the kinetics of nucleation and mass transport in solid-state chemical reactions. Task (i) will be addressed by combining state-of-the-art statistical algorithms for uncovering hidden relations in large computed data sets with high-throughput computation of reaction enthalpies and novel DFT-based crystal field and compressive sensing lattice models for predicting electronic and configurational entropies. Task (ii) will be addressed by developing predictive high-throughput framework for defect energetics and diffusivity calculations, combined with symmetry-adapted structure prediction methods. Our materials focus extends from hydrogen storage materials

(which was the focus of this project in the previous period) to include materials with applications in thermochemical water splitting reactions and other energy materials problems.

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Proximity Effects in Graphitic Nanostructures

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Project Scope

Dispersive electromagnetic interactions and related proximity phenomena encompass a wide range of problems in many areas. Casimir and van der Waals forces in various settings together with related energy exchange processes have received new directions with the discovery of materials, such as graphene and their derivatives. The unique electronic and response properties of such systems have proven to be a source of new discoveries for the fundamental science of long ranged interactions in different conditions by uncovering novel functionalities and new theoretical methods. The scope of the current project is to continue building a comprehensive theoretical understanding of the nature of graphitic Casimir and van der Waals forces and related phenomena. Our primary focus is to consider the dimensionality, specific properties, and external factors in equilibrium and out of equilibrium conditions involving graphitic systems. We develop theoretical methods that allow us to determine how the magnitude and sign of the Casimir/van der Waals force can be modulated by using graphitic systems. We also investigate the intriguing role of temperature in the interactions of such materials concerning temperature fluctuations and out of temperature equilibrium heat exchange processes.

Recent Progress

Graphene, Graphene Nanoribbons and Thermal Fluctuations in Dispersive Interactions

Casimir interactions are prominent in the μm range and for most materials the quantum mechanical effects and retardation due to the finite speed of light play a dominant role. Thermal fluctuations are unimportant and one must consider larger distances (which reduces the Casimir effect as a whole) or go to very high temperatures in order to enhance their manifestation. When graphene is involved, however, the Casimir force is determined by thermal fluctuations down to 50 nm separations at room temperature [1-3]. This is perhaps the first system in which quantum effects are unimportant in such ranges and the thermal effects may be detected experimentally [4]. The Dirac-like carriers and 2D nature are responsible for this behavior are credited for such behavior. However, doping and external electric fields contribute towards decreasing the thermal fluctuations and enhancing the role of quantum mechanics and retardation [2]. Graphene nanoribbons, on the other hand, have a very different behavior when it comes to their long-ranged interactions. We developed a Lifshitz-like formalism for van der Waals interactions, which allowed us to make significant progress in understanding of how temperature affects not only graphene nanoribbons but other 1D materials when it comes to their dispersive forces (Table I) [5]. In fact, the van der Waals force has a behavior typical for interacting semiconductors, however, increasing the chemical potential transforms the force from quantum mechanical to thermal at room temperature – Fig. 1. These results can potentially be used by experimentalists to achieve previously unattainable regimes for probing dispersive interactions.

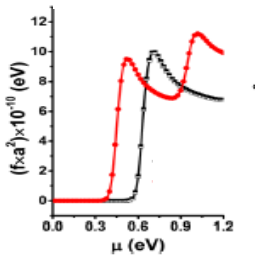

Fig. 1 Thermal van der Waals force between two graphene nanoribbons as a function of their chemical potential is shown.

TABLE I. Approximate vdW forces for 1D materials

1D materials	Force per unit length
Metals	$-\frac{\hbar}{8\pi d^3}\sqrt{\frac{n_{1D}e^2}{m}}\frac{1}{[2\ln(d/w)]^{3/2}}$
Insulators	$-\frac{135\pi}{4096}\frac{\hbar}{\omega_0^3}\left(\frac{n_{1D}e^2}{m}\right)^2\frac{1}{d^6}$
$\sigma = \text{const}$	$-\frac{3\hbar\sigma}{128}\frac{1}{d^4\ln(d/w)}$
Thermal	$-\frac{\pi k_B T}{64}\frac{1}{[d\ln(d/w)]^2}$

Theoretical Developments – Perturbative Approach, Mode Summation Method

Besides the electronic structure and dielectric response of the interacting systems, another important factor affecting the long ranged interactions stems from the particular boundary conditions. Designing objects with various boundaries can be an effective method in controlling the magnitude and sign of the Casimir force. Calculating the necessary electromagnetic fields, however, is a formidable task in general. We have found that for dilute systems one can construct an infinite perturbative series of this force for systems of all shapes [6]. In some cases, the series can be summed exactly. When this is not possible, each successive term in the series can be evaluated in order to obtain dominant effects from the boundary conditions. This approach is especially beneficial for systems with edges and/or reduced dimensions.

The zero-point photon energy summation method is another way to compute Casimir forces. This method is particularly useful when the absorption in the system is less important. The mode summation method is an elegant way to obtain the

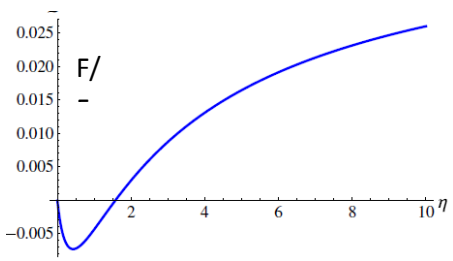

Fig. 2 Normalized Casimir force as a function of $\eta=2\pi\sigma/c$, where σ is the conductivity. Also, $F_0=hc/R^3$ with R being the radius of the sphere.

Casimir energy for objects with circular, cylindrical, or elliptical forms. However, removing the occurring divergencies cannot be done in a unified manner. We have found, however, that for spherical shells characterized with a constant conductivity no divergencies appear and all expressions are finite [7]. A prototype of such object can be a graphene bucky-ball with very large radius. It turns out that the transverse electric and magnetic modes can have competing roles in terms of positive and negative contributions for small values of the conductivity. Interestingly, the strength of the Casimir interaction does not depend on the radius, but it can be repulsive for smaller conductivity – Fig. 2 [7].

Radiative Heat Exchange

The radiative power exchange between two objects at different temperatures is a phenomenon with the same origin as Casimir and van der Waals interactions. It is due to the electromagnetic fields exchange in out of thermal equilibrium conditions. The near-field radiation is of significant interest for many problems as researchers find new materials and schemes for an enhanced transfer. In fact, materials that support resonant surface plasmons or surface polaritons can deliver many orders of magnitude enhancement compared to the far-field regime. Graphene has emerged as a system that not only supports strong surface plasmons, but external fields or doping can be used for their modulations. This is very desirable from experimental point of view which allows achieving control of the heat exchange process. Our recent investigations show that enhanced near-field radiation between two dissimilar materials can be achieved if graphene plasmons are used to achieve resonance [8]. In most other cases, one must utilize two materials that are the same for the resonance condition to occur. We also find that the near-field radiation process can be utilized to obtain fingerprints of the graphene transvesre electric surface modes [8]. This new mode has been predicted by several groups, however, no experimental signature of such excitations has been found. The transverse magnetic modes are usually dominant. We propose that a certain class of metamaterials can be used to enhance and probe the transverse electric contributions in the near-field heat exchange. We show that the near-field heat exchange coefficient in a graphene/metamaterial system is sensitive to the graphene scattering times and chemical potential. By properly designing the metamaterial components, the graphene transverse electric contribution can be maximized [8]. A microscopic approach for graphitic nanostructures was also developed, which is advantageous in the atomic design to module the heat transfer, as well [9].

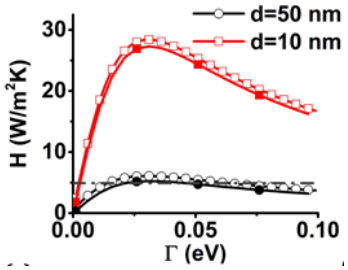

Fig. 3 Near-field radiation heat exchange coefficient vs. graphene scattering time. The substrate is a metamaterials as specified in [8] at two separations *d*. Other parameters are also found in [8]. The total H is determined by the transverse electric contribution mainly.

Van der Waals Interactions and Mechanical Stimulations

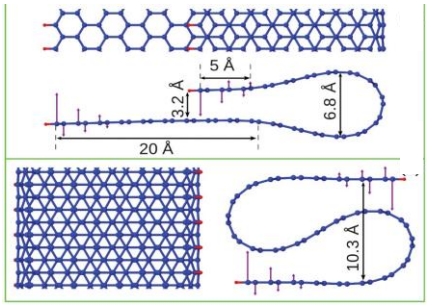

Fig. 4 Zigzag graphene nanoribbon folds from density functional theory calculations. Characteristics distances and localized spins are denoted.

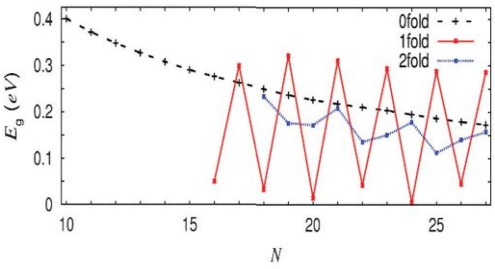

Fig. 5 Energy band gap vs. zigzag carbon lines for unfolded (0), single (1), and double (2) folded graphene nanoribbons from density functional theory calculations.

The van der Waals force plays an important role for the formation and stability of various graphene composites. Here we show that this interaction can be a driving force for making graphene folds (origami), which results in electronic structure modulations, stacking patterns, etc… The folding process is a balance between the van der Waals attraction and the elastic bending repulsion from the curved regions [10, 11]. Such folds can be achieved in the lab and they can potentially be used to modify the energy gap of the graphene system. The stacking patterns and van der Waals force play an important role in the microscopic nature of the energy bands, changes in spin polarization from zigzag edges, and the transport characteristics in general [10, 11].

Planned Activities

Graphene/Substrate Systems and Charge Accumulation

The Casimir/van der Waals interactions are strongly dependent on the dielectric and magnetic response of the involved objects as well as the boundary conditions. According to the fluctuations dissipation theorem, dipolar fluctuations are responsible for giving rise to this universal force [10]. In situations where graphene is used in a transistor setting an external voltage is applied. As a result, net charges are accumulated on both plates. The fluctuating charges and their contribution to the Casimir force is a much less studied problem. It is our goal to investigate this Casimir-like phenomena and determine the role of temperature for typical materials. Further, our plan is to see if the unique graphene properties can be utilized in order to enhance (or inhibit) this charge-fluctuating force and compare it with the "traditional" Casimir interactions in polarizable media.

Drift Currents and Van der Waals Interactions

We also plan to pursue another interesting possibility for modifying the Casimir/van der Waals force using directed motion of carriers. DC currents flowing in graphene systems is especially relevant since these materials are often used in electronics applications. Appreciable drift velocities can be achieved in graphene and graphene nanoribbons yielding currents having several orders of magnitude larger than the capacity of most other materials. The drift of the carriers affects the fluctuating evanescent fields and the dielectric response. Sometimes these changes can be quite significant, which can lead to major

modulations in the Casimir force. This is a novel direction which we plan to pursue by developing a theoretical formalism for the description of such non-equilibrium effects.

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Accurate density functionals for heterogeneous materials

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Project Scope

Density functional theory (DFT) offers a generic procedure to describe the equilibrium and ground state properties of condensed matter and chemical systems in terms of the one-body density profiles. Although the original concepts, as introduced first by Pierre Hohenberg and Walter Kohn in 1964, were intended to provide an alternative to solving the Schrödinger equation for electronic systems at 0 K, the mathematical framework can be similarly applied to electronic systems at finite temperature, to the thermodynamic models of simple fluids or polymeric systems, and to multicomponent mixtures of quantum and classical particles. Despite tremendous progress in the past 50 years, present applications of DFT have been mostly focused either on the ground state properties of electronic systems at 0K, or on the thermodynamic properties of classical inhomogeneous systems that are represented by various semi-empirical/coarse-grained models. Although the mathematical foundations of the electronic and classical DFT methods are strikingly similar, their integration into a self-consistent computational framework applicable to heterogeneous materials with both quantum and classical components remains essentially unexplored.

This research aims to establish DFT as a unified theoretical tool for predicting the microscopic structure and thermodynamic behavior of heterogeneous condensed mater from first principles. The theoretical development follows a generalization of the Hohenberg-Kohn-Mermin theorem for multi-component systems at finite temperature wherein the free energy functional will be formulated in terms various perturbation methods with the quantum effects described by classical mapping. To facilitate applications of DFT to classical systems, we have already formulated a number of accurate density functionals to account for molecular excluded volume effects, van der Waals attractions, inter- and intra- molecular associations and hydrogen bonding, electrostatic correlations in ionic fluids, and intra-chain correlations in polymeric systems. These classical functionals empower us, as well as others, to predict the structure and interfacial properties of a broad range of complex molecular systems beyond the computational reach of conventional mean-field theories or simulation methods. In future developments, we will establish new density functionals for heterogeneous quantum and classical systems by incorporating the universality of bridge functional and direct and pair correlation functions of the corresponding uniform reference systems. The ultimate goal of this project is to establish a new procedure for multiscale modeling of complex heterogeneous materials without invoking different quantum and classical theoretical frameworks. We expect that the new theoretical methods will be most useful for systems that exhibit non-negligible nuclear quantum effects even at ambient conditions, in particular those consisting of metallic or organic metallic crystals in contact with a fluid phase containing hydrogen gas or liquid water.

Recent Progress

Recently we introduced a systematic procedure to calculate the correlation functions and the exchange-correlation (XC) free energy of uniform quantum systems by using the integral-equation methods. One key idea of our liquid-state approach to quantum systems is to account for the Pauli exclusion principle using a classical mapping method originally proposed by Dharma-wardana and Perrot (Physical Review Letters **84**, 959, 2000). The classical mapping method allows us to describe the exchange and degeneracy effects of electron systems by using an effective, pairwise additive potential. Key results from our recent work for electronic systems include:

1) Bridge functional for electronic systems

We have developed a bridge-functional-based classical mapping method for calculating the correlation functions of uniform spin-unpolarized electron gases at finite temperature. The bridge functional is formulated following Rosenfeld's universality *ansatz* in combination with the modified fundamental measure theory. The theoretical predictions are in good agreement with recent quantum Monte Carlo (QMC) results but require negligible computational cost, and the accuracy is better than a previous attempt based on the hypernetted-chain approximation. We find that the classical mapping method is most accurate if the effective mass of electrons increases as the density falls. Efficient and accurate prediction of the correlation functions of uniform electron gases is of great importance for both practical and theoretical applications.

2) Electrons at finite temperature

We have revised the classical mapping method for uniform electron gases (HEG) at finite temperature by introducing improved correlations for the classical reference temperature. The semi-empirical correlations were parameterized on the basis of the correlation energies from recent QMC studies and the asymptotic behaviors of classical mapping. The new theoretical procedure was calibrated with the correlation energy, exchange-correlation free energy and pair correlation functions of HEG at finite temperature from QMC and/or previous theoretical predictions. Specifically, the correlation energy and pair correlation functions were compared with those based on the classical temperature proposed by Dharma-Wardana *et al*. and with QMC results, while the exchange-correlation free energy was compared with the semi-empirical correlations proposed earlier by Karasiev *et al*. (Physical Review B **88**,161108, 2013). The new theoretical procedure yields the correlation energy in excellent agreement with QMC and shows significant improvement over the classical mapping method originally proposed Dharma-Wardana *et al*. It predicts the dependence of the exchange-correlation free energy on the electron density in good agreement with that from Karasiev and coworkers. However, noticeable disagreement exists at high temperature between these two approximations. The new correlations for the classical temperature show improvement also on the prediction of the classical mapping for the pair correlation functions at long-range region.

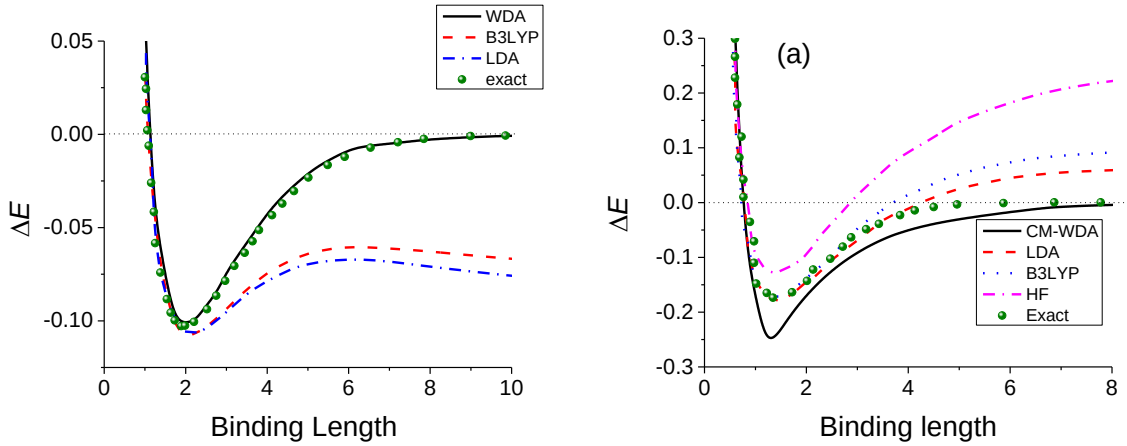
2) Relativistic effect

In quantum systems relativistic effect is important but complicated from both fundamental and application perspectives. We introduced an efficient computational procedure to predict the

structure and energetic properties of relativistic quantum systems by mapping the Pauli principle into effective potentials such that the relativistic non-quantum systems that can be readily solved with liquid-state methods. We applied the new theoretical procedure to relativistic electron gas and compared the pair correlation functions with those for non-relativistic electrons. A simple analytical expression has been developed to correlate the exchange-correlation free energy of relativistic uniform electrons.

4) A new exchange-correlation functional

We have proposed a new functional for the exchange-correlation energy of inhomogeneous electronic systems based on the weighted density approximation and classical mapping. The new functional is free of the delocalization and static correlation errors commonly suffered in alternative methods. We have tested the numerical performance of the new functional for predicting both H_2^+ and H_2 binding curves, a standard test set for calibrating the strong correlations. For H_2^+, it exactly reproduces the whole binding curve; while for H_2, the theory reduces the correct asymptotic limit when $r \to \infty$.



(Left) Binding energy curves (atom units) for H_2^+ calculated from different versions of KSDFT. B3LYP, LDA and exact results are from reference. The binding length is referred to the center-to-center distance between the two H atoms. (Right) Binding energy curves for H_2 calculated from different methods (atom units).

Future Plans

Conventional approaches to multiscale modeling follow cascade computations that are inappropriate to describe physiochemical phenomena that entail strong coupling between different quantum and classical components. By contrast, DFT offers a generic procedure to describe the properties of many-body systems in terms of the one-body density profiles, which are continuously applicable to molecular as well as macroscopic systems. A major focus of our future theoretical developments will thus be directed at closing the gaps among different theoretical frameworks in condensed matter physics to describe heterogeneous materials. Specifically, we will extend the classical mapping method and several perturbation strategies established for classical systems to systems containing both quantum and classical components. By using different mathematical procedures to account for short-range and long-range

correlations, we will introduce new density functionals that are conceptually sound, numerically reliable, and computationally convenient. In addition to theoretical derivations, we will demonstrate the numerical performance of these functionals and their application to a wide variety of heterogeneous materials systems with strongly correlated electronic, atomic and molecular interactions that are difficult to describe with conventional multiscale modeling methods. To seek practical applications of these new functionals, we will investigate the properties of heterogeneous materials containing metallic elements and liquid water or hydrogen gas. Despite the tremendous importance of such systems in many technological applications, existing computational methods are insufficient to describe hydrogen quantum effects and electron-proton correlations for many systems of practical concern.

Publications exclusively acknowledge the DMSE support

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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. Here we report our progresses in searching for new topological properties of graphene-based two-dimensional materials.

Recent major progress in 2D Topological insulators

Since graphene can be fabricated and manipulated easily, it is highly desirable to artificially enhance spin-orbit coupling strength in graphene so as to elevate the gap protecting the quantum spin Hall effect (QSHE) to a level that is suitable for room temperatures applications. Through systematic density functional calculations, we found a route to have graphene inheriting strong spin-orbit coupling from a dilute concentration of heavy adatoms. Although the system appears to be simple, many complex competing effects such as local magnetic moments, Rashba spin-orbit coupling, and random scattering are involved that may suppress the quantum spin Hall phase. Even adatoms may also bring in complexities since the may favor different sites and aggregate under ambient conditions. Our results indicate that Indium and Thallium are good adaptors for this purpose. Indium and Thallium adatoms take the hollow site and thus are able to efficient mediate the desired intrinsic spin-orbit terms present in the Kane-Mele model, without the local sublattice symmetry-breaking problem. Neither element forms a magnetic moment, and although they do generate significant Rashba coupling, for symmetry reasons this remarkably does not suppress the QSHE. The topological band gaps are large and robust, e.g., 11 meV at a coverage of 2.0%, and 6 meV at a coverage of 1% for Thallium on graphene, and the high mobility of electrons in graphene can be mostly reserved.

Furthermore, we introduced a new concept for engineering a two-dimensional topological insulator by hybridizing graphene π-orbitals with the partially filled d-orbitals of heavy adatoms, in particular, osmium and iridium. Fig. 1 shows the evolvement of the

band structure of a model Hamiltonian for the adatom/graphene with the inclusion of adatom-graphene interaction and the spin-orbit coupling term. First-principles calculations predicted that the gaps generated by this means exceed 0.2 eV over a broad range of adatom coverage as shown in Fig. 1(d). Moreover, tuning of the Fermi level is not required to enter the QSHE state of Os/graphene and Cu-Ir/graphene. The mechanism is expected to be rather general and may open the door to designing new topological phases in many two-dimensional materials.

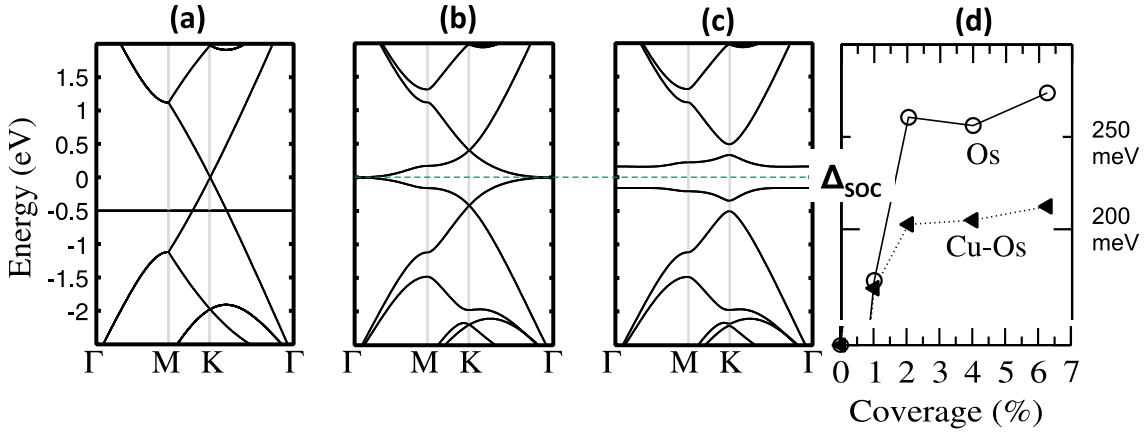

Fig. 1 Sketches of tight-binding band structures for (a) non-interacting graphene and adatom (one orbital only for the adatom as shown by the flat line), (b) with hoping between adatom and graphene, and (c) with hoping between adatom and graphene and spin-orbit coupling in adatom. (d) shows the change of spin-orbit coupling induced band gap as a function of coverage of adatoms.

Another interesting new phenomenon in spin-topotronics is the quantum anomalous Hall effect (QAHE). So far, the QAHE has been observed only in Cr-doped $(Bi,Sb)_2Te_3$ yet at extremely low temperature, due to the tiny topological gap, and also the complicities in dealing with surfaces of three-dimensional topological insulators. Therefore, the search of new topological insulators that may demonstrate the QAHE is a cutting-edge research topic in condensed matter physics and material science. For the realization of the QAHE, the time-reversal symmetry must be broken by *intrinsic* magnetization rather than external magnetic field, through magnetic impurities, adatoms, or substrate. In addition, it is necessary to align the magnetization along the surface normal, in analog to the geometry of conventional anomalous Hall effect. The QAHE was indeed predicted in graphene covered by Fe or W, with topological band gaps of 5.5 or 30 meV. The main drawback of these predictions is that both Fe/graphene and W/graphene prefer the in-plane spin orientation rather than as assumed to be perpendicular to the graphene plane as required by the QAHE. To solve this issue, we recently performed *ab-initio*

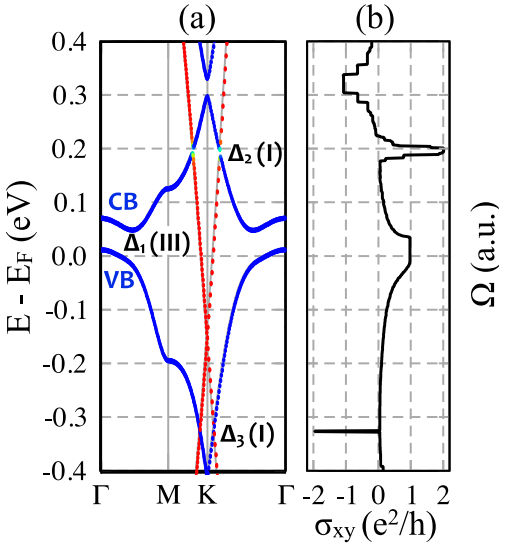

FIG. 2: (a) Band structure of Co/graphene with SOC (red and blue lines for the majority spin and minority spin states, respectively). (b) Fermi level-dependent anomalous Hall conductivity (σ_{xy}).

calculations for various adatom/graphene systems and found that Co/graphene and Rh/graphene can be excellent magnetic topological (or Chern) insulators, with a large topological band gap in the minority spin channel and a Dirac cone in the majority spin channel at the Fermi level. Through DFT calculations and tight-binding model analyses, we found that the topological gaps of Co/graphene and Rh/graphene are 50 and 100 meV, and they also have large perpendicular magnetic anisotropy energies of 5.3 and 11.5 meV, respectively. Therefore, they are ideal model systems for the observation of the QAHE at elevated temperature. As shown in Fig. 2, there are three topological band gaps for Co/graphene in the energy range we display, with Chern numbers of -2, 1 and +2, respectively. If one can tune the Fermi level into these gaps, different topological states should be observable.

Future Plans

For the next year, we plan to continue our studies of electronic and magnetic properties of different materials. In particular, we will study:

- Topological band gaps of innovative two-dimensional materials for the realization of quantum spin Hall effect or quantum anomalous Hall effect;
- Magnetic anisotropy and spin dynamics in small structures including single molecular magnets;
- Origin of magnetic noise in “non-magnetic” qubits.

The uniqueness of our project is the determination of magnetic anisotropy energies of large systems, which is essential for the understanding of spin dynamics and spintronics.

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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

Transitions between Semimetal and Semiconductor in Graphene Induced Geometrically. How the long-range ordering and local defect configurations modify the electronic structure of graphene remains an outstanding problem in nanoscience, which precludes the practical method of patterning graphene from being widely adopted for making graphene-based electronic and optoelectronic devices, because a small variation in supercell geometry could change the patterned graphene from a semimetal to a semiconductor, or vice versa. We employ a tight-binding model to reveal that a semimetal-to-semiconductor transition can be induced geometrically without breaking the sublattice symmetry. For the same patterning periodicity, however, breaking the sublattice symmetry increases the gap, while phase cancellation can lead to a semiconductor-to-semimetal transition in non-Bravais lattices.

Figure 1 shows electronic band structures of H-passivated and BN-doped graphene with various numbers of defected areas in a suoercell. Here phase cancellation in H-passivated graphene can induce a transition from insulator to semimetal, while in BN-doped graphene, E_g is significantly reduced when phase cancellation

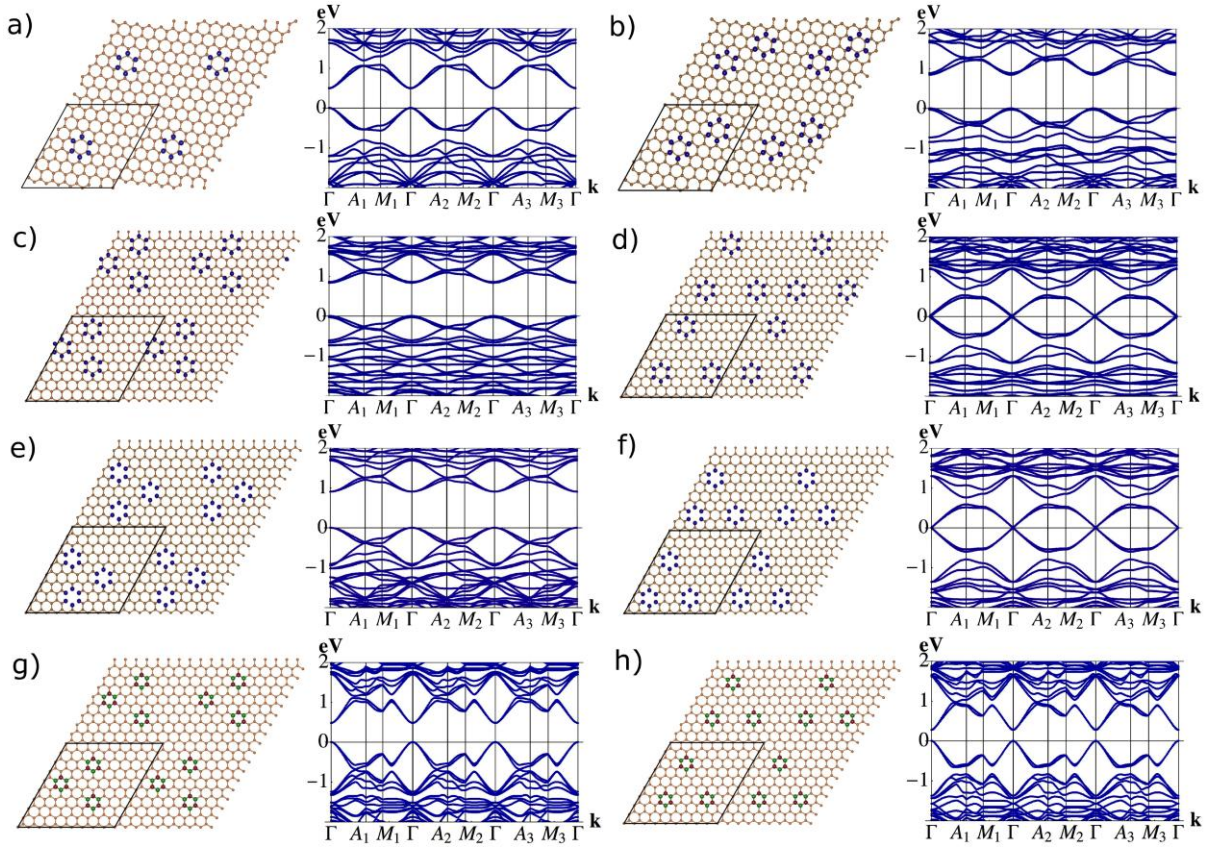

Figure 1. Crystal (left) and electronic band (right) structures of defected graphene sheets, which have (7, 1, 8, −7) supercells in (a) and (b) and (9, 0, 0, 9) supercells in (c–h). Except for panel (a), defects in these graphene structures form non-Bravais lattices. (a–d) H-passivated graphene. (e) and (f) GNMs. (g) and (h) BN-doped graphene. Supercells in these graphene structures are indicated by black rhombuses.

occurs. Our theory predicts the analytic relationship between the long-range defects ordering and bandgap opening/closure in graphene, which is in excellent agreement with our numerical *ab initio* calculations of graphene nanomeshes and partially H-passivated or BN doped graphene.

While it is simple to treat symmetric, idealized defects numerically, experimentalists lack the precision to make such perfect structures. In the past, we only considered defects that affect a single 6-carbon (6-C) ring of graphene. We have recently extended our model to include defects with arbitrary geometry and find that the Dirac points move in accordance with the anisotropy induced by the defect. This movement of Dirac points, as illustrated in Figure 2, is entirely predictable, and we have performed extensive numerical calculations to confirm our analytic model that is based on the anisotropic honeycomb lattice. When the Dirac points drift onto a reciprocal lattice vector, inter-valley scattering is induced and a band gap opens. By understanding the effect of the defect geometry, we can help experimentalists design new materials for optoelectronic devices, especially photovoltaics.

Band gap engineering of silicon nanowires via twisting. Si NWs are among the most promising semiconductor nanomaterials, whose electronic and optical properties can be well tuned by size and surface chemistry. Recently, there have been a lot of efforts focusing on tuning the electronic structures of Si NWs by applying external strains. Besides conventional stretching and compressing approaches, twisting is also a promising and practical method to apply external strains on Si NWs, however, the effect of twisting on electronic properties of Si NWs remains unexplored.

Figure 3 summarizes our DFT results of band gap as a function of the twisting angle for Si NWs along the [001], [111] and [011] directions with d = 0.7, 1.1 and 1.2 nm, respectively. As twisting angle

increases, Eg increases slightly except for the [111] NW, then it decreases dramatically for the [001] and [011] NWs, while Eg in the [001] NW decreases nearly linearly with twisting angle. Thus our calculations suggest that electronic structures of Si NWs can be tuned by twisting. However, twisting leads to very large unit cells, especially small twisting angles. We are working on new method to treat such modified periodic boundary conditions, so that we can carry out DFT calculations for twisted nanowires and other systems using the original size of unit cells.

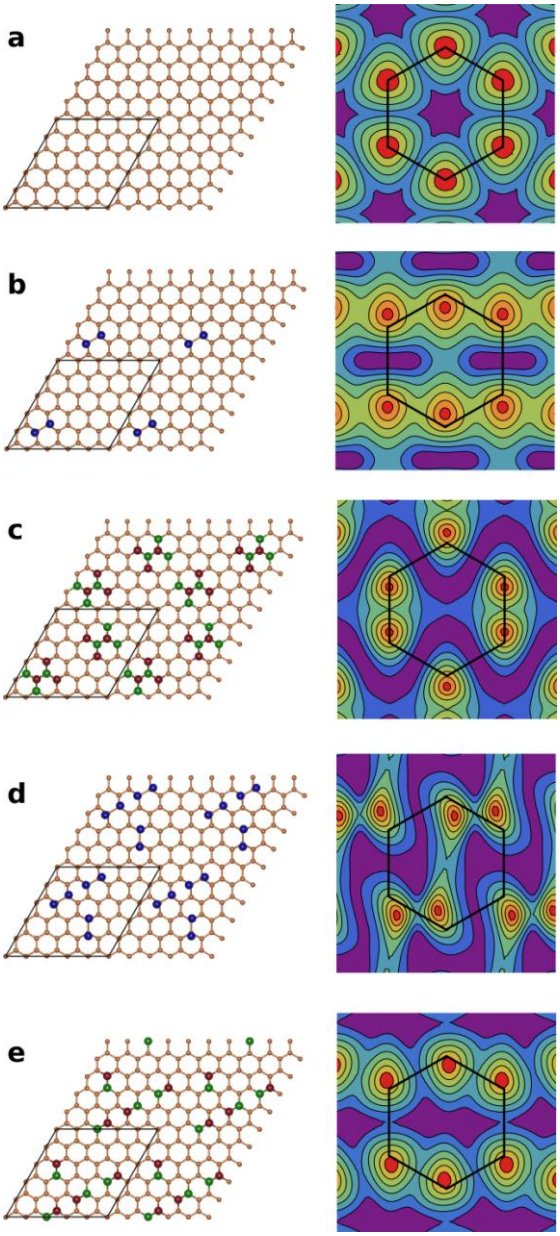

Figure 2. Contour plots (right) show contours of the lowest conduction band in the Brillouin zone (black hexagon). Structural defects are adsorbed H atoms (blue dots) and hexagonal BN dopants (red and green atoms).

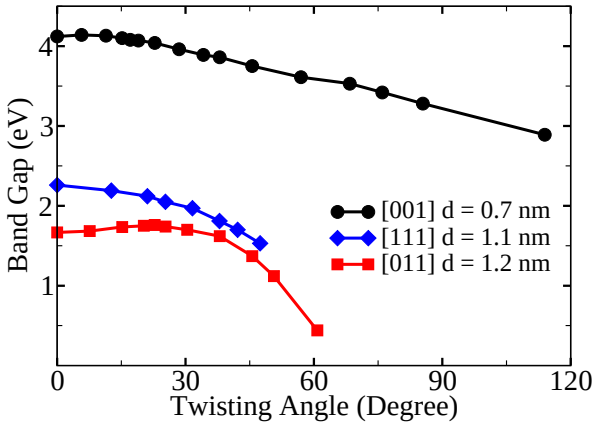

Figure 3: Calculated band gap as a function of twisting angle for Si nanowires.

Tailoring the optical gap of silicon quantum dots for photovoltaic cells. The absorption of photons through the direct generation of spatially separated excitons at dot-ligand interfaces is proposed as a promising strategy for tailoring the optical gap of small silicon quantum dots independent of their size. This removes a primary drawback for the use of very small dots in broad range of applications. For instance, the strategy can be applied to solar energy technologies to align the absorption of such dots with the peak of the solar spectrum. The key is to establish both a Type-II energy level alignment and a strong electronic coupling between the dot and ligand.

Our first principles analysis indicates that connecting conjugated organic ligands to silicon quantum dots using vinyl connectivity can satisfy both requirements. For a prototype assembly of 2.6 nm dots, we predict that triphenylamine termination will result in a 0.47 eV redshift along with an enhanced near-edge absorption character, as shown in Figure 4. Robustness analyses of the influence of oxidation on absorption and of extra alkyl ligands reveal that the control of both factors is important in practical applications.

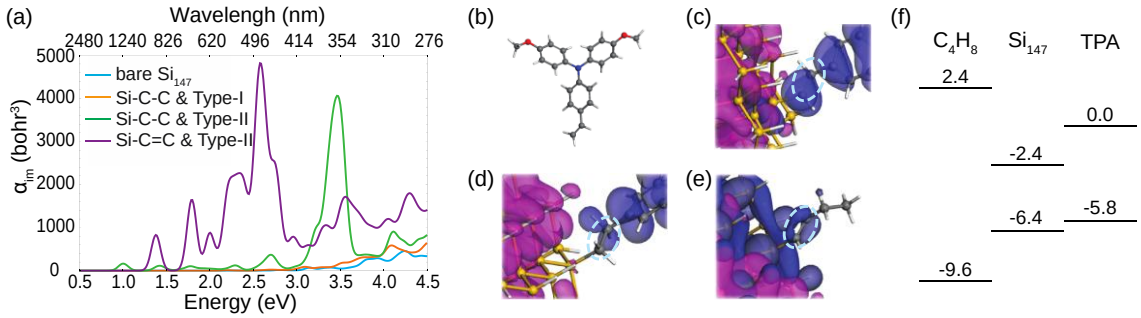

Figure 4. (a) Calculated absorption spectra of bare Si_{147}, 4 TPA on Si_{147} with C=C connections, 4 TPA on Si_{147} with C-C connectivity and 4 C_4H_7 on Si_{147} with C=C connectivity. (b) Structure of the TPA molecule. The dot-ligand interfaces of Si_{147} capped by: (c) 4 TPA with C=C connectivity, (d) 4 TPA with C-C connectivity and (e) 4 1-butenes along with HOMO (blue) and LUMO (purple). The light blue ellipses highlight the relevant C=C and C-C bonds. (f) Energy level alignment between Si_{147}, C_4H_8 and TPA in eV.

III. Planned Activities for the Next Year

Method development. (**a**) Improving our QP-DFT method and solving the problem for degenerate bands. (**b**) Assessing GW approximation and hybrid functionals for materials with strong correlations and/or strongly-localized electrons, in order to better understand the success and failure of these widespread methods in first-principles electronic structure calculations. (**c**) Implementing the electron-phonon code for large-scale calculations of electronic properties affected by lattice vibrations, and computing the effects of electron-phonon coupling in electronic excitations in silicon nanowires and carbon nanotubes. (**d**) Develop theoretical formulism for DFT to treat the modified periodical boundary conditions, such as those encountered in twisted silicon nanowires.

Method applications. (**a**) Defected graphene: (1) the exact energy gap using the GW method (partially done already); The optical absorption spectra and excitonic binding energies of semiconducting defected graphene by solving the Bethe-Salpeter equation (partially done already); (3) inducing magnetism by controlling defects structures and periodicity; (4) optoelectronic behaviors of interfaces between defected graphene and other materials, such as silicon quantum dots and polymers. (**b**) Bilayer graphene and sillicene for optoelectronic applications. (**c**) The dynamics of interfacial charge transfer: effects of the electron-phonon coupling and thermal fluctuations.

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LASER-INDUCED ULTRAFAST MAGNETIZATION IN FERROMAGNETS

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Project Scope

Our research focuses on the theoretical investigation of laser-induced femtosecond magnetization in ferromagnets or femtomagnetism. Our goal is to understand the laser-induced demagnetization and spin switching in a group of transition metals and rare-earth materials. Since on the femtosecond time scale multiple interactions are involved, our theory has multiple thrusts. One line of the research is to develop the theoretical tool to investigate the interaction between the laser field and the system. We employ the first-principles density functional theory to compute optical and magnetic properties, and then we employ the Liouville equation to couple the laser field to the system. The entire precession of the spin can be calculated. Another focus is on the electron-electron interaction, in particular exchange interaction through the functional itself and the exchange integral during the laser excitation. In ferromagnets, the exchange interaction plays a critical role. Our current study will provide much needed insights into the dynamics on the shortest time scale.

Recent Progress

Effect of strain and stress on magnetization change

Ruthenium-based perovskite systems are attractive because their structural, electronic, and magnetic properties can be systematically engineered. The $SrRuO_3/RrTiO_3$ superlattice, with its period consisting of one unit cell each, is very sensitive to strain change. Our first-principles simulations reveal that, in the high tensile strain region, it transits from a ferromagnetic metal to an antiferromagnetic insulator with clear tilted octahedra, while in the low strain region, it is a ferromagnetic metal without octahedral tilting. Detailed analyses of three spin-down Ru-t_{2g} orbitals just below the Fermi level reveal that the splitting of these orbitals underlies these dramatic phase transitions, with the rotational force constant of RuO_6 octahedron high up to 16

meV/Deg^2, 4 times larger than that of TiO_6. Differently from nearly all the previous studies, these transitions can be probed optically through the diagonal and off-diagonal dielectric tensor elements. For a 1% change in strain, our experimental spin moment change is 0.14±0:06μ_B, quantitatively consistent with our theoretical value of -0.1μ_B. This result has been published in Physical Review Letters **109**, 157003 (2012).

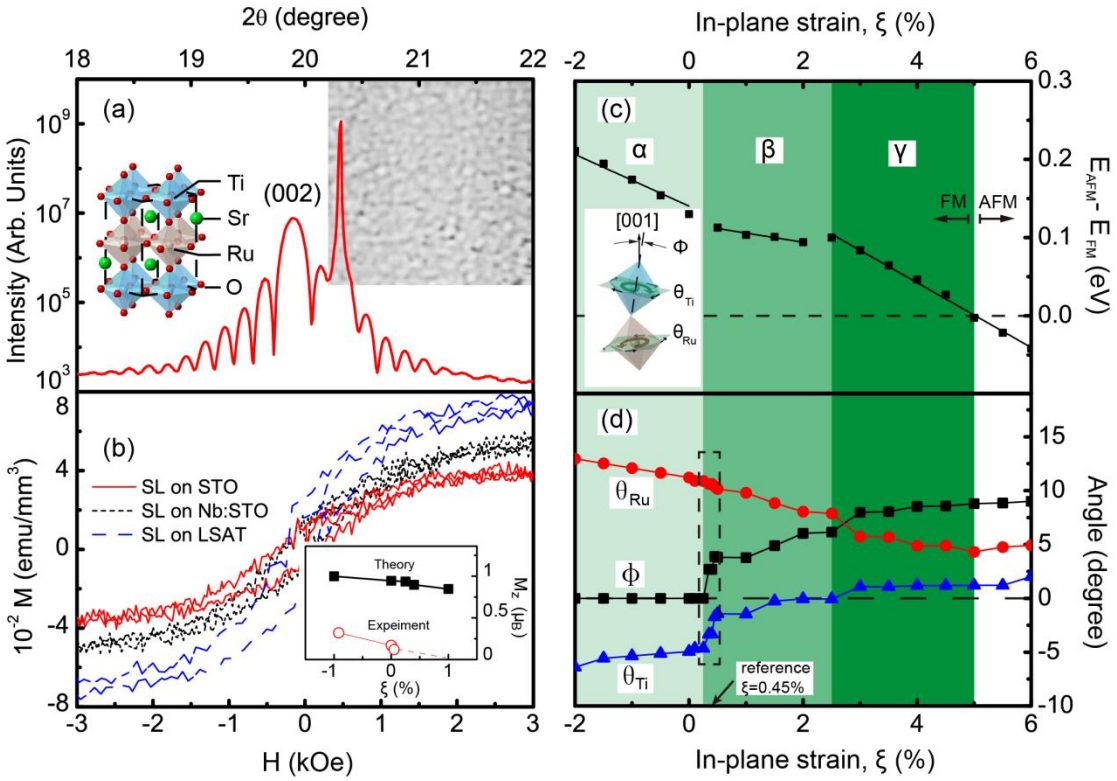

Figure 1. (a) X-ray diffraction pattern for the sample grown on the STO substrate. Left inset: Superlattice structure, where Sr, Ru, Ti and O atoms are directly shown in the model. Right inset: Surface AFM image for this sample. (b) Hysteresis loops for $[SRO/STO]_{30}$ superlattices grown on STO (red solid line), Nb:STO (black dotted line), and LSAT substrates (blue dashed line), respectively. The inset shows the magnetic moment of the Ru atom as a function of strain.(Exp: open symbols and theory: closed symbols.) (c) Theoretical in-plane strain dependence of the total energy difference between AFM and FM phases. Three phases α, β and γ in FM phase are highlighted by shading in three different colors. The slopes for the three fit lines are -0.03, -0.01 and -0.04 eV for 1% change in strain, respectively. The inset shows the tilting angle ϕ and two rotational angles θ_{Ru} and θ_{Ti} . (d) Optimized ϕ, θ_{Ru} and θ_{Ti} as a function of ξ.

Manipulating femtosecond magnetism through pressure: First-principles calculations

Inspired by a recent pressure experiment in fcc Ni, we propose a simple method to use ressure to investigate the laser-induced femtosecond magnetism. Since the pressure effect on the electronic and magnetic properties can be well controlled experimentally, this leaves little room for ambiguity when compared with theory. Here we report our theoretical pressure results in fcc Ni: Pressure first suppresses the spin moment reduction and then completely diminishes it; further increase in pressure to 40 GPa induces a demagnetization-to-magnetization transition. To reveal its microscopic origin, we slide through the L-U line in the Brillouin zone and find two essential transitions are responsible for this change, where the pressure lowers two valence bands, resulting in an off-resonant excitation and thus a smaller spin moment reduction. In the spin-richest L-W -W plane, two spin contours are formed; as pressure increases, the contour size retrieves and its intensity is reduced to zero eventually, fully consistent with the spin-dipole factor prediction. These striking features are detectable in time- and spin-resolved photoemission experiments. This result has been published in PHYSICAL REVIEW B 88, 144425 (2013).

Resolving the controversy over the thermal or nonthermal spin switching in GdFeCo

GdFeCo is among the most interesting magnets for producing laser-induced femtosecond magnetism, where light can switch its spin moment from one direction to another. This paper aims to set a criterion for the thermal/nonthermal mechanism: we propose to use the Fermi-Dirac distribution function as a reliable criterion. A precise value for the thermalization time is needed, and through a two-level model, we show that since there is no direct connection between the laser helicity and the definition of thermal/nonthermal processes, the helicity is a poor criterion for differentiating a thermal from a nonthermal process. In addition, we propose a four-site model system (Gd_2-Fe_2) for investigating the transient ferromagnetic ordering between Gd and Fe ions. We find that states of two different kinds can allow such an ordering. One state is a pure ferromagnetic state with ferromagnetic ordering among all the ions, and the other is the short-ranged ferromagnetic ordering of a pair of Gd and Fe ions. This result has been published in J. Phys.: Condens. Matter 25 (2013) 366002 (7pp).

Future Plans

In the next year, we plan to focus on the effect of the exchange interaction on the magnetization process and spin switching.

(1) It is well known that in ferromagnets, the exchange interaction plays a critical role, but there has been almost no study on the femtosecond time scale. We plan to employ the density functional theory to investigate the exchange interaction change due to the laser pulse. The goal is to get the time-dependence of exchange interaction under laser excitation.

(2) Then with the time-dependent exchange interaction, we will carry out a massively parallel calculation with a big unit cell. This can be directly compared with the experimental results, in particular in the rare earth compounds.

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Project Title: Theory of Defects in Electronic Materials

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Project Scope:

This scope of the research supported by this project includes carrying out theoretical development for accurate predictions of defects properties in electronic materials, and performing, 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 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), time-dependent DFT (TDDFT), hybrid functional methods, and the many-body GW quasiparticle perturbation theory for accurate prediction of defect properties in electronic materials. One of the focuses of this research is to investigate accuracy and limitations of the hybrid functional methods for defect calculations, especially for localized states in wide gap semiconductors, and to 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) Anisotropic Polaron and Shallow Dopants in Wide Band-Gap (WBG) Semiconductors

Wide band gap semiconductors (E_g > 3 eV) are key materials for optoelectronics and power electronics. Doping these materials to specific conductivity is often among the most difficult steps towards such applications. GaN is one of the most successful WBG semiconductors for making short wave-length light-emitting devices largely owing to the successful p-type doping with Mg. As a promising low-cost alternative to GaN, ZnO has attracted significant attention in recent years. However, stable p-type doping of ZnO is still a major obstacle towards its widespread applications. Even for GaN, further improving the p-type conductivity is highly desirable. The doping bottleneck has been found to be intimately related to the formation of small polarons in WBG semiconductors.

We have made important progress in understanding the p-type doping problem in ZnO. We find a new type of polaron which explains why GaN can be p-doped with Mg, whereas ZnO cannot be effectively p-doped with Li. The novel feature of the Mg related polaron in GaN lies in its highly anisotropic localization (Fig. 1), i.e., effective-mass-like in one direction but strongly localized in the

other directions. Our results resolve a long-standing puzzle why band conduction can still be possible in some polaronic materials. We find that GaN is a borderline WBG material whose p-type conductivity is facilitated by an incomplete polaron localization. In contrast, doping ZnO with Li falls on the other side of the borderline. The system cannot sustain an anisotropic hole state. The Li-on-Zn defect undergoes a spontaneous symmetry breaking, leading to a fully localized, therefore deep, hole state. Overcoming the doping bottleneck in ZnO and other WBG semiconductors thus hinges on our ability to find dopants that can stabilize the anisotropic polaron.

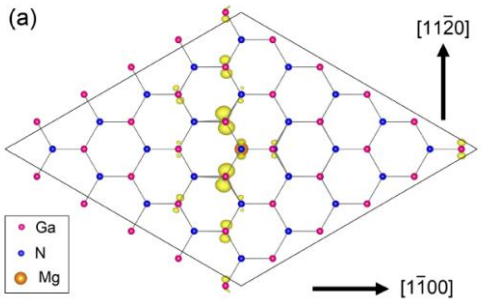

Fig. 1. Charge density of the hole state of Mg substitution in GaN showing the anisotropic hole localization.

(2) Prediction of Carbon Kagome Lattice

Kagome lattices have attracted great research attention for understanding the physics of frustration. They were first studied in the context of spin frustration of anti-ferromagnetic systems, where a spin cannot find an orientation which simultaneously favors all spin-spin interactions with its neighbors. Spin frustration is known to yield fascinating effects such as the formation of spin ices, spin liquids, and spin glasses. Frustration can also lead to new fundamental phenomena such as fractional quantum numbers, magnetic monopoles and exotic forms of superconductivity. Beyond spin, other fundamental physical quantities such as electronic orbitals should also show frustration in a Kagome lattice. For example, a p-orbital can be viewed as a rank-one tensor (i.e., a vector) with a clearly defined polarity pointing from its negative lobe to positive lobe, in analogy to a spin vector.

Based on the above consideration, we recently proposed a three-dimensional (3D) elemental carbon Kagome lattice (CKL), whose stability is comparable to the fullerene C_{60}. This investigation is performed at the crossroad between the physics of orbital frustration with that of graphene and graphene-derivatives. We show that orbital frustration in this system not only exists, but it is also responsible for the emergence of a direct band gap of 3.43 eV at the Γ point of the Brillouin zone (BZ), as determined by hybrid-functional calculations [see Fig. 2(a)]. Our study of the transition of a zero-gap graphene-like network for which no orbital frustration takes place to a fully frustrated CKL reveals that the gap is a direct result of frustration-induced metal-insulator transition. We further show that the electronic and optoelectronic properties of the CKL are excellent for applications since both the electron and hole effective masses are comparable to those of Si, while the imaginary part of the dielectric function, which determines the optical properties, is similar to that of direct-gap GaN and ZnO [Fig. 2(b)-(c)].

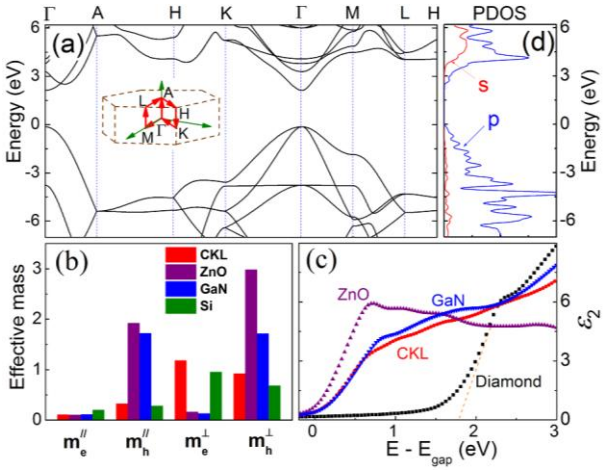

Fig. 2. (a) band structure, (b) projected density of states, (c) effective masses, and (d) optical absorption of CKL.

(3) Diamond NV$^-$ like color center in cubic boron nitride

A successful transition from a transistor-based computing paradigm to quantum computing requires identifying systems with desired properties such as having a long quantum coherence time and being

scalable. In this regard, the negatively charged nitrogen-vacancy (NV^-) center in diamond, with its unique spin and optical properties, has emerged as a promising solid system for quantum information applications. The promise of the NV^- center has inspired unprecedented research interests in optical manipulations of defect states, and has fostered the search for alternative isoelectronic and possibly low-cost defect systems. Since c-BN shares many of the interesting properties with diamond, it is likely the best system to host an NV−like isoelectronic defect center. We predict a diamond NV−like color center in c-BN. This defect center consists of a substitutional oxygen and an adjacent boron vacancy, ON−VB (shown in Fig. 3) and displays most of the interesting properties found in the NV center. We find that the electronic structure of the ON−VB center resembles that of the NV center in diamond, thus providing a potentially low-cost alternative to the NV center. The ON−VB center is optically accessible with a zero-phonon line of about 1.6 eV, to be compared with 1.95 eV for the NV center. The ON−VB center also shares much of the characteristics of the GC-2 center often observed in c-BN.

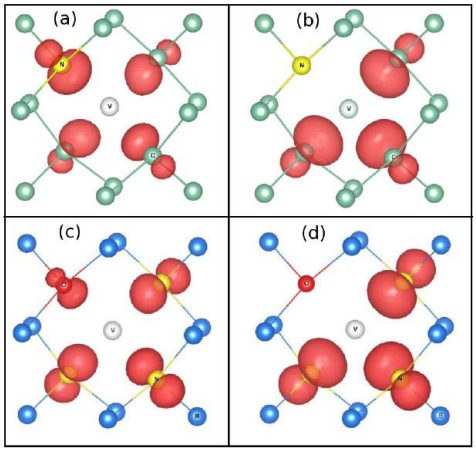

Fig. 3. Charge density plots for the minority-spin a1 [(a) and (c)] and e [(b) and (d)] defect states for the NV^- center in diamond and the O_N–V_B center in c-BN, respectively.

Future Plans (2014-2015):

(1) Charged defect energy in two-dimensional (2D) systems

We are currently investigating the feasibility of calculating charged defect formation and transition energies in two-dimensional systems. The widely-used jellium charge background model is notorious inaccurate, as it is mathematically proven to diverge with the size of the vacuum region used in the calculation. We have reformulated the problem and preliminary results for defects in 2D boron nitride suggest that one should be able to obtain accurate and converged results using an extrapolation method.

(2) Transient non-radiative recombination centers in wide-gap semiconductors

Current defect theories attribute non-radiative recombination either to a pre-existing defect or defect complex via the Shockley-Read-Hall mechanism or to a defect-free intrinsic materials property known as the Auger effect. We recently found that there could exist a transient mechanism for non-radiative recombination where defect formation and annihilation play a pivotal role in the recombination process but the formation of actual permanent defects may never happen. We are currently investigating such a mechanism for non-radiative recombination in GaN and its alloys with InN under a high density carrier injection.

(3) Defects and metastability of organic-inorganic hybrid solar cell materials

Recent progress in organic-inorganic hybrid solar cell material *MA*PbI_3, where *MA* stands for methylammonium, represents a real breakthrough in fabricating low-cost, high-efficiency solar cell devices. Yet, the magic of the exceptional efficiency in such a low-cost material is not necessarily understood. We are currently investigating the physical origin for the exceptional defect tolerance of the material and the origin for the dissociation of the material under illumination, as well as due to interaction with moisture.

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Magnetization dynamics at elevated temperatures

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Project Scope

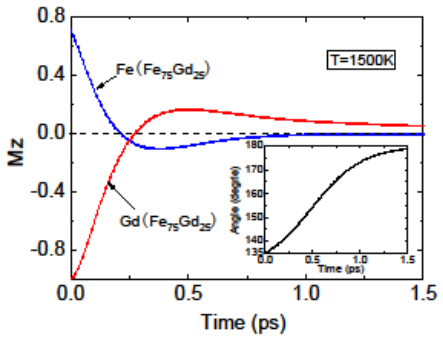
The present research program aims at better understanding of fast magnetization dynamics at high temperatures. Fast magnetization dynamics excited by external perturbations, such as laser pumping, high- current heating and strong THz electromagnetic radiation, involves physics on the time scale of picoseconds and femtoseconds, several orders of magnitude faster than conventional nanosecond magnetization dynamics in hard disk drive devices. While a number of qualitative and phenomenological theories had been established previously, there were very limited connections between these theories with vastly available experimental data. In the last several years, we have developed a new formulation which is based on the quantum kinetic approach, capable of addressing novel magnetization dynamics at elevated temperature for many ferromagnetic materials. The project was started four years ago and we were wrapping it up last year. At present, we focus on a related and broader project on novel quantum spintronic phenomena such as quantization and coherence of spin-polarized currents in metal-based multilayers beyond the present-day semi-classical physics.

Recent Progress (2013-14)

Modeling fast magnetization

Experimentally, the fast magnetization dynamics excited by laser pimping and picosecond current pulses have been studied for various magnetic compounds and structure. We utilize the self-consistent Bloch (SCB) equation which we established a few years ago to investigate element specific dynamics in ferromagnetic multilayers and alloys. Among other things, we find that 1) the time scale in which the magnetization relaxes to its equilibrium states could be vastly different for each magnetic element even though the exchange coupling of the magnetic layers are strongly coupled—this quantitatively and qualitatively agrees with available experiments. We found that the time scales of individual magnetic element are not directly related to the magnetic momentum as previously reported, instead, it depends mainly on the relative exchange coupling parameters among magnetic ions as well as equilibrium temperature and alloy concentration; 2) for ferrimagnetic materials such as FeGd, the

antiparallel alignment between Fe and Gd can be simultaneously switched at certain ranges of temperature and laser intensity, as shown in the figure below; 3) the critical slowdown can be explicitly shown when the temperature is approaching Neel or Curie temperature, and the dynamic scaling is consistent with the conventional analytic theory on dynamic critical exponents. These simulations validate our CBS equation developed earlier.

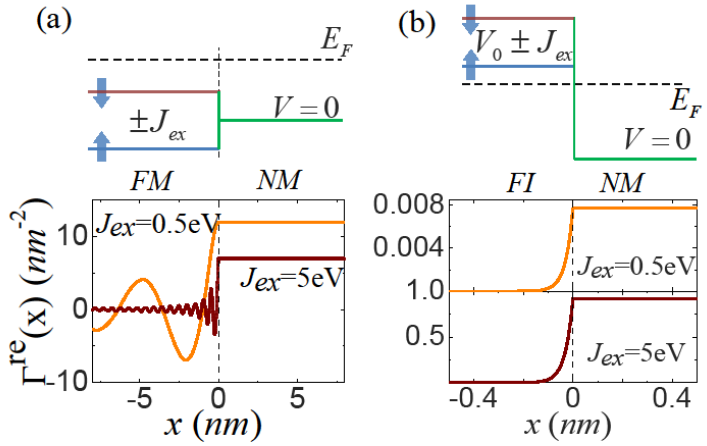


(Caption) The magnetization reversal of Fe and Gd in a ferrimagnetic alloy Fe$_{75}$Gd$_{25}$ at a temperature T=1500K. We assume the initial direction of Fe is along the z-axis, while the angle of Gd is 135^0 relative to Fe.

Spin pumping in magnetic multilayers

Most recently, our research is slightly deviated from our origin proposed subject. We consider this work as a preliminary result for the continuation of the DOE project (if funded).

Spin pumping, which describes generation of a spin current in a non-magnetic metal layer by an adjacent processing ferromagnetic layer, has emerged as one of the most important spin transport phenomena. Up until now, theoretical description of the spin pumping current is formulated by the scattering approach in which spin conductance is solely determined by reflection and transmission coefficients between the leads and the conductor. While this approach has been successfully used for explaining and predicting several novel experiments, it also suffers a few serious drawbacks. We have used the time-dependent linear response approach to reformulate the spin pumping conductivities. We obtained a few salient features beyond the current scattering theory: 1) the mixing conductance is non-local, not just simply related to the interface reflection coefficients; 2) the effect of disorders on spin pumping current can be explicitly included and thus, spin pumping depends on the interface as well as bulk scattering parameters; 3) an oscillatory spin current exists inside the processing magnetic layer; 4) in the disorder-free case, the theory reduces to that of the scattering formalism. These results have an immediate impact on most of the spin pumping experiments recently performed.



(Caption) Position-dependence of the real part of the spin pumping conductance of two semi-infinite bilayers. (a) Both magnetic (M) and non-magnetic (N) layers are metallic. (b) The M layer is a ferromagnetic insulator (FI) and the N layer is a metal. In both cases, the spin current in the N layers are constants. The spin current decays oscillatory in the metallic FM and exponentially in the FI. The Fermi energy is 6 eV and the exchange parameters are J_{ex}=0.5 and 5, respectively. The spin-dependent potentials relative to the Fermi level are also shown.

Future directions

With the completion of the current project, we have moved onto emerging topics in spintronics. In the next several years, we will take on the following topics, based on the preliminary results outlined above.

- With a strong interface spin-orbit coupling, e.g., Pt/Co, the spin pumping into Pt layer would be strongly altered. We should expand the spin conductivity calculation and correlate the spin current loss at the interface to the charge current generation observed experimentally.
- When the spin current is injected into a topological interface via spin pumping, an unconventional conversion to a charge current occurs. We will apply our approach to such highly non-trivial scenario.
- As the lateral dimension shrinks, we expect robust quantum effects: the quantization of the spin pumping current (the integer number of Bohr magnetron per cycle) and coherence of spin current.
- We will evaluate the experimental feasibility of quantum spin transport in metal-based magnetic nanostructure.

Publications (2013-14)

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Theory of semiconductor Nanostructures in 0D, 1D and 2D (Since 8/2013)

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Project scope: Testing our fundamental understanding of the basic interactions that govern the electronic properties of semiconductor nanostructures requires access to spectroscopically rich and highly resolved data. Alas, this is afforded mostly by rather *large* nanostructures such as self-assembled epitaxial systems (InAs/GaAs; HgTe/CdTe; GaAs/AlAs), containing typically 100,000 or 1,000,000 atoms per computational unit cell. This size regime is well outside the range of DFT methodologies. At the same time, continuum-like methods (based on envelope functions) that can handle large nanostructures lack the atomistic resolution needed to describe the underlying electronic structure phenomenology. Using our previously developed screened-pseudopotential plus configuration interaction approach we can directly address million–atom nanostructures of the sort described above. Our scope is to use this methodology for understanding fundamental electronic processes in nano and eventually meso scopic systems..

Recent Progress (synopsis): The way large scale calculations lead to theoretical discovery of new nanostructure mechanisms (i) Discovery of a first-order, giant Rashba spin splitting in semiconductor nano wires; (ii) the discovery of a novel channel of light-hole to heavy-hole coupling in strained quantum dots, mediated by intermediate states (analogous to super exchange in magnetism), (iii) prediction of emergent density of states features in nanowires that are not associated with the conventional, orbitally classified states such a 1S, 1P, 1D. (iv) Microscopic explanation of the spectroscopic features observed in million-atom quantum dots embedded in nanowires. (v) Careful calculation of the electronic states in HgTe/CdTe quantum wells at the critical well thickness where topological band inversion occur shows that the relevant HH1 and E1 states *anti-cross* rather than cross, leading to *gapped Dirac cones*.

Some details on these and other, in-progress ideas follow.

(a) Supercoupling explains the heavy-hole and light-hole mixing in Self-assembled quantum dots (with Jun-Wei Luo and Gabriel Bester)

Heavy-hole (HH) and light-hole (LH) mixing is a key property to explore fundamental building blocks for spin-based quantum computation using semiconductor quantum dots. Like in the case of a diatomic molecule the eigenstates of atom A mix with the ones of atom B to form molecular orbitals, the magnitude of HH-LH mixing is inversely proportional to the energy separation between unperturbed HH and LH states. By studying various types of self-assembled quantum dots, we show that HH states can significantly mix with LH states, despite the fact that they are energetically well separated, through a novel supercoupling — a coupling meditated by

intermediate states amplifying the interaction (analogous to super-exchange in magnetism mechanism). This supercoupling offers a control which has far reaching consequences for quantum dot spintronics, such as the generation of entangled photon pairs, the decoherence of hole states, the optical polarization anisotropy and the preparation of qubits.

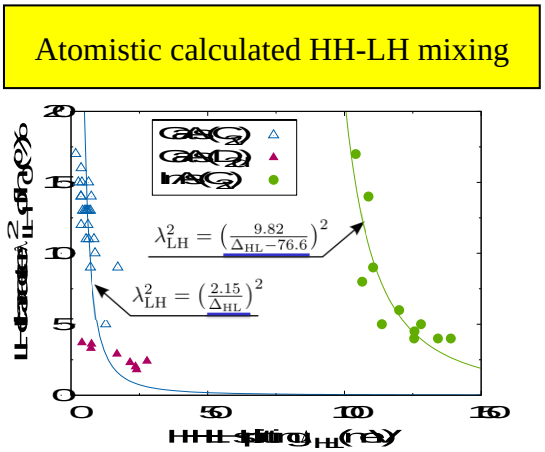

FIG. 1: Bulk LH character of the QD's ground hole states **h**0 as a function of HH-LH splitting for unstrained (GaAs/AlAs left hand side) and strained InAs/GaAs (in green ,right hand side) dots. Whereas the LH-HH coupling for unstrained dots can be described by a simple curve (left), for strained dots (right) the description of the coupling requires a reduced denominator that represents the enhanced interaction ('super coupling') due to intermediate HH states, (analogous to super exchange)

(b) Quantum dots in a nanowire System for quantum photonics

NATURE MATERIALS VOL 12 p. 440 (2013)

[With :M. Heiss, Y. Fontana, A. Gustafsson G. Wüst, C. Magen, D. D. O'Regan, J.W. Luo, B. Ketterer1 S. Conesa-Boj, A. V. Kuhlmann, J. Houel, E. Russo-Averchi, J. R. Morante, M. Cantoni, N. Marzari J. Arbiol, A. Zunger, R. J.Warburton and A. Fontcuberta i Morral]

Quantum dots embedded within nanowires represent one of the most promising technologies for applications in quantum photonics. Whereas the top-down fabrication of such structures remains a technological challenge, their bottom-up fabrication through self-assembly is a potentially more powerful strategy. However, present approaches often yield quantum dots with large optical linewidths, making reproducibility of their physical properties difficult. We present a versatile quantum-dot-in nanowire system that reproducibly self-assembles in core–shell GaAs/AlGaAs nanowires. The quantum dots form at the apex of a GaAs/AlGaAs interface, are highly stable, and can be positioned with nanometre precision relative to the nanowire centre. Unusually, their emission is blue-shifted relative to the lowest energy continuum states of the GaAs core. Large-scale electronic structure calculations show that the origin of the optical transitions lies in quantum confinement due to Al-rich barriers. By emitting in the red and self-assembling on silicon substrates, these quantum dots could therefore become building blocks for solid-state lighting devices and third-generation solar cells.

(c) Future plans (in progress): Reinterpretation of the expected density of states of semiconductor nanowires (With Jianping Wang, Jun-Wei Luo, Lijun Zhang, and Alex Zunger)

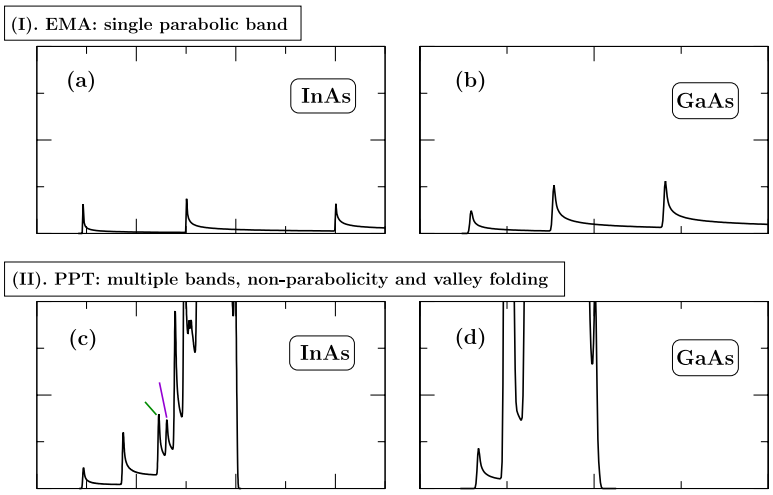

Figure 1: The DOS of conduction bands for InAs (a and c) and GaAs (b and d) nanowires at the diameter of 5 nm calculated in the framework of (I, upper panels) the EMA approach, and atomistic (non-self consistent) pseudo potential theory (PPT). All the nanowires are in the zinc blende structure and oriented along the [111] direction. The quantum-confined shell-like feature (S in orange, P in blue, D in green) of identified peaks is labeled and in (II) for those peaks with unknown feature the question mark (in red) is placed. Note that for the same material (a and c, or b and d) the scales of both x-axis and y-axis are same.

One-dimensional semiconductor nanowires hold the promise for many optoelectronic applications since they combine the advantages of *quantized* in-plane energy levels (as in zero-dimensional quantum dots) with a *continuous* spectrum along the growth direction (as in three-dimensional bulks). This dual characteristics is reflected in the density of states (DOS) which is thus the key quantity describing the electronic structures of nanowires, central to the analysis of transport and spectroscopy. By comparing the widely used, 'standard model' of wire DOS--the effective mass approximation (EMA)--with direct atomistic pseudopotential calculations of the wire DOS for GaAs and InAs, we uncover significant qualitative and quantitative shortcomings of the standard description. The EMA description renders the wire DOS as a series of sharply rising peaks having slowly decaying tails, with characteristic peak spacing, all being classifiable in the language od *orbital momenta* 1S, 1P, 1D... Herein we predict that for wire diameters of the order of ~ 50 A the picture changes significantly in that not only does the profile of each DOS peak loses its pronounced asymmetry, with significant changes in peak spacing and heights, but that also the *origin* of the high- energy peaks changes fundamentally: Below a critical wire diameter, the orbitally- classified states disappear and a new set of DOS peaks folded-in from other valleys emerge. We describe how distinct physical effects beyond the conventional EMA contribute to these realistic DOS features. These include effective mass discontinuity between nanowire and its environment, non-parabolicity of bands, coupling among multiple bands and band folding of non-□ valleys]. These results represent a significant step toward understanding the intriguing electronic structure of nanowires reflecting the coexistence of discrete and continuum states. Experimental examinations of the predicted novel DOS features are called for.

(d) Future plans (in progress): Different types of band edge transitions in layered group-VIB transition metal dichalcogenides as a function of layer thickness (Lijun Zhang* and Alex Zunger)

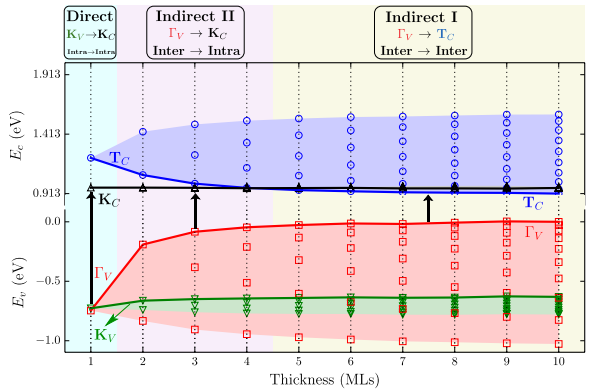

Fig 2: Evolution of various band-edge states (as labeled in Fig. 1) from the multiple-layered films (with the AB-type stacking) to the monolayer film of MoS_2. The energy levels corresponding to different band-edges are shown in different colors: Γ_V (red), K_V (green), T_C (blue) and K_C □□□□ck□. For each state, the span of energy levels is shaded in lighter color, where the boundary governing band-gap is shown in solid line. The valence band maximum (i.e. Γ_V) at 10 MLs is set to zero once the relative energy levels were alignment with respect to vacuum. The first y-axis tick of the upper panel (for conduction bands) corresponds to the calculated band-gap at 10 MLs. The band-gap transition shows three distinct regions (see text for more detailed description): Indirect I ($\Gamma_V \rightarrow T_C$, in yellow background), Indirect II ($\Gamma_V \rightarrow K_C$, in pink), and Direct ($K_V \rightarrow K_C$, in cyan).

Group VIB transition metal dichalcogenides with the hexagonal 2H structure show indirect band gaps in bulk form but become optically active direct band gap materials at monolayer thickness, thus converting the system into a useful absorber. While it is tempting to associate orbital energy changes vs thickness with kinetic energy quantum confinmemt (as in nanostructures), in this case it is clear that the band edge states Kv and Kc forming the initial and final states of the direct gap system are, in fact, spatially localized within the layers at all thicknesses and so are not subject to wavefunction confinement as thickness is reduced. By classifying the main band edge states into interlayer delocalized (Tc and Gama v) and intra-layer localized (Kv , Kc) states we find that as the film thickness decreases, there appear three distinct regimes of band-gap transition: (i) For thick films we encounter transitions between k-space indirect Gamav-Tc states connecting interlayer delocalized initial and final states (direct ,or "type I" in real space) (ii) For intermediate thickness films we find transitions between k-space indirect Gamav-Kc states, connecting layer-localized initial state with interlayer delocalized final states (indirect ,or "type II" in real space) (iii) Finally, for monolayer thickness we encounter transitions between k-space direct Kv-Kc states connecting interlayer localized initial and final states (direct ,or type I in real space). We show how the various regimes are predictedto change with modification of cations and anions in the MX_2 (M= Cr, Mo,W and X= S, Se, Te) series.

Unconventional Spin and Orbital Ordering in Semiconductor Nanostructures

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PROJECT SCOPE

Semiconductor nanostructures, such as quantum dots (QDs), provide an interesting interplay of interaction effects in confined geometries and novel opportunities to control the spin and orbital ordering at the nanoscale. However, owing to the computational complexity of including even a small number of magnetic impurities (~10), there is a need to apply various approximation schemes to accurately describe magnetic QDs. Unfortunately, a widely used mean-field theory leads to spurious phase transitions and an incorrect description of the carrier density in small magnetic systems. These difficulties impede the progress in understanding the fundamental properties and potential applications of semiconductor nanostructures. To systematically address this situation, our main objectives are: (i) developing a comprehensive framework suitable to study the interplay of many-body effects and quantum confinement in small magnetic systems, focusing on the inclusion of spin fluctuations and developing computational methods beyond the mean-field approximation. (ii) exploring novel possibilities for the control of spin and orbital ordering in semiconductor nanostructures, as well as to providing proposals for their experimental implementation.

RECENT PROGRESS

Robust Magnetic Polaron Formation in (II,Mn)VI Quantum Dots

The formation of a magnetic polaron (MP), studied for over 50 years, is seemingly well-understood. A cloud of localized impurity spins, aligned through exchange interaction with a confined carrier spin, leads to an energy gain by MP formation, E_{MP}. Almost all previous MP studies in QDs relied on systems with Type-I band alignment [the position of a conduction band (CB) minimum and valence band (VB) maximum coincide], promoting fast electron-hole recombination and thus suppressing the carrier-mediated magnetic ordering. In collaborations with experimentalists at U. Buffalo [1], we explored paths to overcome those limitations by focusing on Type-II QDs (Fig. 1) with a strong electron-hole spatial separation, leading to a much slower recombination—the carriers have more time to align nearby Mn-spins. A conventional MP behavior of a strong E_{MP} suppression with temperature (T) and magnetic-field (B) is observed for Mn-doping outside of the QD [Figs. 1(c) and (e)]. Both thermal disorder and B-field [partially pre-aligns Mn spins and thus the energy gain through the subsequent exchange-driven alignment would be suppressed] give the expected behavior. In contrast, a qualitatively different behavior of robust MPs is seen for Mn-doping in the QDs with a strong hole-Mn overlap [Figs. 1(d) and (f)]. We explain theoretically such a peculiar $E_{MP}(T,B)$ behavior and suggest a the feasibility of a thermally *enhanced* magnetic ordering in QDs. We also explore the possibility for the emergence of strongly-correlated states in magnetic QDs with multiple occupancy.

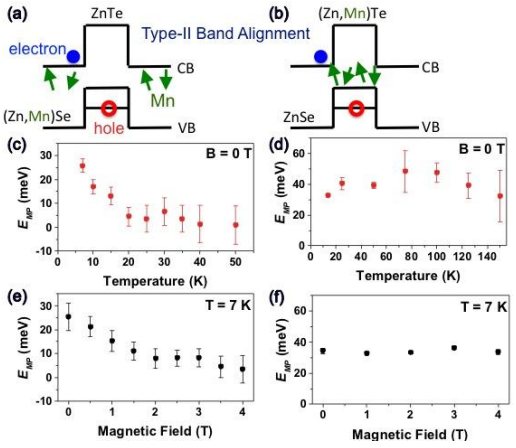

Fig. 1 Type-II band alignment in (a) (Zn,Mn)Se/ZnTe and (b) ZnSe/(Zn,Mn)Te QDs. (c), (d) Temperature dependence of the MP energy. (e), (f) B-field dependence of the MP energy [1].

Nodal Ground States and Orbital Textures in Semiconductor Quantum Dots

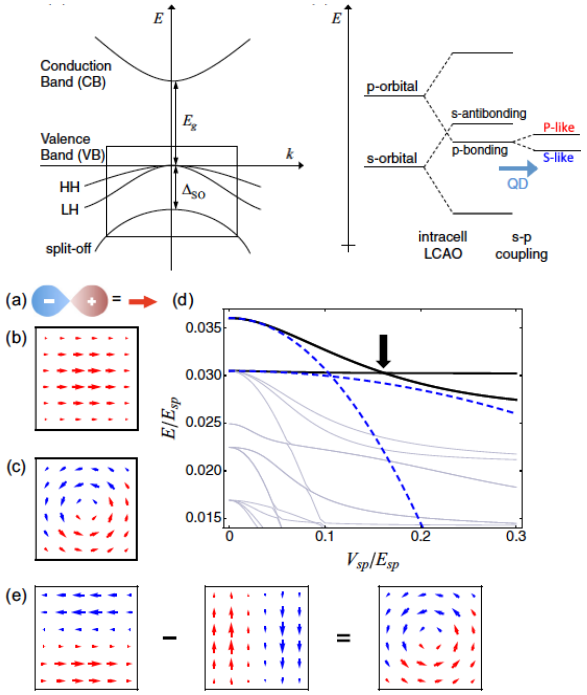

Fig. 2 Top: A sketch of a band structure in zinc-blende semiconductors. E_g is the energy gap, Δ_{so} the spin-orbit gap, HH, LH are heavy and light hole bands. The s-p coupling influences the bonding and ordering of QD levels. Bottom: (a) Vector representation of $p_{x,y}$ orbitals. (b) S- and P-like vortex states without s-p coupling V_{sp}=0. (d) At larger V_{sp} there is a crossing of nodeless a S-like state and a nodal P-like (vortex) state that becomes the ground state. Dashed lines are perturbative results. (e) A vortex state as a superposition two P-like states [2].

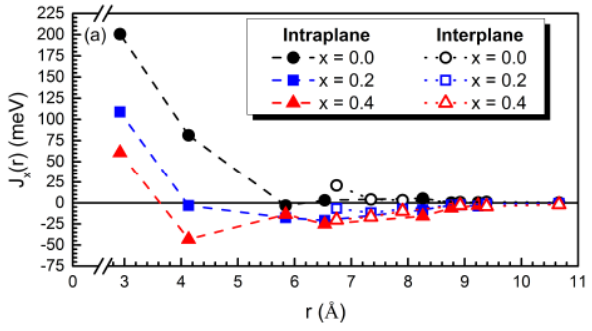

Fig. 3 The magnetic interaction's doping dependence as a function of distance between Mn pairs for different hole dopings, x in (Ba,K)(Zn,Mn)$_2$As$_2$. A corresponding sign change, as a function distance, reveals the competition of the antiferromagnetic short-range superexchange and ferromagnetic carrier-mediated indirect changes, leading to frustrated magnetism [3].

Conventional understanding implies that the ground state of a nonmagnetic quantum mechanical system should be nodeless. While this notion also provides a valuable guidance in understanding the ordering of energy levels in semiconductor nano-structures, there are reports that *nodal* ground states for holes are possible. However, the existence of such nodal states has been debated and even viewed as a merely theoretical artifact. Using complementary approaches of both $\boldsymbol{k}\cdot\boldsymbol{p}$ and tight-binding models, further supported by a novel effective Hamiltonian for a continuum model, we reveal that nodal ground states in QDs are not limited to a specific approach [2]. Remarkably, the emergence of nodal hole states at the top of the valence band can be attributed to the formation of orbital vortex textures (Fig. 2) through the competition between the hole kinetic energy and the coupling to the conduction band states. We propose an experimental test for our predictions of reversed energy ordering and the existence of nodal ground states. Our findings of orbital textures could be also relevant for other materials systems.

Theory of Novel Frustrated Dilute Magnetic Semiconductors

A novel magnetic semiconductor (Ba,K)(Zn,Mn)$_2$As$_2$, isostructural to 122 Fe-based superconductors, has a decoupled spin and charge doping, unlike the vast majority of magnetic semiconductors. This provides a unique opportunity to elucidate the microscopic origin of the magnetic interaction and ordering in dilute magnetic semiconductors (DMS). We show that (i) conventional density functional theory accurately describes this material, and (ii) the magnetic interaction emerges from the competition of the short-range superexchange and the longer-range

spin-spin interaction mediated by the itinerant As holes, depicted in Fig. 3 [3]. Using thermodynamic arguments we explain the formation of Mn-dimers and reduction of experimentally observed magnetic moments. The carrier-mediated interaction can be viewed as a high-doping extrapolation of double exchange with the Schrieffer-Wolff p − d interaction representing an effective Hund's rule coupling, J_{eff} [3]. The key difference between the classical double exchange and the actual interaction in DMS is that an effective J_{eff}, as opposed to the standard Hund's coupling J, depends on the Mn d−band position with respect to the Fermi level, and thus allows tuning of the magnetic interactions. We predict a clear path to enhance T_C in novel DMS with an already record-high T_C.

Phonon Laser using Quantum Dot Spin States

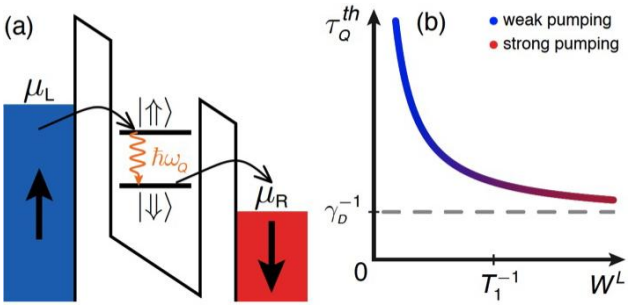

Fig. 4 (a) Phonon emitter: A QD in the sequential-tunneling regime with ferromagnetic leads. (b) The threshold phonon lifetime τ_Q as a function of the tunnel rate W_L, showing the crossover between the weak ($W_L << 1/T_1$) and the strong ($W_L >> 1/T_1$) pumping regimes, where T_1 is the spin relaxation time [5]. For $\tau_Q < 1/\gamma_D$, where γ_D is the rate of the generation of phonon population in a laser, no lasing is possible regardless of the pumping regime [4].

Realizing acoustic analogues of active optical devices has been a long-standing challenge. Phonon lasers could provide versatile sources of coherent acoustic waves used for 3D imaging of nanostructures or creating periodic strain of a material to rapidly modulate its optical and electronic properties. We propose a nanoscale realization of a phonon laser utilizing phonon-assisted spin flips in QDs to amplify sound, depicted in Fig. 4 [4]. Owing to a long spin relaxation time, the device can be operated in a strong pumping regime, in which the population inversion is close to its maximal value allowed under Fermi statistics. In this regime, the threshold for stimulated emission is unaffected by spontaneous spin flips. Considering a nanowire with QDs defined along its length, we show that a further improvement arises from confining the phonons to one dimension, and thus reducing the number of phonon modes available for spontaneous emission. Our work calls for the development of nanowire-based, high-finesse phonon resonators.

Other Topics

We have studied the influence of spin-orbit coupling on spin decoherence and magnetic ordering in quantum dots and described the similarities between the role of nuclear spins and magnetic impurities [5]. In the presence of spin-orbit coupling, the impurity-impurity interactions are no longer spin conserving. We quantify the degree of this symmetry breaking and show how it relates to the spin-orbit coupling strength. We identify several ways how the impurity ensemble can in this way relax its spin by coupling to phonons. A typical resulting relaxation rate for a self-assembled Mn-doped ZnTe quantum dot populated by a hole is 1μs. We also show that decoherence arising from nuclear spins in lateral quantum dots is still removable by a spin echo protocol, even if the confined electron is spin-orbit coupled. The PI's (DOE-supported) postdoc, Karel Vyborny (now a permanent staff member at the Institute of Physics, Prague, Czech Republic) has led a large collaborative project [6] to develop a systematic understanding of measured magneto-optical effects in (Ga,Mn)As, a prototypical dilute magnetic semiconductor. The focus was on polarization-resolved effect of magnetic linear dichroism and birefringence,

arising from the polarization-dependent index of refraction. An accurate description of such magneto-optical studies is one of the key requirements for a successful theory of dilute magnetic semiconductors.

FUTURE PLANS

We plan to investigate several peculiar effects for magnetic ordering and frustration in QDs arising from the interplay of quantum confinement, Coulomb interactions, and distribution of magnetic impurities. The focus will be on applying Monte Carlo simulations to complement more phenomenological methods of including spin fluctuations. We will explore the influence of spin-orbit coupling on orbital textures in quantum dots and develop effective Hamiltonians to elucidate the interplay of competing interactions. In quantum dot and quantum ring geometries we will investigate topological states and their detection. In our studies of semiconductor/ superconductor junctions, in the presence of spin-orbit coupling, we have preliminary results for novel anisotropic Andreev reflection (a phase-coherent scattering process where at the superconducting interface an incident electron is reflected as a hole, while two electrons are transferred to the superconducting region). We plan to explore the prospect of using such Andreev reflection to probe the strength of interfacial spin-orbit coupling in different superconducting junctions.

List of Papers Supported by this DOE Award (2013-2014):

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