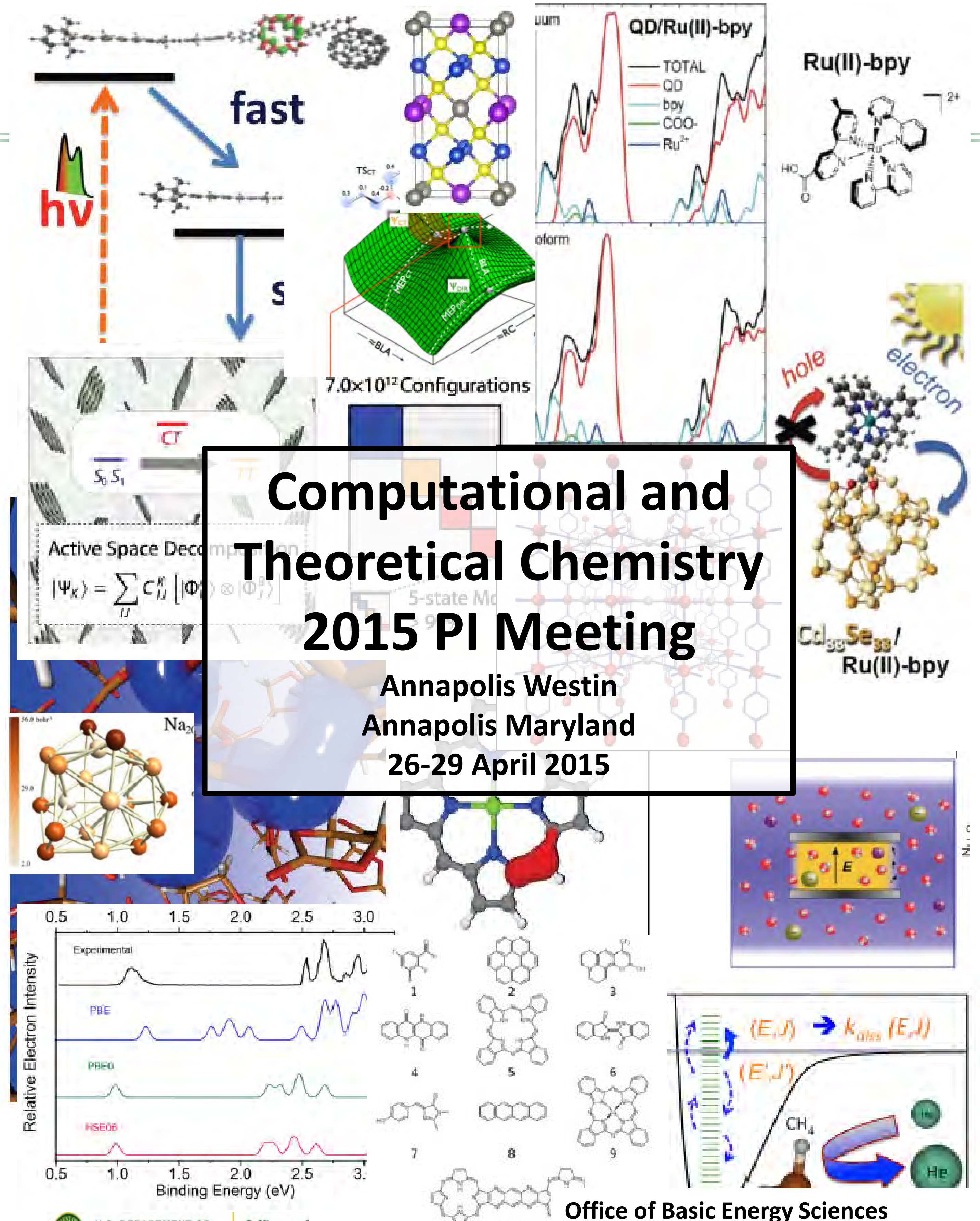


Computational and Theoretical Chemistry 2015 PI Meeting

Annapolis Westin
Annapolis Maryland
26-29 April 2015

U.S. DEPARTMENT OF ENERGY
Office of Science

Office of Basic Energy Sciences
Chemical Sciences, Geosciences , and Biosciences Division

FORWARD

This abstract booklet provides a record of the U.S. Department of Energy first annual PI meeting in Computational and Theoretical Chemistry (CTC). This meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and includes invited speakers and participants from BES predictive theory and modeling centers, Energy-Frontier Research Centers, SciDAC efforts and an SBIR/STTR project.

The objective of this meeting is to provide an interactive environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually complementary expertise, will identify needs of the research community, and will focus on opportunities for future research directions. The agenda has several invited talks and many brief oral presentations. In response to a questionnaire about meeting organization, many of the participants noted that it would be desirable to provide all CTC researchers with the opportunity for an oral presentation since this is the first annual meeting. There should be ample time during the evenings for detailed follow-up discussions and the meeting room is available during this time for informal breakout sessions.

We thank Mark Gordon, Martin Head-Gordon, and Bruce Garrett for participating in pre-meeting discussions about the organization and goals of the afternoon strategic planning session and hope that everyone will be ready to actively contribute their ideas during these discussions.

We thank all of the researchers whose dedication and innovation have enhanced the goals of Basic Energy Sciences and made this meeting possible and, we hope, productive. We look forward to seeing this community build upon your successes and look forward to the next joint meeting.

We thank Diane Marceau of the Chemical Sciences, Geosciences and Biosciences Division and Connie Lansdon of the Oak Ridge Institute for Science and Education for their important contribution to the technical and logistical features of this meeting.

Warmest regards and best of luck to all!

Mark Pederson, Wade Sisk, Gregory Fiechtner, and Larry Rahn

SHORT AGENDA 2015 CTC PI Meeting

26 April Evening	**Dinner in Groups on Your Own**	
27 April 7:00	Continental Breakfast	
27 April 8:00	**Welcome**	Mark Pederson
27 April 8:05	**News From CGBS**	Tanja Pietraß
CHAIR: Nandini Anath		
27 April 8:30	**Simulation of Photochemical Processes and Transport**	Truhlar, Baruah, Dunietz, Galperin, Shiozaki
27 April 10:30	Coffee	
CHAIR: David Yarkony		
27 April 10:50	**Beyond Born-Oppenheimer Dynamics**	Furche, Lewis, Niklasson
27 April 11:50	Working Lunch	
CHAIR: Eric Schwegler		
27 April 13:30	**Beyond Density Functional Theory**	Carter, Krakauer, Miller, Zgid, Wasserman, Ruzsinszky, Gagliardi, Ogut
27 April 15:50	Coffee	
27 April 16:10	**Crosscutting Challenges for Theory and Computation**	Garrett, Windus, Gordon, Head-Gordon
27 April 17:50	The Semantic Web for Chemistry	Neil Ostlund
27 April 18:10	DINNER AT HOTEL	
28 April 7:00	Continental Breakfast	
CHAIR: Lee Woodcock		
28 April 8:00	**Large Scale Methods**	Yang, Gordon
	CHAIR: Heather Kulik	
28 April 9:00	**Surfaces and Plasmonics**	Kara, Schatz, Jackson
28 April 10:00	Coffee	
CHAIR: Margaret Cheung		
28 April 10:20	**Methods for Liquids, Electrolytes, and Polarization**	Pask, Panagiotopoulos, Herbert, Fernandez Serra, Car, Luzar
28 April 12:20	Working Lunch	
CHAIR: Gregory Schenter		
28 April	**Porous Materials**	Siepmann, Paesani, Johnson, Evans, Mundy

13:30		
28 April 15:30	Coffee	
28 April 16:00	**Crosscutting Challenges for Theory and Computation**	Mundy, Truhlar, Perdew, Gagliardi, Carter, de Jong
	DINNER IN GROUPS IN ANNAPOLIS	
29 April 7:00	Continental Breakfast	
CHAIR: Theresa Windus		
29 April 8:00	**Spin, Spin-Orbit, and Magnetism in Molecular Systems**	Long, Krylov, Peralta, Jasper, Khanna, Li
29 April 10:00	Coffee	
CHAIR: Jim Evans		
29 April 10:30	**Surfaces, Plasmonics, and Excitonics**	Shuford, Greeley, Jang, Kilina, Govind
29 April 11:45	**Closing Remarks**	Pederson

CTC 1

U.S. DEPARTMENT OF ENERGY | Office of Science
Office of Basic Energy Sciences
Chemical Sciences, Geosciences & Biosciences Division

First Computational and Theoretical Chemistry (CTC) Research Meeting

Registration at: http://www.orau.gov/comptheo2015/

Sunday, April 26

3:00-6:00 pm **** Registration (General Session Room – Capital Ballroom) ****

Sunday Evening --- Dinner on our own in Annapolis

Monday, April 27

7:00 am **** Continental Breakfast (foyer near General Session)****

8:00 am **Mark Pederson**, DOE Basic Energy Sciences
Welcome

8:05 am **Tanja Pietraß**, DOE Basic Energy Sciences
News from Chemical Sciences, Geosciences and Biosciences

Session Ia *Simulation of Photochemical Processes and Transport*
Chair: **Nandini Anath (Cornell University)**

8:30 am **Donald Truhlar,** University of Minnesota
Quantum Photochemistry

9:10 am **Tunna Baruah,** University of Texas El Paso
Excited States in Photovoltaic Molecules

9:30 am **Barry Dunietz,** Kent State University
Photo induced charge transfer processes in organic semiconducting materials: A Fermi golden rule perspective

9:50 am **Michael Galperin,** University of California – San Diego
Energy transport and heating in an open quantum nanoscale device

10:10 am **Toru Shiozaki,** Northwestern University
Diabatic model Hamiltonians of exciton dynamics from many-body wavefunctions

10:30 am **** **Break** ****

Session Ib *Beyond Born-Oppenheimer Dynamics*
Chair: **David Yarkony, Johns Hopkins University**

10:50 am **Filipp Furche,** University of California – Irvine
Non-Adiabatic Molecular Dynamics Simulations

11:10 am **James Lewis**, **University of West Virginia**
Efficient non-adiabatic molecular dynamics for high-throughput design of photo-active materials

11:30 am **Anders Niklasson, Los Alamos National Laboratory**
Extended Lagrangian Born-Oppenheimer Molecular Dynamics

11:50 am **** Lunch ****

Session II *Beyond Density Functional Theory*
Chair: **Eric Schwegler, Lawrence Livermore National Laboratory**

1:10 pm **Emily Carter, Princeton University**
Embedded correlated wavefunction theory for semiconductors with applications to solar energy conversion

1:30 pm **Henry Krakauer, College of William and Mary**
Random walks with Slater determinants: A framework for tackling many-body problems

1:50 pm **Tom Miller, California Institute of Technology**
Quantum embedding methods for the simulation of inorganic catalysts and battery materials

2:10 pm **Dominika Zgid, University of Michigan**
New generation of embedding methods: Stochastic methods for environment with deterministically treated system

2:30 pm **Adam Wasserman, Purdue University**
Non-decomposable, non-additive, and non-interacting kinetic energy functionals: Why they matter

2:50 pm **Adrienne Ruzsinszky, Temple University**
Ground state energy differences within the random phase approximation

3:10 pm **Laura Gagliardi, University of Minnesota**
Multi-Configurational Pair Density Functional Theory

3:30 pm **Serdar Ogut, University of Illiniois – Chicago Circle**
First-principles real-space studies of electronic and optical excitations in TiO_2 nanocrystals and organic molecules

3:50 pm **** Break ****

4:10 pm *Crosscutting challenges for theory and computation (Breakout Style Session)*
Bruce Garrett (PNNL), Theresa Windus (Ames), Mark Gordon (Ames), Martin Head-Gordon (LBNL)

5:50 pm **Neil Ostlund**, The Semantic Web for Chemistry

6:10 pm **** Dinner (at hotel) ****

Tuesday, April 28

7:00 am **** Continental Breakfast (foyer near General Session)****

Session llla *Large Scale Methods*
Chair: **Lee Woodcock** (University of South Florida)

8:00 am **Chao Yang, LBL**
Fast numerical algorithms for electronic structure calculation

8:30 am **Mark Gordon, Ames Lab**

Methods for calculations on large molecular systems

Session IIIB *Surfaces and Plasmonics*
Chair: **Heather Kulik** (MIT)

9:00 am **Abdelkader Kara**, **University of Central Florida**
Recent advances on the role of van der Waals interactions in molecules/metal-surfaces system

9:20 am **George Schatz*,* Northwestern University**
Hybrid plasmonics: coupling plasmons with excitons, and plasmons with optical modes

9:40 am **Koblar Jackson, Central Michigan University**
Universal behavior of small and intermediate-sized metal clusters based on a site specific polarizability analysis

10:00 am **** Break ****

Session lV *Methods for Liquids, Electrolytes, and Polarization*
Chair: **Margaret Cheung, University of Houston**

10:20 am *Methods for Liquids, Electrolytes, and Polarization*
John Pask, Livermore National Laboratory
Discontinuous methods for large-scale quantum molecular dynamics: Li-ion solid-electrolyte interface

10:40 am **Thanos Panagiotopoulos**, **Princeton University**
Simulations of phase equilibria and self-assembly in aqueous solutions

11:00 am **John Herbert, Ohio State University**
Accurate and efficient quantum chemistry methods for non-covalent interactions

11:20 am **Marivi Fernandez-Serra, Stonybrook University**
Trajectory-Based Assessments of DFT: Applications to Water

11:40 am **Roberto Car, Princeton University**
Ab-initio molecular dynamics of soft matter via Van der Waals inclusive density functionals

12:00 pm **Alenka Luzar, Virginia Commonwealth University**

Novel modeling approaches to multiphase electrolytes

12:20 **** Lunch ****

Session V *Porous Materials*
Chair: **Gregory Schenter, PNNL**

1:30 pm **Ilja Siepmann, University of Minnesota**
The Nanoporous Materials Genome
2:10 pm **Francesco Paesani, University of California – San Diego**
Spin-dependent potentials for separations in metal organic frameworks
2:30 pm **J. Karl Johnson, University of Pittsburgh**
Design of Lewis pair functionalized metal organic frameworks for CO_2 *reduction*
2:50 pm **Jim Evans (Ames Lab)**
Non-equilibrium statistical mechanical modeling and coarse-grained mesoscale modeling of catalytic reaction-diffusion processes
3:10 pm **Chris Mundy (PNL)**
A microscopic approach to the mesoscale problem

3:30 pm **** Break ****

4:00 pm *Crosscutting Challenges for Theory and Computation*
Christopher Mundy (PNL), Don Truhlar (UMN), John Perdew (Temple), Laura Gagliardi (UMN), Emily Carter (Princeton), Bert de Jong (LBNL)
6:00 pm **** Dinner (in groups in Annapolis) ****

Wednesday, April 29

7:00 am **** Continental Breakfast (foyer near General Session)****

Session VI Chair: **Theresa Windus (Ames Lab)**

8:00 am **Jeffrey Long, University of California - Berkeley**
Spin Dependent Transformations in Metal-Organic Frameworks and Molecular Magnets
8:30 am ***Anna Krylov, University of Southern California***
Spin-Flip Methods
The role of spin in chemical and photochemical transformations
9:00 am **Juan Peralta**, **Central Michigan University**
The reliability of DFT approximations to characterize spin-forbidden reactions
9:15 am **Ahren Jasper, Argonne University/Sandia National Lab**
Spin-dependent effects in gas-phase chemical physics
9:30 am **Shiv Khanna, Virginia Commonwealth University**
Towards chemically stable magnetic order in clusters and nano-assemblies and transport through molecules

9:45 am **Xiaosong Li, University of Washington**
Time-Dependent Spin Frustration and Exciton Diffusion

10:00 am *Coffee*

Session VII *Surfaces, Plasmonics, and Excitonics*
Chair: **Jim Evans**

10:30 am **Kevin Shuford, Baylor University**
Plasmon enhanced photovoltaics: Energy and charge transfer in solar nanoassemblies

10:45 am **Jeff Greeley, Purdue University**
Structure and reactivity of model oxyhydroxide/metal interfaces: applications to electrochemical hydrogen evolution

11:00 am **Seojoo Jang, Queens College – CUNY**
Computational modeling and theory development of energy and charge flow dynamics in photosynthetic units and conjugated polymers

11:15 am **Svetlana Kilina, North Dakota State University**
Simulating phonon-induced photoexcited dynamics in ligated and core/shell quantum dots

11:30 am **Niri Govind, PNNL**
Excited states with real-time TDDFT: Molecular complexes, doped metal oxides, core excitations and non-Hermitian dynamics

11:45 am **Mark Pederson, Closing Remarks**

12:00 noon **** Meeting Adjourns ****

Quantum Photochemistry

Donald G. Truhlar
Department of Chemistry, Chemical Theory Center, and
Supercomputing Institute
University of Minnesota
207 Pleasant St. SE
Minneapolis, MN 55455-0431

Presentation Abstract

We are integrating and applying a number of methods for carrying out dynamics calculations on photochemical reactions of complex molecules. This lecture will present a recent study of the photodissociation of phenol:

> Xu, X.; Zheng, J.; Yang, K. R.; Truhlar, D. G. Photodissociation Dynamics of Phenol: Multi-State Trajectory Simulations including Tunneling. *Journal of the American Chemical Society* **2014**, *136*, 16378-16386.

This study combines four methods:

- the fourfold way for diabatization of potential energy surfaces calculated by multi-configuration-quasidegenerate perturbation theory,
- the anchor points reactive potential for fitting diabatic surfaces of systems with both active and spectator degrees of freedom,
- the coherent switches with decay of mixing (CSDM) semiclassical dynamics method, and
- the army ants tunneling method for incorporating tunneling in electronically adiabatic or electronically nonadiabatic molecular dynamics simulations.

DE-SC0008666: Developing Advanced Methods for Excited State Chemistry

Lead PI: Christopher J. Cramer
Research associates: Xuefei, Xu, Jingjing Zheng
Graduate student: Ke R. Yang (Ph. D., 2014)

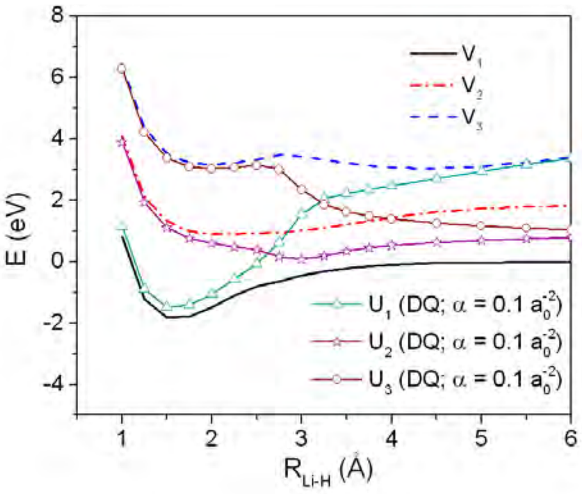
SELECTED RECENT PROGRESS

Multi-Configuration Pair-Density Functional Theory

We presented a new theoretical framework, called Multi-Configuration Pair-Density Functional Theory (MC-PDFT), which combines multi-configurational wave functions with a generalization of density functional theory (DFT). A multi-configurational self-consistent-field (MCSCF) wave function with correct spin and space symmetry is used to compute the total electronic density, its gradient, the on-top pair density, and the kinetic and Coulomb contributions to the total electronic energy. We then use a functional of the total density, its gradient, and the on-top pair density to calculate the remaining part of the energy, which we call the exchange-correlation energy by analogy to the exchange-correlation energy of Kohn–Sham DFT. Because the on-top pair density is an element of the two-particle density of density functionals by translating conventional density functionals of the spin densities using a simple prescription, and we performed post-SCF density functional calculations using the total density, density gradient, and on-top pair density from the MSCSF calculations. Double counting of dynamic correlation or exchange does not occur because the MCSCF energy is not used. The theory is illustrated by applications to the bond energies and potential energy curves of H_2, N_2, F_2, CaO, Cr_2, and NiCl and the electronic excitation energies of Be, C, N, N^+, O, O^+, Sc^+, Mn, Co, Mo, Ru, N_2, HCHO, C_4H_6, c-C_5H_6, and pyrazine. The method presented has a computational cost and scaling similar to MCSCF, but a quantitative accuracy, even with the present first approximations to the new kinds of density functionals, that is comparable to much more expensive multireference perturbation theory methods.

Diabatization Based on the Dipole and Quadrupole: The DQ Method

In this work we presented a method, called the DQ scheme (where D and Q stand for dipole and quadrupole, respectively), for transforming a set of adiabatic electronic states to diabatic states by using the dipole and quadrupole moments to determine the transformation coefficients. It is more broadly applicable than methods based only on the dipole moment, for example it is not restricted to electron transfer reactions, and it works with any electronic structure method and for molecules with and without symmetry, and it is convenient in not requiring orbital transformations. We illustrated the new method by prototype applications to two cases, LiH (see figure) and phenol, for which we compare the results to those obtained by the fourfold way diabatization scheme.



Diabatic potential energy curves for the three lowest lowest-energy $^1\Sigma^+$states for LiH. The adiabatic states from which these were obtained were computed at the SA(3)-CAS(2,5)SCF/aug-cc-pVTZ level of theory and diabatized with the DQ method with $\alpha = 0.1\ a_0^{-2}$.

Testing Time-Dependent Density Functional Theory with Depopulated Molecular Orbitals for Predicting Electronic Excitation Energies of Valence, Rydberg, and Charge-Transfer States and Potential Energies Near a Conical Intersection

Kohn-Sham (KS) time-dependent density functional theory (TDDFT) with most exchange-correlation functionals is well known to systematically underestimate the excitation

Orbital on an extensive dataset of valence and Rydberg excitation energies of various atoms, ions, and molecules. We found that the method can significantly improve the accuracy of predicted Rydberg excitation energies while preserving reasonable accuracy for valence excitation energies.

Ten Publications Acknowledging this Grant in 2014

1. Zheng, J.; Xu, X.; Meana-Pañeda, R.; Truhlar, D. G. Army Ants Tunneling for Classical Simulations, *Chemical Science* **2014***, 5*, 2091-2099. dx.doi.org/10.1039/C3SC53290a.
2. Li, S. L.; Marenich, A. V.; Xu, X.; Truhlar, D. G. Configuration Interaction-Corrected Tamm-Dancoff Approximation: A Time-Dependent Density Functional Method with the Correct Dimensionality of Conical Intersections. Journal of *Physical Chemistry Letters* **2014**, *5*, 322-328. dx.doi.org/10.1021/jz402549p
3. Yang, K. R.; Xu, X.; Truhlar, D. G. Anchor Points Reactive Potential for Bond-Breaking Reactions. *Journal of Chemical Theory and Computation* **2014***, 10*, 924-933. dx.doi.org/10.1021/ct401074s
4. Xu, X.; Yang, K. R.; Truhlar, D. G. Testing Noncollinear Spin-Flip, Collinear Spin-Flip, and Conventional Time-Dependent Density Functional Theory for Predicting Electronic Excitation Energies of Closed-Shell Atoms. *Journal of Chemical Theory and Computation* **2014***, 10*, 2070-2084. dx.doi.org/10.1021/ct500128s
5. Zheng, J.; Meana-Pañeda, R.; Truhlar, D. G. Including Tunneling in Non-Born-Oppenheimer Simulations. *Journal of Physical Chemistry Letters* **2014**, *5*, 2039-2043. dx.doi.org/10.1021/jz500653m
6. Li Manni, G.; Carlson, R. K.; Luo, S.; Ma, D.; Olsen, J.; Truhlar, D. G.; Gagliardi, L. Multi-Configuration Pair-Density Functional Theory. *Journal of Chemical Theory and Computation* **2014***, 10*, 3669–3680. dx.doi.org/10.1021/ct500483t
7. Yang, K. R.; Xu, X.; Zheng, J.; Truhlar, D. G. Full-Dimensional Potentials and State Couplings and Multidimensional Tunneling Calculations for the Photodissociation of Phenol, *Chemical Science* **2014***, 5*, 4661-4680. dx.doi.org/10.1039/c4sc01967a
8. Hoyer, C.; Xu, X.; Ma, D.; Gagliardi, L.; Truhlar, D. G. Diabatization Based on the Dipole and Quadrupole: The DQ Method. *Journal of Chemical Physics* **2014***, 141*, 114104/1-11. dx.doi.org/10.1063/1.4894472
9. Li, S. L.; Truhlar, D. G. Testing Time-Dependent Density Functional Theory with Depopulated Molecular Orbitals for Predicting Electronic Excitation Energies of Valence, Rydberg, and Charge-Transfer States and Potential Energies Near a Conical Intersection. *Journal of Chemical Physics* **2014***, 141*, 104106/1-8. dx.doi.org/10.1063/1.4894522
10. Xu, X.; Zheng, J.; Yang, K. R.; Truhlar, D. G. Photodissociation Dynamics of Phenol: Multi-State Trajectory Simulations including Tunneling. *Journal of the American Chemical Society* **2014***, 136*, 16378-16386. dx.doi.org/10.1021/ja509016a

Density functional studies on light harvesting molecules

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The project concerns development and applications of efficient density functional theory based methods that can provide a framework to study the light-harvesting molecular systems. The goal is to gain the predictive capability of quantum mechanical computational methods, which could be used for high-throughput material screening. Such a framework needs to be efficient enough to handle large system sizes for molecular calculations since most of the interesting light-harvesting molecular systems contain hundreds of atoms. We have earlier demonstrated the predictive power of a density functional method for charge transfer excitations. It was shown that even using pure generalized gradient approximation to exchange-correlation functionals such systems could be described both efficiently and accurately [1-4]. Further developments include calculation of other parameters such as electronic coupling from first principles which combined with the previous developments can be used to gain insight into photoinduced charge transfer process. Application of the developed method to light harvesting systems, which are of interest to experimentalists, is another aspect of the project. Another goal is to study the electronic structure of light-harvesting molecular systems in an environment such as on surfaces or in the presence of spectator molecules where the effects due to morphology and polarization can be large.

We have applied our method to two novel acceptor systems, which are being tested in the laboratories of our collaborators at UTEP and UCSB. These two types of acceptors are endohedral fullerenes with a metallic endohedral unit and C_{60} molecules functionalized with dye molecules. We have shown that using a tri-metallic nitride endohedral C_{80} fullerene in a porphyrin-fullerene dyad can enhance the charge transfer excitation energies by about 25% compared to C_{60}. Such dyads are bound through van der Waals interaction with a small amount of charge transfer in the ground state from the porphyrin to the fullerene. The CT excitation energy depends on the endohedral unit. Replacing the metal atoms by a heavier one raises the excitation energy but the orientation of the endohedral unit does not affect it [5]. The outer carbon cage of the fullerene completely shields the endohedral unit from external electric fields. We also find that the polarizability of the endohedral fullerene is smaller compared to the outer cage only. Applications to dye-attached fullerenes showed that the linker addition site strongly influences the electronic structure of the dye-attached fullerene resulting in higher electron affinities for some of the systems. The charge transfer exciton binding energy in the dye-functionalized fullerene:P3HT systems is lower that the corresponding value in PCBM:P3HT system.

Recent progress in treating the self-interaction errors by means of Fermi orbitals offers a promising route to study the effect of self-interaction errors on the electronic structure of molecules. One advantage of using the Fermi orbitals is that the corrected Hamiltonian is unitarily invariant. We have parallelized the Fermi orbital-based scheme to correct for SI errors in DFT calculations of molecules. The Fermi orbitals depend on the location of the electronic positions, called as Fermi orbital centroids. Minimization of the corrected energies leads to an optimized set of centroid positions. The preliminary results on small and medium size molecules such as benzene, Mg-porphyrin, C_{60} show very encouraging results. For example, the eigenvalue of the highest occupied molecular orbital of benzene with LDA+SIC is 9.24 eV, which is in close agreement with perturbative delta-SCF value of 9.29 eV with PBE functional and experimental value of 9.44 eV.

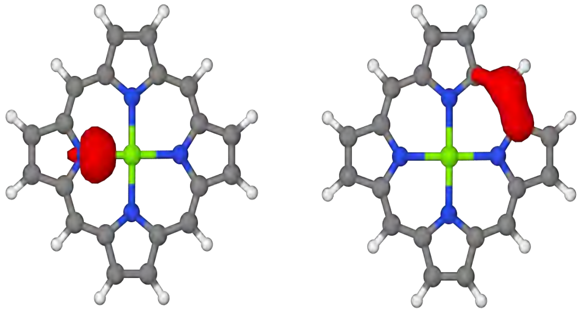


Fig. 1: Two Fermi orbitals of the Mg-porphyrin.

References:

1. Charge transfer excited state energies by perturbative delta-self consistent field method, T. Baruah, M. Olguin, R. Zope, J. Chem. Phys. 137, 084316 (2012).
2. Charge transfer excitations in co-facial fullerene-porphyrin complexes, R. Zope, M. Olguin, T. Baruah, J. Chem. Phys. 137,084317 (2012).
3. Effect of geometrical orientation on the charge transfer energetics of supra-molecular (tetraphenyl)-porphyrin-C60 dyad, M. Olguin. R. Zope, T Baruah, J. Chem. Phys., 138, 074306 (2013).
4. The effect of structural changes on the charge transfer states in a light-harvesting carotenoid-diaryl-porphyrin-C60 molecular triad. M. Olguin, L. Basurto, R. Zope, and T. Baruah, J. Chem. Phys. 140, 204309 (2014).
5. Electronic structure and charge transfer excited states of endohedral rtimetallic nitride C_{80}(Ih) fullerene-Zn tetraphenyl porphyrin dyads, L. Basurto, F. Amerikheirabadi, R. Zope and T. Baruah, Phys. Chem. Chem. Phys. 17, 5832 (2015).

Abstract

Modeling Molecular Electron Transport for Thermal and Photo Energy Conversion

Dunietz, Barry: Department of Chemistry, Kent State University, Kent, OH.

PROGRAM SCOPE

The goal of the research program is to reliably describe electron transport and transfer processes at the molecular level. Such insight is essential for improving molecular applications of solar and thermal energy conversion. We develop electronic structure models to study

(1) photoinduced electron transfer and transport processes in organic semiconducting materials,
(2) charge and heat transport through molecular bridges.

We seek fundamental understanding of key processes, which lead to design new experiments and ultimately to achieve systems that demonstrate improved properties.

RESEARCH HIGHLIGHTS

In one thrust, we investigate charge and heat transfer processes in molecular bridges. These systems are investigated as candidates for thermoelectric applications. We analyzed the role of the anchoring group in the reorganization of frontier molecular orbitals (FMOs), which was found to strongly determine the bridge transport and thermoelectric properties. In another project, we addressed the challenge of achieving control of heat transfer, where we propose that molecular bridges can function as spin filters to actively control the heat flow using a magnetic field

- "End-Group Influence on Frontier Molecular Orbital Reorganization and Thermoelectric Properties of Molecular Junctions", Janakiraman Balachandran, Pramod Reddy, Barry D. Dunietz, and Vikram Gavini *J. Phys. Chem. Lett.*, 2013, *4* (22), pp 3825–33.
- "Active control of thermal transport in molecular spin valves", Myeong H. Lee, Barry D. Dunietz *Phys. Rev. B* 2013, 88, pp 045421.

In the second main research thrust we study photoinduced charge transfer processes through interfaces involving organic semiconducting materials. We developed and implemented a fully quantum mechanical protocol to compute the charge transfer (CT) kinetics. The approach is based a Fermi-Golden rule picture. (We first reported our approach in a JPCC 2013 paper v117, pp 23391). We showed that a fully quantum mechanical scheme is necessary for achieving reliable modeling of CT processes in organic semiconducting materials, in contrast to the pervading semi-classical Marcus picture that grossly underestimates the transfer rates. In follow up studies we reported the study of important aspects involving donor-acceptor molecular interfaces that are relevant to photovoltaic applications. In a recent JCP communication, we showed that molecular-scale means can tune the kinetics through stabilization of CT states affected by the polar environment. The success in controlling CT rates is crucial for achieving high efficiency optoelectronic applications using organic semiconducting materials.

- "Communication: Charge-transfer rate constants in zinc-porphyrin-porphyrin-derived dyads: A Fermi golden rule first-principles-based study" Arun K. Manna and Barry D. Dunietz *J. Chem.*

Phys., 2014, 141, pp121102.

We implemented our electronic structure approach combining charge constraint DFT and range separated based DFT to study solvated charge transfer states of functionalized organic materials, and to calculate orbital gaps of organic materials at the condensed phase to advance the design of related materials

- "Solvated charge transfer states of functionalized anthracene and tetracyanoethylene dimers: A computational study" Shaohui Zheng, Eitan Geva, Barry D Dunietz *J. Chem. Theo. Comp.* ,2013, 9, pp1125-1131
- "Orbital Gap Predictions for Rational Design of Organic Photovoltaic Materials" *Org. Elect.* , Heidi Phillips, Zilong Zheng, Eitan Geva, and Barry D. Dunietz 2014, 15, pp1509-1520.

. Recent studies highlight the potential role of hot CT states to achieve charge separation in organic photovoltaic applications. We consider the possible role of hot CT states and other high energy CT states in complicated molecular structures. Towards this aim we showed the need to properly tune the range separated parameter in DFT approach that models properly CT processes:

- "Calculating High Energy Charge Transfer States Using Optimally Tuned Range-Separated Hybrid Functionals" *J. Chem. Theory Comput.*, 2015, *11* (3), pp 1110–1117.

Finally, we investigated two high profile systems, where in both cases our research was inspired by presentations provided in the previous CTC DOE meeting (2012):

In one study, a solvated tri-nuclear complex (two iron and one platinum ligand bridged centers) is investigated. Such mixed nuclear complexes in both solution and crystal phases are widely studied as models for charge transfer (CT) reactions using advanced spectroscopical and electrochemical tools. Complementing earlier studies, we find that the most stable gas solvated geometry is substantially different from the crystal phase structure, resulting from changes in the oxidation numbers of the metal centers. Importantly, our novel structural assignment achieves a substantially improved agreement to experimental measurements of vibrational and electronic spectra and of the photo induced kinetics. We therefore find that the solvated complex differs substantially from the complex crystal structure.

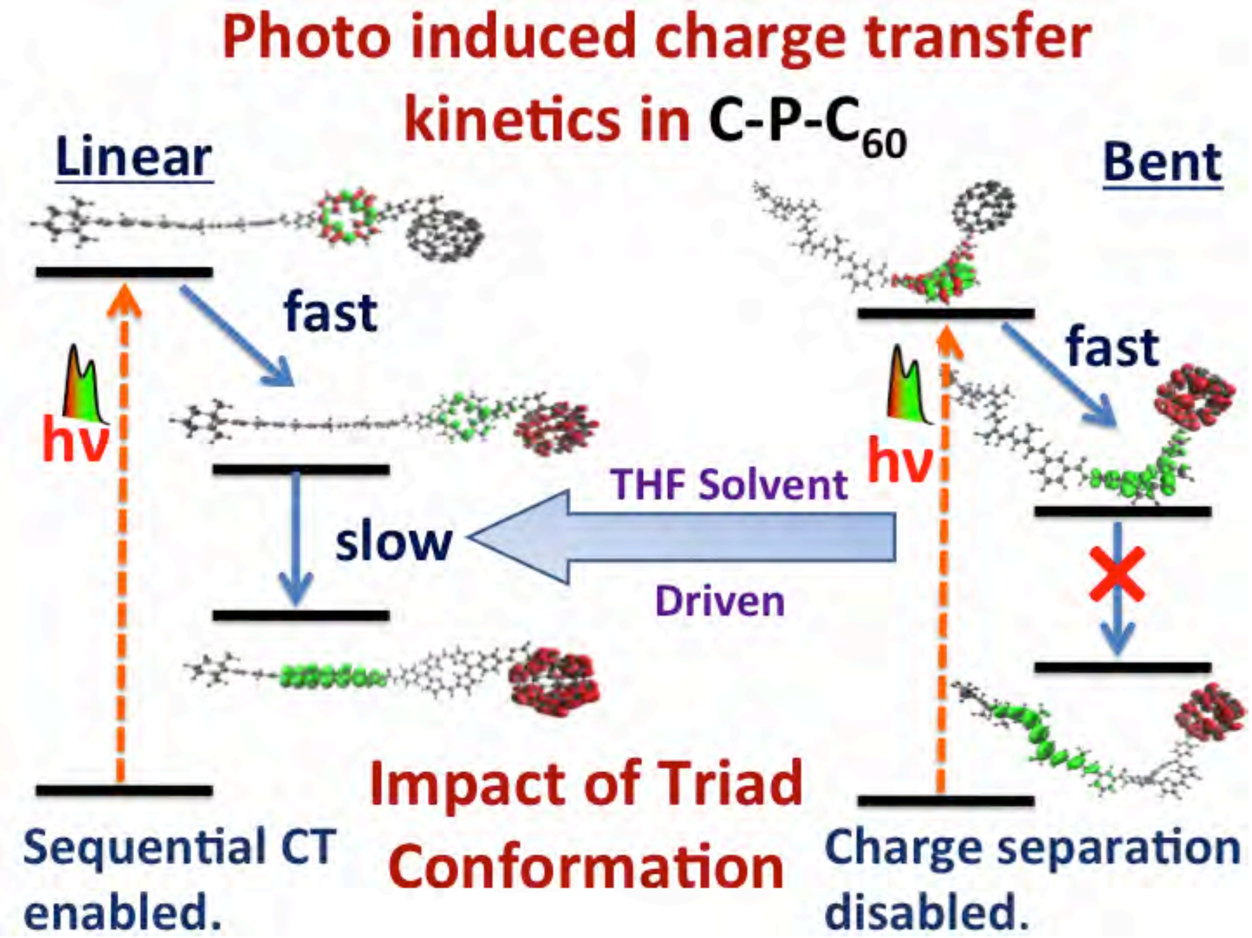
- "Molecular Structure, Spectroscopy, and Photoinduced Kinetics in Trinuclear Cyanide Bridged Complex in Solution: A First-Principles Perspective" Zilong Zheng, Arun K. Manna, Heidi P. Hendrickson, Morgan Hammer, Chenchen Song, Eitan Geva, and Barry D. Dunietz J. Amer. Chem. Soc., 2014, 136, pp16954–16957

In the second study, a molecular triad composed of carotene-porphrin-fullerene is investigated. The molecular triad has been widely studied to explore conformational flexibility of molecular systems relationship to photoinduced charge-transfer. In collaboration with Prof Cheung (University of Houston) we report the charge transfer properties of two key triad conformations: An entropically preferred conformation (bent) versus the energetically preferred conformation (linear). [Find a figure demonstrating this key finding in the triad study next page]

- "Unraveling the Mechanism of Photoinduced Charge Transfer in Carotenoid–Porphyrin–C_{60}" Arun K. Manna, D. Balamurugan , Margaret S. Cheung and Barry D. Dunietz *J. Phys. Chem. Lett.*, 2015, *6* (7), pp 1231–1237.

FUTURE PLANS

We will develop our quantum mechanical scheme to model photo induced processes. Importantly our implementation of the Fermi golden role will address non equilibrium conditions. In this way the role of hot CT state will be addressed as well as the potential role of other high energy CT processes. We will also integrate our model with large scale molecular models by incorporating molecular dynamical simulations that address the effect of the molecular environment in crystal structure, thin films and solvent phase. We will study CT processes in several molecular systems that can be used in organic photovoltaic applications. In one important direction the role of disorder at the interface of the donor and acceptor materials to improve the charge separation in PV systems will be investigated.
In molecular bridges we will develop NEGF formalism that is based on modern DFT, solve the electronic equation of motion in model Hamiltonian to explore dynamical driven phenomena as Coulomb-drag, and study effects of molecular contacts to result with bridges of varying conductance in collaboration to relevant experimental efforts..



Energy Transport and Heating in an Open Quantum Nanoscale Device

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Program Scope. Understanding and controlling charge and energy transport at nanoscale is at the forefront of experimental research from cells in biology to memory chips and optoelectronic devices in molecular electronics. Progress in measurement techniques poses challenges to theory [1-10]. For example, a nontrivial task of description of simultaneous energy conversion and charge transport in open nanoscale systems [8,9] have direct relation to research in photo-voltaic devices. Proper theoretical treatment should include development of appropriate theoretical tools capable of describing experimental data [4-6], suggesting new experiments [3], and establishing theoretical characteristics suitable in the realm of open non-equilibrium systems [1,2].

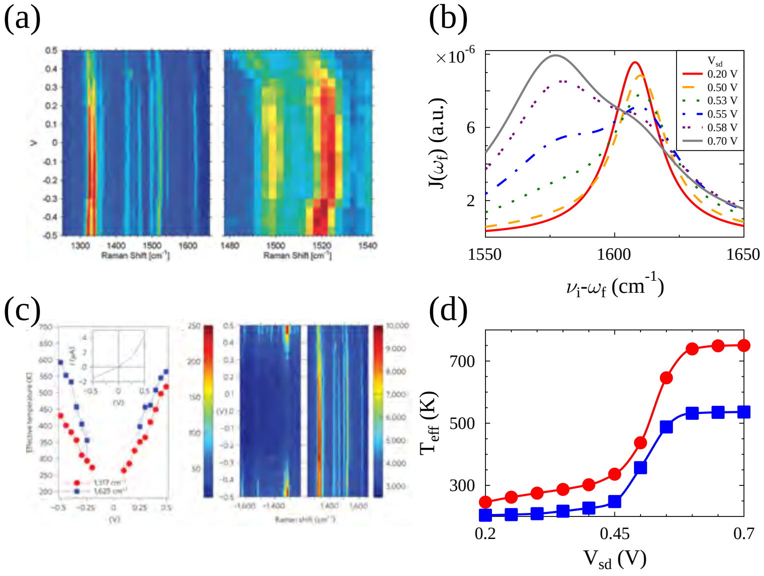
Many-body effects (e.g. electron-electron, electron-vibron, and excitonic interactions), are essential in predicting response of these systems to external perturbations (bias, gate voltage, light sources, temperature gradients). Although quantum chemistry has developed methods for dealing with correlated many-electron effects within the context of isolated molecules, *ab inito* calculations of open molecular systems mostly employ methods formulated within an effective single-electron picture. The latter (quasi-particle or molecular orbitals methods) is well developed and is especially useful in situations, when system allows description in terms of non- or weakly interacting elementary excitations (quasi-particles). This is the case for mesoscopic devices (e.g. quantum dot junctions) or nanoscale devices (e.g. molecular junctions) in the off-resonant tunneling regime. The description becomes inconvenient when intra-molecular interactions are dominant (compared to strength of molecule-contacts coupling) or when separation into Fermi and Bose degrees of freedom is cumbersome. The former is the situation encountered e.g. at resonant transport regime in nanoscale devices (this is the regime most relevant for practical applications). The latter corresponds to e.g. breakdown of the Born-Oppenheimer approximation, interaction of plasmons with molecular excitations and intra-molecular optical excitations in junctions held under current-carrying conditions. We develop theoretical tools for **the nonequilibirum atomic limit** (i.e. approaches which account for all the intra-molecular interactions exactly, while molecule-contacts couplings are treated perturbatively), which allow to incorporate quantum chemistry methods developed for isolated systems into the realm of open nonequilibrium junctions. We show that such tools are invaluable in experimentally relevant situations.

Physical quantities applied to description of a device behavior should be chosen with case. For example, in nano-electronics often employed parameters to characterize extent of heating of molecular vibrations and electronic background is “effective temperature” (e.g. measured as a ratio of Stokes and anti-Stokes peaks intensities), while in studies of thermo-electric properties of nano-devices a “figure-of-merit” is the standard characteristic of the device performance. Both concepts are used in description of nonequilibrium nanoscale systems following studies of equilibrium and/or macroscopic systems. Note that both examples essentially describe heating (heat transport) through a nanoscale device, and as such are intimately related to quantum thermodynamics of the device. We show that traditional choices may lead to qualitative failures, propose suitable alternatives, and formulate a consistent thermodynamic description for an open nanoscale system under slow driving.

Recent Progress. As a demonstration of importance of many-body state-based description of electron transport problems we considered in Ref.[6] a molecular junction in Coulomb blockade regime, where intra-molecular charge transfer rather than electron transfer between contacts and molecule defines gate induced switching of conductance in the junction. We show that nonequilibrium conductance channels (i.e. those channels which are defined by both energetics of the problem and nonequilibrium occupation of many-body states of the molecule) in principle cannot be described within the Landauer-DFT methodology. This is an important statement, since it points not to a non-adequate pseudopotential (which in principle can be improved or adjusted for a particular molecule), but to the effective single particle character of the DFT theory (i.e. consideration, as is often done, of the Kohn-Sham orbitals as true molecular orbitals), which makes proper description impossible.

Another example discusses inelastic processes, which are often considered as a source of decoherence in molecular junctions, while coherence induced by electron-vibration coupling is less common. We show that vibration-induced coherence leads to a an observed cooperative effect in multi-molecule junctions, which reveals itself in nonlinear scaling of IETS signal with number of molecules [5]. Note that describing the effect within usual quasiparticle consideration is complicated even in the case of relatively weak electron−vibration coupling, where perturbation theory is applicable. The reason is the effective mean-field character of low-order (e.g. the popular SCBA) considerations.

In Ref.[4] we develop a formulation of Raman spectroscopy in molecular junctions based on a many-body state representation of the molecule. The formulation goes beyond the previous effective single-orbital formalisms and provides a convenient way to incorporate tools of molecular spectroscopy and quantum chemistry into realm of open non-equilibrium systems. We illustrate feasibility of our approach performing first principle simulations of Raman response in an OPV3 junction, and compare our results to available experimental data. In particular, we demonstrate that bending of the Stokes line observed in the experiment can be easily explained within our methodology as shift with bias of dominant contribution to Raman scattering from neutral molecule to cation. Note that description of the effect within the traditional orbital-based language is nontrivial. We also find that calculated vibrational heating by electric current agrees with available experimental data (see Figure below).



Raman spectroscopy of an OPV3 junction:
(a) experimental data on the Stokes line shift with bias;
(b) first-principles simulation of the Stokes scattering for several biases;
(c) experimental data on heating of vibrational modes of the OPV3 molecule;
(d) vibrational heating (the PP-NEGF simulation).
From Ref.[5]

We note that unlike theory of isolated molecule spectroscopy developed in terms of double-sided Feynman diagrams, this consideration is capable not only treat intra-molecular processes exactly, but also molecule-contacts coupling is taken into account in a controlled way (for more details see http://arxiv.org/abs/1503.03890). The formulation of Ref.[4] is an important step toward atomistic quantum *ab initio* modeling of optical response of non-equilibrium electronic dynamics in molecular junctions. A full *ab initio* treatment should include also quantum description of molecule-plasmon interaction, as e.g. proposed in our earlier publication [9].

Although “effective temperature” is often used in experimental research to characterize extent of heating of a device held under current carrying conditions (e.g. see Figure above), the notion of temperature is applicable only at equilibrium. We show that use of temperature in place of the proper characteristic – the heat flux – may lead to both misinterpretations and qualitative failures. While it is generally believed that the later is relevant only for highly biased junctions or in presence of resonances (either intra-molecular or bath-induced), we demonstrate that quantum interference effects may invalidate the concept of Raman temperature even at low (or no) bias and in the absence of resonances. This prediction is confirmed by recent experimental data. Similarly, experimental studies on thermoelectricity in nanoscale junctions make use of the macroscopic theory of thermoelectricity to assess the junction’s performance. The latter is characterized by the figure of merit, a quantity exclusively defined in terms of linear response transport coefficients and thus ill defined out of equilibrium. While the linear theory is reasonable in bulk material, it fails in small thermoelectric junctions, which can operate in the nonlinear regime. This fact motivated a number of semi-classical studies to consider the macroscopic efficiency of the junction as an alternative to the figure of merit. Moreover, small size of nanoscale devices implies importance of quantum effects and thermal fluctuations in their response. We propose a method, based on characterizing efficiency fluctuations, to assess the performance of nanoscale thermoelectric junctions, and propose an approximate method to express efficiency fluctuations in terms of nonequilibrium currents and noises, which are experimentally measurable in molecular junctions [2].

Finally, both studies of opto- and thermo-electric devices utilize concept of heat. The nature of heat is one of the most fundamental questions, which has been driving research in thermodynamics since its origins. Consistent thermodynamic formulation for an open quantum nanodevice coupled to its environment is a highly nontrivial task. For example, contrary to the standard thermodynamic formulation, where energy of coupling between system and bath is assumed to be negligible, such assumption is not applicable for description of nanojunctions. In Ref.[1] we establish the foundations of a non-equilibrium theory of quantum thermodynamics for non-interacting open quantum systems coupled to their reservoirs and controlled by slow external time-dependent force. It allows one to reliably assess the performance of energy-converting devices such as thermo-electrics or photo-electrics, by identifying the system entropy production. It enables one to meaningfully compare these different devices by discriminating the system specific features from the universal ones and to appraise the role of quantum effects. This formulation is the first step in developing a comprehensive theory of quantum thermodynamics.

Future Plans. Conceptually involved directions of future research include:

1. Formulation of nonequilibrium quantum thermodynamics of open interacting systems subjected to arbitrary driving. This will require to go beyoing the gradient expansion and quasiparticle formulations utilized so far.

2. Development of theoretical methodologies beyond quasiparticle or nonequilibrium atomic limit. That is formulations capable of treating systems in the absence of a small energetic parameter (such as intra-molecular interactions for quasiparticles and system-bath coupling fro the atomic limit).

More technical important developments include:

1. Going beyond the small sizes of system accessible within the many-body states formulation by utilizing ideas of divide-and-conquer approaches to formulate a multi-scale approach to atomistic simulations of nano-scale devices, which can combine advantages of atomic limit formualtions (exact treatment of local interactions of any strength and type) and DFT-based approaches (ability to treat systems of big size).
2. Full *ab inito* simulation of optical processes in nanodevices requires development of an interface between quantum (at small scale) and classical (at large scale) electrodynamics. This will allow full atomistic simulations of optoelectrocnic devices.
3. Elucidating role of quantum coherence (coherent control) and local interactions for increase of efficiency of nanoscale devices. This includes also application of recently developed thermodynamic approach to modeling of local heat and entropy fluxes. This provides thermodynamically relevant information on local structure and operation of the devices. Similar modeling of local elastic current yielded information on influence of quantum coherence on charge transport.

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Diabatic model Hamiltonians of exciton dynamics from many-body wave functions

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We will present our recent development of the active space decomposition (ASD) method for excited states of molecular dimers and aggregates. ASD not only enables active space computations of unprecedented size, but also provides accurate model Hamiltonians for exciton dynamics fully *ab initio*. Application to singlet fission processes and extension to multiple-chromophore systems will be presented.

DE-FG02-13ER16398: Electronic Structure Theories of Singlet Fission and Multiple Exciton Generation

Postdocs:	Matthew MacLeod and Inkoo Kim (and, in part, Shane Parker and Jefferson Bates)
Students:	(in part, Xiaotian Deng, Hai-Anh Le, and Ryan D. Reynolds)

PROGRAM SCOPE

There are two major goals in this research program: (1) *Simulations of singlet fission based on active space decomposition*. We propose to develop a new methodology with which one could accurately calculate model Hamiltonians for singlet fission, a carrier multiplication process in organic photovoltaics, using many-body wave function methods. (2) *Non-adiabatic photodynamics based on automated code generation*. It is proposed that we develop analytical nuclear gradient theory and programs and those of non-adiabatic coupling matrix elements on the basis of multireference electron correlation methods to realize quantitative on-the-fly dynamics simulations of non-adiabatic photochemistry.

RECENT PROGRESS

Simulations of singlet fission based on active space decomposition. To accurately calculate the model Hamiltonians of excitonic processes in molecular aggregates and crystals, we have developed an electronic-structure method called active space decomposition (ASD), which compresses the wave functions of such systems using molecular geometry information. For the simplest case of molecular dimers, the wave function is parameterized using the physical states of monomers (labeled as A and B) as

$$\Psi = \sum_{IJ} C^{IJ} \Phi_I^A \Phi_J^B$$

in which Φ_I^A and Φ_J^B are calculated by active-space wave function methods, such as complete or restricted active spaces. We found that the Hamiltonian matrix elements between the product basis functions can be computed without explicitly constructing the product basis as follows:

$$\langle \Phi_I^A \Phi_J^B \left| \hat{H} \right| \Phi_{I'}^A \Phi_{J'}^B \rangle = \Gamma_\zeta^{II'A} H_{\zeta,\eta} \Gamma_\eta^{JJ'B}$$

in which Γ are transition-matrix-like quantities that can be computed from a fragment wave function alone. The ASD ansatz is exact when the complete set of monomer states (i.e., all the charge and spin sectors) is included in the summation, which is somewhat analogous to singular value decomposition of matrices.

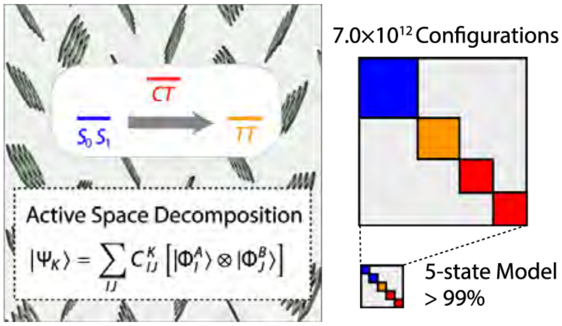

Figure 1: ASD extracts few-state models from the Hamiltonian in a very large configuration space.

We have shown that the ASD method not only enables active-space computations of unprecedented size that are otherwise intractable, but also naturally provides few-state model Hamiltonians in the diabatic representation for electron and energy transfer dynamics (Figure 1).[1] We have applied this methodology to the singlet fission processes in pentacene and tetracene crystals.[2] Singlet fission is a molecular analogue of multiple exciton generation, whose mechanism is still under intense discussions. Our results have numerically proven the effectiveness of the diabatic models in these systems by demonstrating that the model Hamiltonians with 5 states describe more than 99% of the wave functions for low-lying electronic states. Our model has also been used by other researchers to validate more approximate but efficient models.

The ASD method has been recently extended to multiple-chromophore systems. The extension is based on the matrix-product-state approximation in the DMRG algorithm (called ASD-DMRG):[3]

$$\Psi = \sum_{IJK\ldots} C^{IJK\ldots}\,\Phi_I^A \Phi_J^B \Phi_K^C \ldots, \quad \text{where} \quad C^{IJK\ldots} = \mathrm{Tr}[\mathbf{C}^I \boldsymbol{C}^J \boldsymbol{C}^K \ldots]$$

This parameterization can be seen as successive compression of wave functions, and is a natural generalization of the ASD dimer wave-function ansatz. From a theoretical point of view, ASD-DMRG is the first proposal to use chemical fragments to map molecular systems to a lattice model, as opposed to orbitals in the standard *ab initio* DMRG, which (we think) is major advancement in the field.

Non-adiabatic photodynamics based on automated code generation. We have realized, for the first time, the analytical nuclear gradients of complete-active-space second-order perturbation theory (CASPT2) with *full internal contraction*.[4] CASPT2 is a popular method among computational chemists, but its nuclear gradients had not been available due to enormous complexity of the equations arising from the use of full internal contraction. We have overcome this difficulty by employing the automatic code generation approach. The code generator and generated code are both publicly available online (http://www.nubakery.org). The program has been applied to vertical and adiabatic ionization potentials of a free-base porphyrin to show that the cation structure is in a lower symmetry due to the pseudo-Jahn–Teller effect [CAS(4,4), cc-pVDZ consisting of ~400 basis functions]. We did not use any spatial symmetry. One geometry optimization step only took about 30 min without parallelization.

FUTURE PLANS

We are currently extending the ASD model to allow for orbital optimization and treatment of dynamical correlation to make our model predictive. In addition, generalization of the ASD-DMRG ansatz to higher-dimensional tensor network states is under investigation in our research group. Regarding the second component of this research project, we are currently developing an efficient theory and programs for non-adiabatic coupling matrix elements with CASPT2, which would enable accurate surface hopping dynamics simulations on correlated potential energy surfaces.

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Non-Adiabatic Molecular Dynamics Simulations

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Keywords: Ab-initio Molecular Dynamics, Non-Adiabatic Couplings, Electronic Excitations, Time-Dependent Density Functional Theory, Surface Hopping

Project Scope

The goal of this project is to provide robust, predictive, and broadly applicable computational tools enabling non-adiabatic molecular dynamics (NAMD) simulations in real materials with unprecedented accuracy and realism. We aim to develop a general-purpose code enabling 10-100 picosecond ensemble NAMD simulations for molecules and nano-sized clusters with ~100 atoms at the level of hybrid time-dependent density functional theory (TDDFT).

Relevance to MGI and DOE Mission

The rate of breakthrough discoveries in energy-related materials sciences depends crucially on our ability to control non-adiabatic transitions between electronic states. For example, sensitizer dyes for solar cells should exhibit large transition probabilities from the absorbing state to the charge-injecting state and minimal losses through other channels. NAMD simulations are the method of choice for these challenges. They provide direct access to observables such as quantum yields, time constants, and kinetic energy distributions which can be compared to accurate calculations and gas-phase experiments.

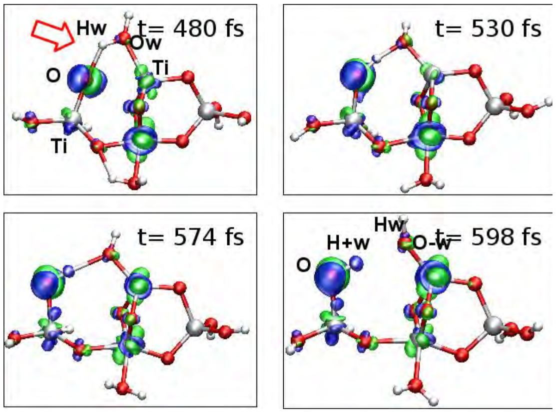

Figure. Sample B3LYP/SVP NAMD trajectory showing photoinduced water splitting in the S_1 state of $(TiO_2)_4$ clusters at 278 K. No reaction is observed in the ground state.

Technical Progress

A highlight in FY 2014 was the development of improved iterative subspace algorithms for large-scale response calculations which lie at the heart of materials simulations. The simple but effective idea underlying this method is to exploit the reduction of the residual norms as convergence is reached. The method is particularly successful when Coulomb and exchange portions of the linear response equations are separated and in combination with fast factorization techniques such as the resolution-of-the-identity (RI) approximation. Up to five-fold speedups were observed in TDDFT calculations, with larger benefits for larger systems. This significantly extends the scope of NAMD simulations. Another important accomplishment was the extension of TDDFT-based NAMD simulations to open-shell systems enabling the simulation of homolytic bond breaking, which is very common in photochemical reactions. Previously, excited-state homolytic dissociation could only be addressed by multi-reference calculations, which are limited to molecules with few atoms. The present developments make it possible to obtain a qualitatively complete picture of photochemical reactivity for systems with up to 100 atoms for the first time. Further, we have completed the derivation and a first implementation of first-order non-adiabatic couplings between two excited states in the hybrid TDDFT framework. The result is consistent with time-dependent response theory, but also reveals an incorrect pole structure of the quadratic TDDFT response within the adiabatic (zero frequency) approximation for the exchange-correlation kernel. This result highlights the importance of frequency-dependent kernels for NAMD simulations. In the meantime, an approximate version of the couplings that becomes exact at conical intersections is the most promising candidate for applications. We have also developed a semi-numerical algorithm for efficient computation of non-local density functional exchange- and correlation energies. The integration over the relative coordinate is performed analytically using a new recursion to generate intermediate integrals that are functions of the electron center-of-mass. Integration over the center-of-mass coordinate is carried out numerically using standard molecular integration schemes. This makes it possible to use of local range-separated hybrids without empirical parameter tuning which is crucial for predictive modeling. First results show a surprisingly good performance for bond dissociation energies. In collaboration with the Heyduk group at UC Irvine, we have characterized the electronic structure of complexes of Group V metals with the redox-active tridentate (ONO) pincer ligand. While (ONO) complexes of Nb and Ta exhibit closed-shell ground states with completely oxidized d^0 metals, the V complex has a diradical ground state with an antiferromagnetic coupling between the d^1 metal atom and the semiquinoidal (ONO) ligand, which explains the intense MLCT band of the V complex in the visible spectrum and demonstrates the promise of the (ONO) ligand platform for charge-transfer dyes. We have performed NAMD simulations on photoexcited titania nanoclusters in collaboration with Enrico Berardo and Martijn Zwijnenburg (UCL) to invesigate the promise of this material in photocatalytic water splitting. First results indicate that photoinduced water splitting can occur in the first excited state of TiO_2 tetramers, see Figure.

Future Plans

In the remaining months, we will complete the shared-memory parallelization of our NAMD code and explore further acceleration by graphics processing units. We will also develop an algorithm to efficiently compute couplings between many states. We will test decoherence corrections and investigate local diabatization methods. We will continue to perform illustrative applications.

Broader Impact

During the past two years, two high school students, three undergraduate students, two graduate students, and two postdoctoral researchers were trained in ab-initio NAMD simulations and their application to molecular materials. Partly as a result of their participation, one high school student accepted an offer to study chemical engineering at Columbia University, two undergraduate students received departmental awards, and one postdoctoral researcher obtained a faculty position at Cal State Long Beach. The material developed in this project is being used for undergraduate and graduate classroom education in theoretical and computational chemistry at UC Irvine. We have developed a 3-minute video introduction to ab-initio NAMD simulations that is publically available on YouTube. The PI has given pedagogical lectures at predominantly undergraduate institutions and high school teacher workshops to educate the broader public on computational materials research.

Data Management and Open Access

The software developed in this project is publically available through the Turbomole program package. The source code is archived in the Turbomole SVN repository after it satisfies Turbomole's coding standards and passes the Turbomole test suite. Once the code has been checked in, it can be accessed by all Turbomole developers. Any outside individual or organization can request Turbomole developer status and obtain access to the entire Turbomole source code by submitting a code development proposal to Turbomole. In addition to the distribution through Turbomole, newly developed code can be shared upon request for research and teaching purposes. While Turbomole is proprietary software, the code developed in this project is co-owned by its developers, and no restrictions are imposed on its use in education and research. Turbomole has adopted an irrevocable non-profit clause in its articles of incorporation, and its balance sheets are published on the web. The license fees are mostly used to provide high quality user support, to develop tools such as a graphical user interface to enhance accessibility, and to maintain long-term code stability. Discounted licenses are available for teaching, undergraduate institutions, and students.

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Efficient non-adiabatic molecular dynamics for high-throughput design of photo-active materials

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Presentation Abstract

Azobenzene functional groups undergo photo-isomerization upon light irradiation or application of heat. Zhou *et al.* (*J. Am. Chem. Soc.* 134:99-102, 2012) reported that porous coordinated polymers (PCPs) utilizing stimuli response, such as light absorption, are potentially highly efficient, and reversible, sorbents, particularly for carbon dioxide uptake. Azo-functional sorbents return to their original state while at ambient conditions for a prolonged period of time or with gentle heating (solar activation). The photo switchable molecules also have potential applications ranging from optical storage devices, photo-orientation of liquid crystals, and control of peptide conformations. Determining optimal functional groups on the photo-responsive organic linkers is a major synthesis and characterization challenge. Our research will provide a unique computational approach to aid in the search for optimal linkers via high-throughput materials-by-design scenarios.

Grant DE-SC0004737: Light-Matter Interactions of Azo-Functional Porous Coordinated Polymers

Postdoc(s): Barry Haycock and Hong Wang
Student(s): Zachary Herberger, Amanda J. Neukirch, and Logan C. Shamberger

RECENT PROGRESS

We have developed and implemented a non-adiabatic molecular dynamics (NAMD) algorithm within FIREBALL to gain insight into photo-physical and photo-chemical processes; for example, the charge carrier dynamics in photoactive materials or the isomerization of molecules due to charge excitation recombination. There are several approaches for going beyond the Born-Oppenheimer ground-state surface; we use the molecular-dynamics with quantum transitions methodology proposed by Tully which is the most widely used and successful method to deal with problems in which coupling between electrons and ions is required. In Tully's approach, the hops between PES are determined using the *fewest switches surface hopping* method minimizes the number of non-adiabatic transitions per trajectory, while imposing the correct state populations. However, as we would like to target large-scale applications with several hundred or thousands of atoms involved, we have focused primarily on implementing a NAMD method within a DFT formalism using a local-orbital basis (FIREBALL). All aspects of the system (electrons and ions) advance in the time domain with coupling between the electrons and ions.

The non-adiabatic coupling vectors (NACVs) provide the link between classical atomic motion and changes in quantum electronic states. Results for several small molecule applications (H_3 and formaldamine) of our exact NACV approach were published in *J. Chem. Phys*. There are two key elements regarding our approach. *Firstly*, we explicitly calculate the non-adiabatic coupling vectors (NACVs). The NACVs play a fundamental role in extending first principles molecular dynamic simulations beyond the adiabatic approximation - they provide the link between classical atomic motion and changes in quantum electronic states. In most methodologies, the NACVs are not calculated explicitly. However, it is useful to explicitly calculate the NACVs, for instance, in order to search for conical intersections or avoid crossing regions. Our *exact* expression for the NACVs efficiently extends to NAMD methods so that we can efficiently investigate photo-isomerization processes in large systems (including hundreds or potentially thousands of atoms). *Secondly,* the efficiency of our NAMD approach means that we can also explore very large statistical ensembles of excitation processes. In each of our photo-isomerization investigations, we explore between 500-1,000 trajectories; thereby, we obtain ensembles that are statistically sound. We then explore the properties of the entire ensemble rather than individual trajectories (*photo-isomerization is a probability event*).

Recently, we have extended the non-adiabatic molecular dynamics formalism to investigate photo-isomerization in stilbene and azobenzene (shown in Fig. 1). In our approach, we consider an ensemble of simulations (a few hundred simulations) and investigate the properties of the system for the entire ensemble; these results are published in *J. Chem. Theory Comp*.

Azo-functional Linkers for Porous Coordinated Polymers

More recently, we have been investigating the photo-isomerization processes in azo-functional organic linkers through non-adiabatic molecular dynamics. We are exploring the impact of functional groups (*e.g.* CH_3, NH_2, *etc.*) on the optical properties, isomerization reaction time, and quantum yield and we find that the photo-isomerization properties are *strongly dependent* on the functional groups attached to the azobenzene derivative. We will report on non-adiabatic molecular dynamics simulation results for a few model azobenzene derivative systems and we will discuss our theoretical understanding of the *trans*- to *cis*- transformation mechanisms, and timescale variations, resulting from different functional groups. Our long term goal is to use high-throughput calculations to rationally design highly efficient photo-isomerization response in porous coordinated polymers for gas separation.

We can elucidate more information about the pathway towards relaxation and isomerization by studying the projections of the nonadiabatic coupling vectors onto individual atoms in the molecular systems. In all cases we found that the central CNNC atoms contribute the most to the nonadiabatic coupling terms, hence, they are the most influential atoms in this process. Table 1 shows that in the three systems with organic linkers, the magnitudes of the coupling vectors are larger than those in the pure

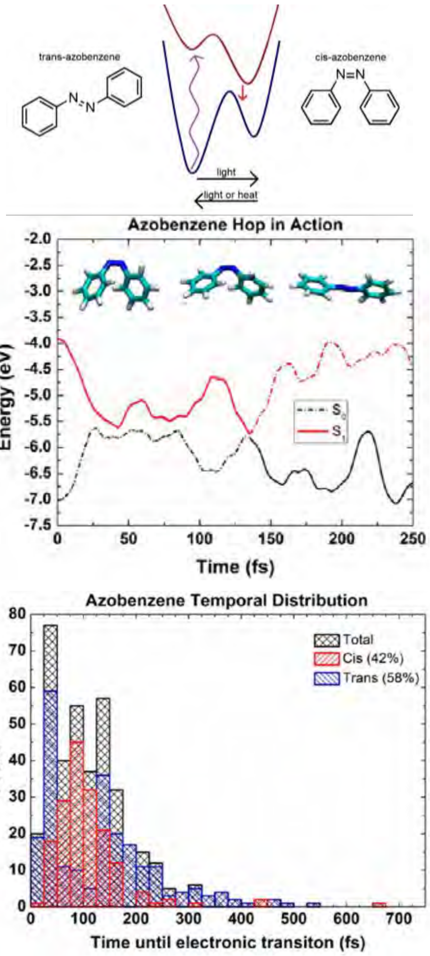

Figure 1. Molecules such as azobenzene exist in two stable conformations: *trans* and *cis*, and are converted from one configuration to the other when they are optically (or thermally) excited (top panel) in a process known as photo-isomerization. In NAMD simulations, the system evolves on an excited state PES with a probability that the electron will transition to the ground state (middle panel). We perform ensembles of simulations to describe isomerization mechanism, time, and quantum yield (bottom panel).

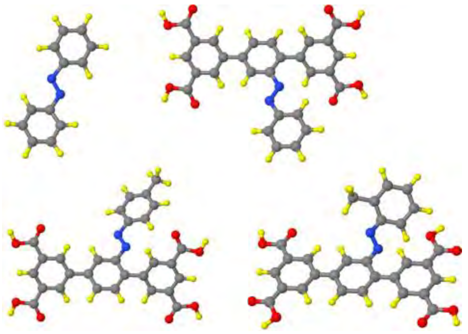

Figure 2. Azobenzene and various azo-functional organic linkers for porous coordinated polymers.

azobenzene system. In all four systems, we found that the nitrogen atoms possessed the nonadiabatic coupling vectors and terms with the largest magnitude. The greatest difference is that while the magnitude of the nitrogen coupling terms are about the same for all four systems, the magnitude of the nitrogen coupling vectors are much smaller in the pure azobenzene system. These results indicate that the velocities of nitrogen atoms in the non-linker system are either larger or are “more parallel” (hence increasing the dot product) with the nonadiabatic coupling vectors. More aligned velocities will lead to a more concerted motion and potentially a higher quantum yield. In all of the cases with linkers the nonadiabatic coupling term for the carbons are larger, suggesting that there may be more contribution from the phenyl rings during the rotation process. We also observed that the least efficient 4-methylazobenzene case has very asymmetric contributions between both the two central nitrogen atoms and the two central carbon atoms perhaps explaining the decreased isomerization efficiency.

Table 1. Ensemble averages for values of modulus of projection on the central atoms CNNC atoms of the nonadiabatic coupling vectors and absolute value of the nonadiabatic coupling terms between the HOMO and LUMO at time preceding electronic transition into the ground state of azobenzene, azobenzene with organic linkers, and 2-methylazobenzene with linkers.

	Azobenzene		Azo w/linkers		4-methylazo w/linkers		2-methylazo w/linkers	
	$\lvert d_{ij}\rvert(A^{-1})$	**$\lvert d_{ij}\cdot V\rvert$(THz)**	**$\lvert d_{ij}\rvert(A^{-1})$**	**$\lvert d_{ij}\cdot V\rvert$(THz)**	**$\lvert d_{ij}\rvert(A^{-1})$**	**$\lvert d_{ij}\cdot V\rvert$(THz)**	**$\lvert d_{ij}\rvert(A^{-1})$**	**$\lvert d_{ij}\cdot V\rvert$(THz)**
C1	7.33	33.4	9.94	47	9.54	48	8.81	44
N2	9.94	151	13.66	160	12.74	149	12.35	153
N3	10.44	176	13.93	144	14.31	184	12.95	157
C4	7.33	33.8	9.63	41	9.4	36	8.46	43

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Extended Lagrangian Born-Oppenheimer Molecular Dynamics

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Presentation Abstract

We are developing a modern framework for quantum based molecular dynamics simulations that combines some of the best features of regular Born-Oppenheimer and Car-Parrinello molecular dynamics. The new framework is based on an extended Lagrangian formulation of Born-Oppenheimer molecular dynamics that allows, for the first time, efficient energy conserving quantum based molecular dynamics simulations with a computational complexity that scales only linearly with the system size. The efficiency and accuracy of the new dynamics can be understood from a backward analysis. Instead of integrating an underlying exact dynamics with approximately converged forces, exact forces that do not rely on the fulfillment of the Hellmann-Feynman theorem are used to integrate an approximate shadow Hamiltonian. In this way properties of a Hamiltonian dynamics, such as the total energy, can be rigorously controlled. This geometric approach to integration is widely used in classical molecular dynamics, e.g. in the velocity Verlet algorithm. Our new framework allows this geometric technique to be applied also to self-consistent field models. A number of applications can take direct advantage of the new formalism, including I) orbital-free density functional based molecular dynamics for matter under extreme conditions, II) dynamics using classical polarizable force fields, III) occupation or charge constrained excited state molecular dynamics, and IV) advanced sampling techniques, such as statistical or path-integral molecular dynamics.

FWP # LANL2014E8AN:
Next Generation First Principles Molecular Dynamics

PI: Anders M.N. Niklasson

RECENT PROGRESS

Generalized extended Lagrangian Born-Oppenheimer molecular dynamics

A generalized, more rigorous and transparent, theoretical framework based on the concept of a shadow Hamiltonian was developed that allows applications to a broader class of materials in the limit that requires only a single Hamiltonian construction and diagonalization per time step. The generalization is given through the introduction of a kernel that acts like a preconditioner for the equations of motion of the electronic degrees of freedom. Previous *ad-hoc* formulations of the 0-SCF limit appear from local approximations of this kernel.

Constrained extended Lagrangian quantum based molecular dynamics

Constrained Kohn-Sham density functional theory can be used to describe diabatic excited state potential energy surfaces. Formulations and molecular dynamics applications of a charge constrained extended Lagrangian framework have been performed.

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Ab Initio DFT+ U and Embedded Correlated Wavefunction Theories for Semiconductors with Applications to Solar Energy Conversion

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Presentation Abstract

This talk will present recent work employing *ab initio* DFT+U theory and embedded correlated wavefunction (ECW) theory aimed at understanding and optimizing mechanisms of solar energy conversion to electricity by non-standard light-absorbers made from abundant elements. Here we focus on the promising material Copper Zinc Tin Sulfide/Selenide (CZTS). CZTS is a zincblende-like compound, with a tunable direct band gap (in the ideal range of 1.0 to 1.5 eV) that contains only cheap, non-toxic elements. The record efficiency for CZTS is still too low (~11%), limited by a low open circuit voltage and fast non-radiative recombination of charge carriers at point defects, interfaces, secondary phases or grain boundaries. We will show that carefully exploitation of surface and interface properties may reduce formation of recombination centers and thereby improve efficiency. Secondly, density-based ECW theory has been extended to semiconductors for the first time. The density functional embedding theory, which derives a unique, exact embedding potential from optimized effective potential theory, has been extended to periodic crystals of covalently bonded materials. The theory has been implemented within Blöchl's projector-augmented wave density functional theory (PAW-DFT) formalism within the VASP code. We will present the formalism and first results for examining properties of charged defects in compound semiconductors.

DE-SC0002120: Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications

PI: Emily A. Carter
Postdoc: Kuang Yu

RECENT PROGRESS

Program Scope

Kesterite phase CZTSSe ($Cu_2ZnSnS_{4-x}Se_x$) (see Figure 1) is a quaternary compound that is a promising thin-film solar cell material. It features a tunable band gap which spans the perfect range for solar cell applications (1.0-1.5 eV). Although it has the great advantage of not containing any expensive or toxic elements, the CZTSSe solar cell is limited by its low efficiency, similar to organic solar cells. One of the major limitations lowering the efficiency is the low open circuit voltage, which is related to the unstable Cu/Zn sub-lattice and the possible presence of secondary phases. Another limitation is the short carrier lifetime that is thought to be due to Shockley-Read-Hall (SRH) recombination centers associated with point defects. Utilizing theoretical and computational tools, our project aims to understand these limitations and to explore strategies that can be deployed to improve the CZTSSe efficiency.

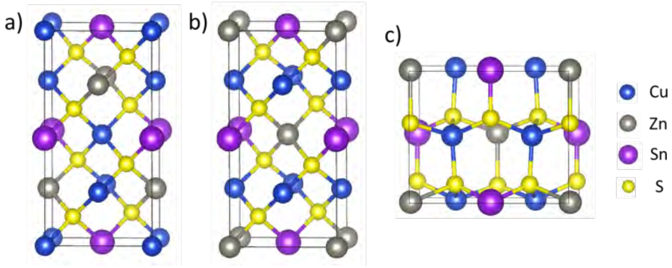

Figure 1. Crystal structures of the three ordered phases of CZTS: a) kesterite phase; b) stannite phase; c) wurtzite phase.

Recent Progress

To study the ground state properties of CZTSSe, we first began our work by computing $U_{eff} = U - J$ parameters for the 3d electrons of Cu(I), Zn(II), and Sn(IV), utilizing the *ab initio* unrestricted Hartree-Fock methodology previously developed in our group. Clusters of increasing size were cut from the experimental structures of the relevant oxides (Cu_2O for Cu(I), wurtzite ZnO for Zn(II), and SnO_2 for Sn(IV)), and the U_{eff} parameters were computed. We converged the results with respect to the cluster size, and obtained the final U_{eff} parameters that exhibit the expected physical trend (Cu(I) < Zn(II) < Sn(IV)) – a feature not always present when derived with alternative methods. We further benchmarked the U_{eff} parameters by studying properties of both the metal oxides (Cu_2O, ZnO, SnO_2) and CZTS (kesterite and stannite). It was shown that with the *ab initio* U correction, both the lattice geometry and the bulk moduli are significantly improved in all systems when compared to experiment, validating this *ab initio* DFT+U methodology.

With the validated *ab initio* DFT+U method in hand, we proceeded to study the phase stabilities of the relevant materials in the CZTS (Cu_2ZnSnS_4) system. We computed the temperature-dependent free energies of various secondary phases including: ZnS, CuS, Cu_2S, SnS, SnS_2, and Cu_2SnS_3, as well as all three ordered phases of CZTS (kesterite, stannite and wurtzite). Our calculations confirm that formation of CZTS is very favored thermodynamically and the desirable kesterite phase is the most stable phase of CZTS. However, the energy differences between the three CZTS phases are very small (3~5 kJ/mol/formula-unit), which can be easily overcome at typical experimental growth temperatures. In particular, the energy of the stannite phase is only 3 kJ/mol/formula-unit higher than the kesterite phase. Both the kesterite and the stannite phases are tetragonal and the only difference lies in the Cu/Zn sub-lattice, so the lattice mismatch between the two phases is also minimal. Therefore, secondary CZTS phases (especially the stannite phase) can form easily during the synthesis, lowering the open circuit voltage (stannite has a lower band gap than kesterite), creating local traps and recombination centers, ultimately decreasing the device efficiency.

In order to search for possible strategies to stabilize the kesterite phase of CZTS, we explored the surface properties of all CZTS phases, aiming to see if there exist some kesterite surfaces with extra stability that could be exploited to preferentially grow kesterite. Slab calculations indicate that the wurtzite phase CZTS has the lowest surface energies in general, explaining why nanoparticles of CZTS preferentially grow in the wurtzite phase (since nanoparticle stabilities are dominated by surface rather than bulk energetics). The calculations also confirm that the most stable surfaces for the tetragonal phases (kesterite and stannite) are (110), (112) and (102), in agreement with experimental PXRD results. Unfortunately, we did not observe lower surface energies for the kesterite phase compared to the stannite phase in these naturally formed orientations. However, we found that the kesterite phase is more stable than the stannite phase in orientations (001) and (100), which we denote as beneficial surfaces that should provide extra stability for the kesterite phase. However, these beneficial surfaces have higher surface energies compared to the natural surfaces, so an external substrate template would be needed to induce formation of these beneficial surfaces.

We then studied the zincblende ZnS(001) surface as a possible substrate, which has a tetragonal lattice that conforms to the kesterite(001) surface. Interface calculations suggest that CZTS-(001)-oriented films would strongly adhere to Zn-terminated zincblende ZnS(001) surfaces. More importantly, we found significant extra stability for the kesterite overlayer deposited on the ZnS substrate compared to the stannite overlayer. Therefore, we conclude that use of a ZnS(001) substrate is worth exploring as a CZTS crystal growth template; this work has been submitted for publication.

Besides phase stability studies, we also examined properties of point defects in CZTS. We computed the free energy of formation for various types of point defects. As many of these defects are charged, and because the study of charged defects within periodic boundary conditions is problematic (despite various corrections that have been proposed), we sought to extend our embedding formalism to be able to treat such charged defects as well as to study local excited states involving such defects in CZTS. We therefore recently developed a new implementation of our density functional embedding theory (DFET). The new DFET implementation combines the original DFET theory with the projector-augmented wave (PAW) formalism. A new real-space projection scheme was developed, allowing us to project the potential expressed on a uniform grid onto the atom-centered radial grids used in PAW in a very efficient way. The new algorithm also enables any optimized effective potential (OEP) computation within the PAW formalism. For our purposes, it allows us to perform DFET calculations at a frozen-core, all-electron level of theory. The new algorithm was implemented in VASP so that it can be used in conjunction with all VASP features, including a wide selection of density functionals, U corrections, and superior parallelization efficiency. We have thus far evaluated the quality of the resulting embedding potentials first using molecules and metals to compare with our earlier norm-conserving pseudopotential implementation of DFET within abinit, and then on a couple of CZTS-related test systems (i.e., Sn_{Zn} and Cu_{Zn} antisites in ZnS). We showed that the embedded cluster models were able to reproduce key features of the electronic structure of the point defects in bulk semiconductors. We also demonstrated that the embedded cluster calculation results are highly transferrable with respect to different types of basis sets (e.g., Gaussian-type and planewave basis sets). Furthermore, we also developed new algorithms allowing us to perform embedded cluster calculations with all-electron Gaussian-type basis sets in a variety of quantum chemistry programs (MOLCAS, NWCHEM, and GAMESS).

These preliminary studies (recently submitted for publication) lay the foundation for future embedded correlated wavefunction (ECW) calculations.

Future Plans

One of the ongoing directions we are working on currently is studying the effect of the disordered Cu/Zn sub-lattice on the CZTS electronic structure. Experimentally, the Cu/Zn sub-lattice disorder was observed and has been suggested to be a major cause for the low open circuit voltage. We plan to explicitly study the disordered phase and quantify the local potential fluctuations caused by the disordered arrangement of the Cu and Zn atoms.

Another direction is to utilize the DFET method we developed previously to study point defects of CZTS. We plan to conduct ECW calculations for the point defects in CZTS and compute their electron binding energies. Via these calculations, we will assess their capacity to trap free carriers, as well as determine their natural charge states and understand how they perturb the local electrostatic potentials.

In the long term, we are also interested in exploring various other possible strategies to improve CZTS efficiency. We will consider interfaces between CZTS and other semiconductors, aiming to find better electron/hole extraction materials that have low resistance for carriers and contain no toxic elements. We will also explore possible dopants that can introduce triplet excited states with extended lifetimes. Nanostructured CZTS is another direction worth more exploration, as nanoscale topologies may introduce new features facilitating the separation of electron and hole carriers. To sum up, we will carry on the work we proposed in the original proposal and shed light on fundamental aspects of CZTS solar cell devices with the aim to help improve their performance.

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Henry Krakauer

Random walks with Slater determinants: A framework for tackling many-body problems

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Presentation Abstract

The auxiliary field quantum Monte Carlo (AFQMC) method developed by the PIs provides one of the most accurate descriptions of strongly correlated electronic systems, from molecules to solids. Unlike other explicit many-body approaches, QMC scales as a low order polynomial of systems size, similar to mean-field methods such as density functional theory (DFT). The AFQMC algorithm has the form of an entangled ensemble of mean-field calculations, so it is significantly more expensive than DFT. This creates a bottleneck for applications to extended systems, such as large molecules and solids. A principal objective of this grant is to develop new AFQMC computational strategies to achieve improved efficiency for large systems, using downfolding and localization schemes, without sacrificing the predictive power of the calculations.
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DE-SC0001303: Quantum Monte Carlo calculations of chemical binding and reactions

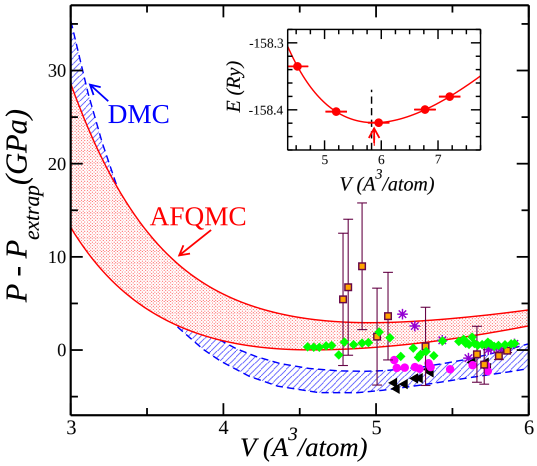
PI: Henry Krakauer; **co-PI:** Shiwei Zhang
Postdocs: Fengjie Ma, Wirawan Purwanto
Student: Yudistera Virgus

RECENT PROGRESS

Stability, Energetics, and Magnetic States of Cobalt Adatoms on Graphene: Adsorbed magnetic atoms on graphene are of interest for possible spintronic applications. We investigated the stability and energetics of adsorbed Co with near-exact many-body calculations. A frozen-orbital embedding scheme was combined with AFQMC calculations to increase the reach in system sizes. Several energy minima were found as a function of Co adsorption site and height. The findings provided an explanation for recent experimental results on nearly free-standing graphene. [Virgus, PRL 2014]

Accurate calculation of Cr_2 potential energy curve: The chromium dimer presents an outstanding challenge for many-body electronic structure methods. Unconstrained (exact) AFQMC calculations were first carried out for a medium-sized but realistic basis set. Elimination of the remaining finite-basis errors and extrapolation to the complete basis set limit were then achieved with a combination of phaseless and exact AFQMC calculations. Final results for the PEC and spectroscopic constants are in excellent agreement with experiment. This hybrid approach enabled us to obtain one of the most accurate theoretical results of Cr_2 ground-state properties to date. [Purwanto, JCP 2015]

Quantum Monte Carlo calculations with downfolded Hamiltonians: We presented a combination of downfolding many-body approach with AFQMC for extended systems. Many-body calculations operate on a simpler Hamiltonian which retains material-specific properties. The Hamiltonian is systematically improvable and allows one to dial between the simplest model and the original Hamiltonian. As a by-product, pseudopotential errors are essentially eliminated using frozen orbitals constructed adaptively from the solid environment. The computational cost of the many-body calculation is dramatically reduced without sacrificing accuracy. Excellent accuracy is achieved for a range of solids, including semiconductors, ionic insulators, and metals. We applied the method to calculate the equation of state of cubic BN under pressure [see figure (Ma, arXiv 2015): AFQMC (red), DMC (blue), shading is statistical uncertainty; expt. (symbols)] and determined the spin gap in NiO, a challenging prototypical material with strong electron correlation effects. This approach greatly extends the reach of general, ab initio many-body calculations in materials. [Purwanto, JCTC 2013*;* Ma, arXiv 2015]



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Quantum embedding methods for the simulation of inorganic catalysts and battery materials

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The use of computational methods for the study of renewable energy applications faces important challenges from the perspective of electronic structure theory. Relevant applications exhibit both large system sizes and subtle electronic structures, often involving transition metal complexes with strong multi-reference character. To address these challenges, we have developed quantum embedding methods [1-3] to leverage the efficiency of density functional theory (DFT) methods and the accuracy of rigorous wavefunction theory (WFT) methods (such as CCSD(T) or MRCI). This approach provides a promising and straightforward tool for the investigation of a range of molecular systems and processes, including the oxidative decomposition of lithium-ion battery electrolytes [4] and the rational design of a new class of cobalt-based hydrogen-evolution catalysts.

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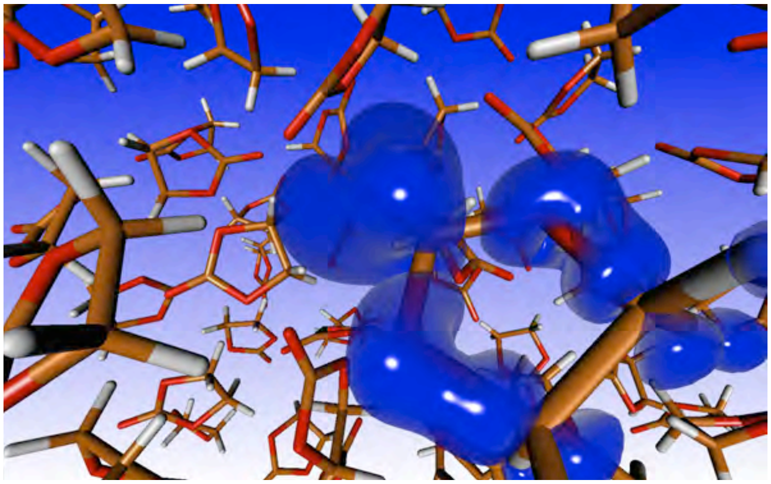

An electron hole:
Electron density change upon oxidation of ethylene carbonate, as computed using WFT-in-DFT embedding.
Adapted from Ref. 4.

Self-energy embedding theory (SEET)

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Presentation Abstract

The development of numerical methods capable of simulating realistic materials and surfaces with strongly correlated electrons, with controllable errors, is a central challenge in quantum chemistry. Here we describe a framework for a general multi-scale method based on embedding a self-energy of a strongly correlated subsystem into a self-energy generated by a method able to treat large weakly correlated systems approximately. As an example, we present the embedding of an exact diagonalization self-energy into a self-energy generated from self-consistent second order perturbation theory. Using a quantum impurity model, generated from a cluster dynamical mean field approximation to the 2D Hubbard model, as a benchmark, we illustrate that our method allows us to obtain accurate results at a fraction of the cost of typical Monte Carlo calculations. We test the method in multiple regimes of interaction strengths and doping of the model. The general embedding framework we present avoids difficulties such as double counting corrections, frequency dependent interactions, or vertex functions. As it is solely formulated at the level of the single-particle Green's function, it provides a promising route for the simulation of realistic materials that are currently difficult to study with other methods. Finally, I would like to describe our newest development that is stochastic embedding framework where the weakly correlated part is modeled statistically and can describe a realistic solid with thousands of orbitals and electrons. Subsequently, we embed the strongly correlated part of the self-energy into the stochastic self-energy for the weakly correlated part.

Grant title: Accurate ab-initio methods for correlated surface problems
PI: Dominika Zgid
Postdocs: Alexander Rusakov, Jordan Phillips
Students: Alexei Kananenka, Alicia Welden

I. RECENT PROGRESS

Our major goal is to develop an embedding approach capable of delivering quantitative results for realistic systems. When developed to a quantitative level such method will enable studies of both strongly correlated surfaces and solids without the currently done frequently empirical approximations. There are couple of major challenges to overcome in order to make a quantitative method for large system. The first challenge is to create a multi-scale method for solids in which weakly correlated orbitals (s- and p-orbitals) are treated at a different level of theory than the strongly correlated ones (d- and f-orbitals). The second challenge is to determine which orbitals in the problem are the most strongly correlated ones and therefore should be treated with a high level method. The third challenge is to account for neglecting of non-local interactions outside of the chosen region in the embedding methods. Finally, the fourth challenge is to construct the embedding scheme in such a way that the translational invariance of a periodic system remains intact. In my group we working on addressing all these four challenges. We made a very significant progress during the last year and we worked on each of the four aforementioned challenges.

A. The development of the GF2 method

In our original proposal, we promised to develop a multi-scale solver capable of describing strong and weak correlation in periodic systems. The first step of such a procedure is to develop a method that could be used to treat the weakly correlated s- and p- orbitals and has a low computational scaling. In a preliminary implementation such a method can be used to treat moderately sized molecules. We have implemented an iterative Green's function formalism called GF2 that can describe orbitals having both weakly and strongly correlated character. The GF2 theory is based on iterative resummation of diagrams in Fig. 1 that form the self-energy expression

$$\Sigma_{ij}(\tau) = -\sum_{klmnpq} G_{kl}(\tau)G_{mn}(\tau)G_{pq}(-\tau) \times \mathrm{v}_{imqk}\left(2\mathrm{v}_{lpnj} - \mathrm{v}_{nplj}\right) . \tag{1}$$

A cartoon showing a bird's-eye view of our implementation of the GF2 algorithm is presented in Fig. 2. A detailed description of GF2 implementation can be found in J. Chem. Phys. 140, 241101 (2014).

Here, we would like to mention some of the key advantages of the GF2 method. GF2 is an all electron, size-extensive, and peturbative method. Series of diagrams are included due to the implicit resummation in the iterative procedure, thus making possible for GF2 to recover certain static correlation effects even when starting from RHF solution and to avoid the typical MP2 divergencies for cases with decreasing band gaps. In Fig. 4, an exceptional performance of the GF2 is illustrated for nontrivial strongly correlated systems such as stretched H_{32} lattice. This system is multi-reference even at their respective equilibrium lattice spacings. GF2 is an iterative procedure independent of the reference Green's function, thus both HF and DFT starting Green's functions can be used. GF2 calculation can be performed in the atomic orbitals without the AO to MO orbital transformation. This is due to a similar structure of the second order self-energy in the τ domain to the Laplace transformed MP2 expressions. An overall cost with the density fitted AO integrals in the Eq. 1 is $O(n^3 m)$ scaling, where n is the number of orbitals and m is the number of auxiliary functions necessary for density fitting. Thus, as expected the overall scaling of GF2 algorithm is identical up to a prefactor with Laplace transformed density fitted MP2 scheme.

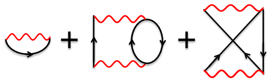

FIG. 1. Diagrams included in second-order self-energy.

GF2 method is explicitly inverse temperature, β, dependent and can be used to calculate energy or band gap as a function of temperature. The GF2 procedure is all-electron, with no selection of an active space of correlated orbitals. It requires no more user input than that of a typical HF or DFT calculation. As such it can be made blackbox. GF2 may be used to determine active space orbitals for complicated strongly correlated molecules studied with QM/QM embedding methods such as DMFT. All the above advantages make GF2 an ideal candidate for the first step of a multi-scale scheme as a method capable of handing weak correlations.

In summary, the developed by us GF2 method shows a great promise to treat both the static and dynamic correlation. By using GF2 as a base for the further development, we can address both the first and the second challenge since we can provide that both weakly and strongly correlated orbitals are correlated at the same time. Additionally, we can calculate the one-body density matrix using the GF2 method and obtain natural orbital occupancies. In this way, the most important orbitals can be chosen for the strongly correlated embedding treatment, thus addressing the second challenge. The GF2 implementation and testing was performed by a postdoctoral fellow Dr. Jordan Phillips, who has been in my group since September, 2013.

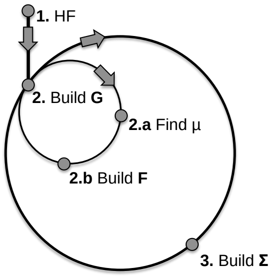

FIG. 2. A bird's-eye view of the GF2 algorithm.

B. The development of the self-energy embedding theory

Despite GF2 being computationally affordable to use it for a treatment of strongly correlated solid such as oxide perovskites, layered materials or surface problems still remains too costly. To mitigate this problem, we developed a method that uses the GF2 treatment only in the embedded region of choice (e.g. single unit cell). Consequently, we can use the GF2 treatment to first determine strongly correlated orbitals in the embedded region for which a strongly correlated method, preferably DMFT, will later be used. The remaining weakly correlated orbitals are treated with perturbative GF2. Since GF2 can be easily used to treat around three hundred of orbitals such a multi-scale approach provides a sufficiently computationally affordable framework to treat realistic systems and large units cells - exactly these components are necessary to treat layered materials and surface problems. The self-energy produced in the self-energy embedding theory (SEET) can be expressed as

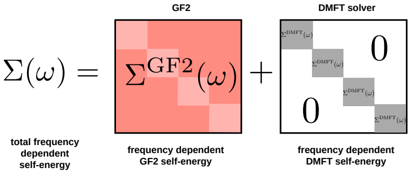

FIG. 3. The SEET self-energy.

$$\Sigma_{\text{unit cell}}(\omega) = \Sigma^{\text{GF2}}_{\text{unit cell}}(\omega) + \Sigma^{\text{DMFT}}_{\text{unit cell}}(\omega) \ . \tag{2}$$

This equation is represented pictorially in Fig. 3.

An extension of the SEET approach to realistic periodic systems requires one additional step to preserve the translational invariance of the original system. This is done using dynamic cluster approximation (DCA) that enables a treatment of a unit cell in the k-space by SEET, thus providing a translational invariant solution for the whole periodic problem. In order to test this approach, we implemented DCA+SEET hybrid for a Hubbard lattice where a significant number of Monte-Carlo results exist providing a good comparison with our data.

To test our conjecture that even for a very complicated systems such as 2D Hubbard model only few orbital are strongly correlated, while the rest of orbitals can be treated with GF2, we performed preliminary calculations with

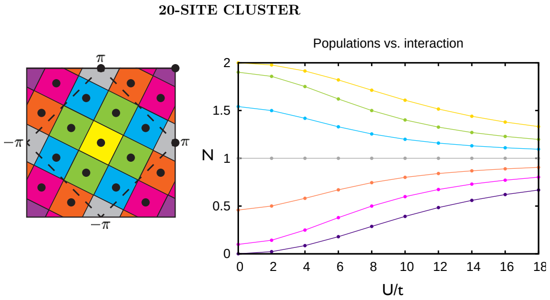

FIG. 5. 20-site Hubbard 2D lattice cluster unit cell and occupation numbers inside it produced with DCA+SEET scheme.

various U/t in order to produce the occupation numbers.

The result of our calculation for 20-site cluster in 2D Hubbard lattice is presented in Fig. 5, where it is visible that two different groups of orbitals exist - strongly correlated with occupancy near 1 and weakly correlated with occupancies near 2. At present these results are preliminary and we plan to explore this topic further by analyzing different cluster geometries and extending our investigations to 3D Hubbard which is closer to the realistic systems.

To summarize, our SEET method has the following advantages:

- Large unit cells with many orbitals are tackled with our scheme and the important strongly correlated orbitals are selected for an accurate treatment while all the remaining orbitals are treated at the GF2 level.
- Non-local Coulomb interactions outside the orbitals treated with impurity solver can be described by GF2, thus screening of local Coulomb interactions is not necessary in the SEET scheme.
- Intercell interactions can be described by SEET with cluster approaches capable of treating few unit cells simultaneously.
- GF2 is iterative, perturbative, and explicitly temperature dependent.
- The scaling is exponential for the accurate solver part (only few orbitals in the unit cell) and $O(n^4)$ for the n orbitals that are treated with GF2.

The SEET implementation was developed in my group a graduate student Alexei Kananenka, who has been in my group since September, 2013. Our first paper featuring SEET approach is currently in press.

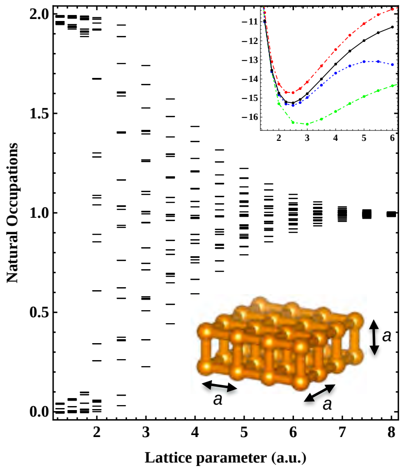

FIG. 4. Natural occupations numbers of H_{32} double plaquette with respect to lattice parameter a. Inset lower-right: structure of H_{32}. Inset upper-right: lattice stretching curves for RHF (red), MP2 (blue), CISD (black), and GF2 (green).

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Avoiding delocalization and static-correlation errors of density-functional approximations

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Presentation Abstract

I will describe how Partition Density Functional Theory (PDFT) can be used to avoid the delocalization and static-correlation errors of approximate exchange-correlation functionals. This is made possible by allowing the fragment densities to be ensemble ground-state densities with fractional charges and spins. I will discuss the behavior of the fragment energies as a function of fragment occupations, and will briefly describe future research directions.

DE-FG02-10ER16196: Partition Density Functionals: Theory and Applications

Student(s): Martin Mosquera, Jonathan Nafziger

RECENT PROGRESS

Correct description of bond breaking

We demonstrated that simple approximations to the partition energy, within the framework of PDFT, can correct almost entirely the delocalization and static-correlation errors incurred in by local and semi-local functionals in standard KS-DFT[8]. For example, the table shows self-consistent calculations employing an "overlap-weighted" approximation to the partition energy: $E_p^{\mathrm{OA}} = \Delta T_s + \Delta V_{\mathrm{ext}} + f\left(N_s, S\right)\Delta E_{\mathrm{H}} + S\Delta E_{\mathrm{XC}}$, where "Δ" stands for the non-additive pieces of the energy components, and the overlap $S[n_1, n_2] = N_s^{-1}\int d\mathbf{r}\sqrt{n_1(\mathbf{r})n_2(\mathbf{r})}$ with $N_s = \sqrt{N_1 N_2}$ and $f\left(N_s, S\right) = \left(\lfloor N_s \rfloor + S\left(1 - \lfloor N_s \rfloor\right)\right)$

Dissociation energies (mH) for H_2^+ and H_2

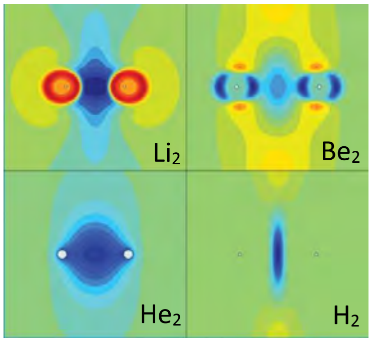
	KS-DFT (LDA)	PDFT (OA-LDA)	exact
H_2^+	18.1	102.0	102.6
H_2	246.1	180.0	174.5

Partitioning the current density

We showed the existence of one-to-one mappings between the total current density of a molecule, a sharply-defined set of fragment current densities, and an auxiliary electromagnetic vector-scalar potential pair (the partition potential). Thus, regarding a molecule as a set of non-interacting subsystems that individually evolve under the influence of the corresponding partition potential, PDFT can be generalized to use the fragment current densities as the main variables. We proved the zero-force theorem for the fragmented systems, established a variational formulation in terms of action functionals, and worked out in detail a simple example for a charged particle in a ring[6].

First benchmark PDFT calculations

We carried out the first benchmark PDFT calculations on homonuclear diatomic molecules and analyzed the associated partition potentials. We derived an exact condition determining the strength of the singularities of the partition potentials at the nuclei, established the connection between charge-transfer and electronegativity equalization between fragments, and tested alternative ways for dealing with fractional charges and spins within PDFT[9].



Partition potentials for the first four homonuclear diatomics[9].

Fractional occupations

The importance of allowing for fractional occupations was highlighted by solving several one-dimensional model systems. We explored in detail two interrelated aspects of PDFT: The connections between fragment densities obtained via different choices of fragmentation, for which we found "near-additivity", and the nature of their corresponding fragment occupations. We found that whereas non-integer occupations arise for very large inter-fragment separations, strictly integer occupations appear for small inter-fragment separations. Cases wherein the fragment chemical potentials cannot be equalized lead to fragment occupations that lock into integers[3].

Future work will involve both formal developments and applications. An adiabatic-connection formula will be used to guide physically-motivated approximations to the partition energy of PDFT; the conditions will be determined under which charge transfer leads to fractional occupations in PDFT; a new algorithm that treats the partition potential as a dynamical variable will be implemented.

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The random phase approximation for delicate ground-state energy differences in materials science

Adrienn Ruzsinszky

Presentation Abstract

In this talk I show the performance of the fully nonlocal random phase approximation (RPA) for the delicate energy differences of interest in materials chemistry and physics. Direct RPA includes the full exact exchange energy and a nonlocal correlation energy from the occupied and unoccupied Kohn-Sham orbitals and orbital energies, with an approximate but universal description of long-range van der Waals attraction . In our work we focus on tests of direct RPA and its corrections for several problems relevant to Department of Energy missions.

The applications in this proposal are challenges for the simpler approximations of Kohn-Sham density functional theory, which are part of the current "standard model" for quantum chemistry and condensed matter physics. The nonlocal RPA approximation with or even without correction fixes long-standing problems such as missing or unreliable long-range van der Waals attraction in certain chemical reactions, too-small energy differences between certain structures in phase transitions, and the wrong magnetic states in strongly-correlated materials [1,2].

We found that the RPA error cancellation is nearly perfect in many solids, including Si, but less perfect in solid SiO_2, as it is in many chemical reactions [2, and a work underway on high-pressure Ca phases is presented in Figure 1]. "Beyond-RPA" methods like SOSEX and r2PT improve upon RPA, but their performance is controversial [3,4,5]. A nonempirical, spatially nonlocal, model for the exchange-correlation kernel could be a more reliable and "intrinsic" approximation to capture accurate ground-state energy differences. This kernel is being implemented in the ABINIT code and tested for energy differences.

Department of Energy under Grant No. DE-SC0007989.
Project title: Exploring the Random Phase Approximation for Materials and Chemical Physics

Postdoc: Savio Laricchia
Student: Bing Xiao

RECENT PROGRESS

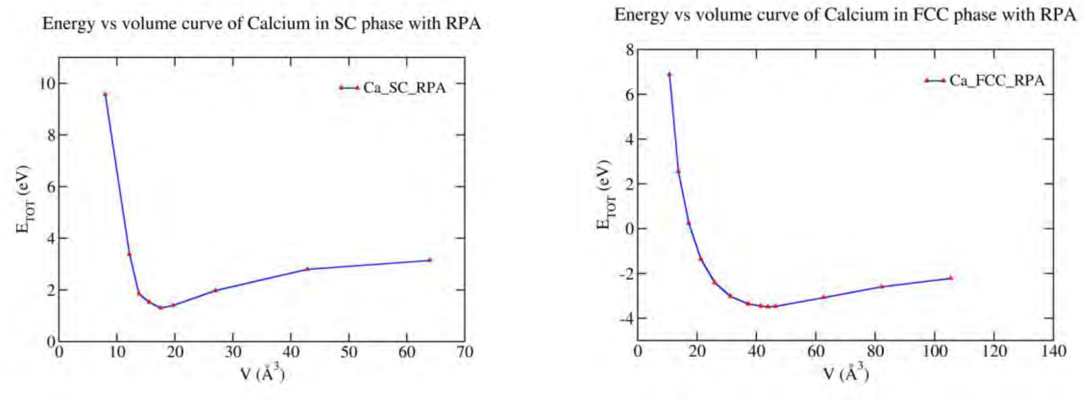
1. High pressure phases of Ca within the random phase approximation

At ambient conditions, Ca crystallizes in the face-centered-cubic (FCC) structure. At higher pressure, the

following transitions have been observed in x-ray diffraction measurements at room temperature: to body-centered-cubic (BCC) at 20 GPa, simple cubic (SC) at 32 GPa.
At this time with the current facilities we could finish the SC and FCC phases. The BCC phase requires more memory.

Parameters used in our calculations with VASP: 10*10*10 k-point grid, ENCUT = 500 eV for ACFDT calculations. Number of bands used: same as maximum number of plane waves using a cutoff. Accurate lattice constants were obtained for both phases with RPA: 2.61 Å for SC, and 5.59 Å for FCC phases, while the experimental values are 2.606 and 5.58 Å respectively, much better than PBE, MS2 and any other approximations tried. Also in the FCC phase the total energy is more negative indicating that SC phase is a high pressure phase compared to FCC, which is correct too. The transition pressure will be determined by the third-order Birch-Murnighan equation. *PRL* **105**, 235503 (2010)

Figure 1.



2.Nonlocal exchange-correlation kernel as a correction to RPA

This kernel is being implemented in the ABINIT code and tested for energy differences between D-Si-beta-tin, and SiO_2(α-quartz)-SiO_2 (stishovite) systems. Currently we obtained the equilibrium energies for ACFD-RPA and for ACFD-RPA+CP07, and ACFD-RPA+CDOP kernel corrections (both uniform electron-gas-based kernels).

Publications acknowledging this Grant in 2013-2015

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[5] Mezei, P.D, Csonka, G.I., Ruzsinszky, A. and Kállay, M. Construction and Application of a New Doubly-Hybrid Random Phase Approximation, *in preparation*.

Future plans

- The future plans include the completion of the ongoing work on high-pressure phases of Ca. We need to finish the energy-volume curve on the third, the BCC phase of Ca. A large memory workstation ordered recently will be appropriate for this memory-bound RPA calculations (DoE mission: materials under extreme conditions).

- Similar to the first plan, our CO_2 adsorption calculations on the Pt(111) surface require the large memory workstation (DoE mission: carbon capture and sequestration). We started doing these calculations on NERSC supercomputers, but noticed that large surface calculations with RPA are largely memory-bound.

- We are currently implementing and testing the nonlocal uniform-electron gas-based kernel of L.A. Constantin and J.M. Pitarke, *Phys. Rev. B* **75**, 245127 (2007). We believe that an "intrinsic" correction to the RPA through the Dyson equation can give more appropriate correction in structural phase transitions than the previous RPA+.

- Other ongoing work is related to DoE mission: multifunctional complex materials**.** The PI is applying *GW* approximations to transition metal monoxide molecules with the FHI-aims code. The *GW* is usually performed perturbatively with an appropriately chosen reference input. The main focus of this research is to understand the role of the exact exchange mixing in the starting point. By tuning the mixing parameter we can minimize the quasiparticle correction in the reference, and determine an optimum parameter which gives accurate photoemission spectrum. This optimum parameter can also deliver the correct dissociation in diatomics. The aim of the work is to understand whether a universal optimized mixing parameter exists, which can deliver accurate ground – and excited-state properties as well (V. Atalla, M. Yoon,F. Caruso, P. Rinke and M. Scheffler, *Phys.Rev. B*, **88**, 165122, (2013). The same scheme will be then applied to transition metal monoxides in the solid state.

Multiconfigurational Pair Density Functional Theory

Rebecca K. Carlson, Chad E. Hoyer, Giovanni Li Manni, Andrew L. Sonnenberger,
Donald G. Truhlar, and Laura Gagliardi

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Presentation Abstract

I will present a method called Multiconfigurational Pair Density Functional Theory, MC-PDFT, which combines multiconfigurational wave functions with density functional theory. A multiconfigurational reference wave function with correct spin and space symmetry, of multiconfigurational SCF type, MCSCF, is used to compute the electronic kinetic energy and classical Coulomb energy, and the rest of the energy is calculated from a density functional, called the on-top density functional, that depends on the density and the on-top pair density calculated from this wave function. The latest development of the theory will be discussed together with results on excited states of organic molecules and systems containing transition metals.

Grant Numbers and Grant Titles

DE-SC0012702 Inorganometallic Catalyst Design Center, an Energy Frontier Research Center.
Postdoc(s): S. Odoh, V. Bernales

DE-SC0008666 Scientific Discovery through Advanced Computing (SciDAC).
Postdoc(s): G. Li Manni
Student(s): Carlson, A. L. Sonnenberger

DE-FG02-12ER16362 Nanoporous Materials Genome Center.
Postdoc(s): S. Odoh, N. Planas, R. Maurice
Student(s): J. Borycz, A. L. Dzubak

DE-SC0001015 Bridging the gap between quantum chemistry and classical simulations for CO_2 capture.
Student(s): J. Borycz, A. L. Dzubak

RECENT PROGRESS

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First-Principles Real-Space Studies of Electronic and Optical Excitations in TiO_2 Nanocrystals and Organic Molecules

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Presentation Abstract

The GW approximation, coupled with the Bethe-Salpeter equation (BSE), allows the first-principles prediction of electronic and optical properties. In this presentation, we examine the efficiency and accuracy of GW-BSE applied to finite systems such as atoms, molecules or nanocrystals. After a brief introduction of the GW-BSE theory, we discuss how a real-space basis, with wave functions defined on a spherical uniform grid, takes advantage of quantum confinement to improve computational efficiency. We present simulations predicting the excited-state properties of titanium dioxide nanocrystals up to ~1.5 nm in size. We also benchmark GW and GW-BSE energies on test sets consisting of transition metal atoms, some of their oxide dimers, and organic molecules, and explore how a LDA-derived vertex function affects the accuracy of quasiparticle and absorption energies on the same benchmark set.

DE-FG02-09ER16072: Manipulating Light with Transition Metal Clusters, Organic Dyes, and Metal-Organic Frameworks

Postdoc: Linda Hung
Student: Bin Shi

PROGRAM SCOPE

The primary goals of our research program are to develop and apply state-of-the-art first-principles methods to predict electronic and optical properties of three systems of significant scientific and technological interest: transition metal clusters, organic dyes, and metal-organic frameworks. These systems offer great opportunities to manipulate light for a wide ranging list of energy-related scientific problems and applications. We focus our investigations on the following areas:

- The development and implementation of many-body Green's function methods (GW approximation and the Bethe-Salpeter equation) to examine excited-state properties of transition metal and transition-metal-oxide clusters.

- The prediction of excited-state properties of free-standing and dye-sensitized titania nanocrystals. For free-standing passivated nanocrystals, we examine the size, shape, and exposed surface dependence of the optical and electronic properties, and investigate whether nanocrystals that are "large" in terms of computational cost can achieve the properties of the bulk limit. We are also interested considering organic dyes attached on various TiO_2 surfaces to investigate how optical properties of the combined system emerge from its individual units.

- Applications of time-dependent density-functional theory and many-body perturbation methods to examine the electronic and optical properties of metal-organic frameworks (MOFs) to shed light on whether they can be utilized as materials for light-harvesting applications. In particular, we plan to focus on two MOFs, the so-called MOF-5 and HKUST-1, and their building units, and perform a systematic study of how their optical properties evolve from their subunits. These studies are expected to lead to significant insights for future design of alternative photovoltaic and photocatalytic materials based on MOFs.

RECENT PROGRESS

We have modeled rutile TiO_2 nanocrystals (NCs) up to ~1.5 nm in size to study the effects of quantum confinement on their electronic and optical properties. Electronic excitations were obtained via the perturbative GW approximation and ΔSCF method for NCs up to 24 and 64 TiO_2 formula units, respectively. These demanding GW computations were made feasible by our implementation of a real-space framework that exploits quantum confinement to reduce the number of empty states needed in GW summations. We used TDDFT to predict the optical properties of NCs up to 64 TiO_2 units. Our computations revealed that the largest NCs modeled are still quantum confined and do not yet have quasiparticle levels or optical gaps at bulk values. Nevertheless, we found that classical Mie-Gans theory can quite accurately reproduce the line shape of TDDFT absorption spectra, even for TiO_2 NCs of sub-nanometer size.

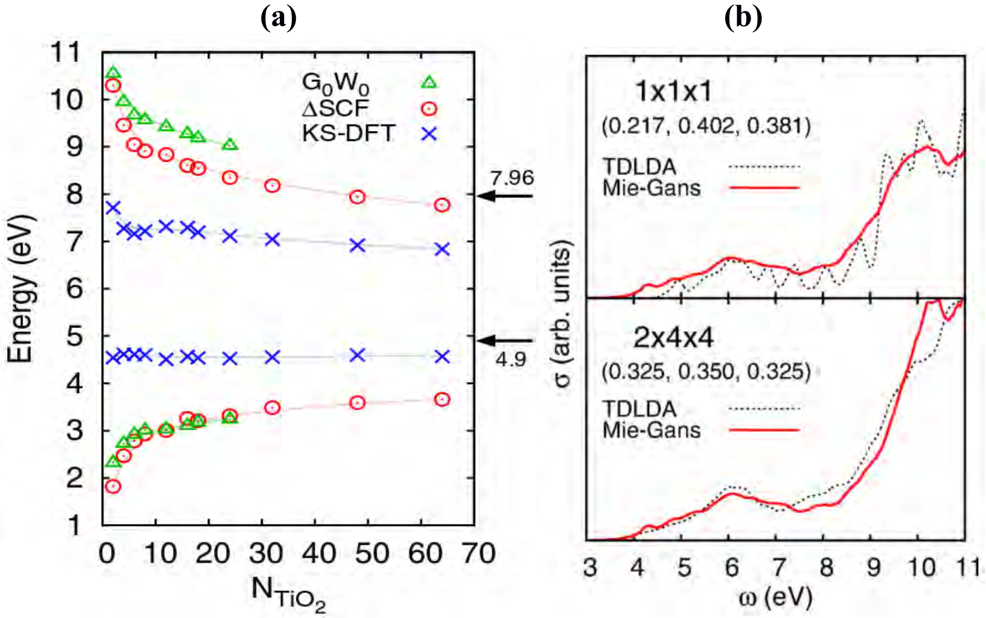

Fig. 1: (a) The ionization energy and electron affinity of TiO_2 NCs of increasing size, computed at three levels of theory: ground state KS-DFT, the ΔSCF method, and "one-shot" GW. The band gap and electronic levels do not yet reach bulk levels, shown by arrows on the right, for the largest NCs (sized ~1.5 nm) in our study. (b) TDLDA and Mie-Gans optical spectra are in good agreement with each other from the smallest to the largest NCs.

We have started a collaboration with two groups (Chelikowsky at UT Austin and Louie at UC Berkeley, in synergy with their SciDAC effort) to benchmark a variety of molecules to determine any trends in the accuracy of GW-BSE computations relative to experiment, particularly in reference to **(i)** the impact of a LDA-derived vertex correction compared to the standard GW (and GW-BSE) calculations without vertex corrections, **(ii)** the effect of self-consistency in GW, **(iii)** the accuracy of TDDFT compared to GW-BSE, and **(iv)** a plane-wave basis compared to a real-space (localized) basis. The set so far includes three inorganic molecules (N_2, H_2O, and NH_3) and six organic molecules (benzene, naphthalene, thiophene, 1,2,5-thiadiazole, benzothiazole, and tetrathiafulvalene). Preliminary results were presented at the 2014 APS March Meeting in Denver, CO, and demonstrate that the LDA vertex correction gives ionization energies in worse agreement with experiment, in comparison to standard GW (no vertex).

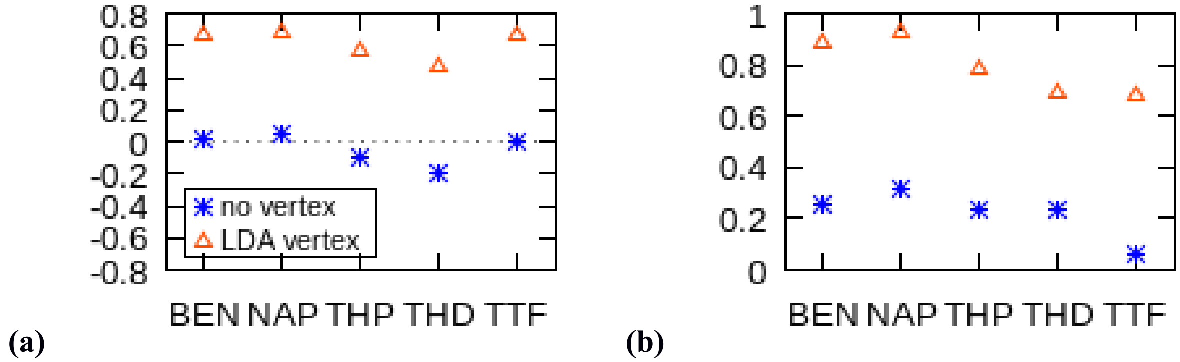

Fig. 2: (a) Error of the first ionization energy, as predicted by GW (real-space framework) without and with a vertex correction, in comparison to experiment, for a test set consisting of benzene, naphthalene, thiophene, thiadiazole, and tetrathiafulvalene. (b) Mean absolute error of the multiple ionization energies for each molecule, from GW calculations without and with a vertex correction.

We also are performing a GW-BSE benchmark study of transition-metal atoms (Cu, Zn, Ag, and Cd), as well as their monoxide molecules. This test set allows us to analyze the accuracy of GW and GW-BSE for states with *s*, *p*, and *d* symmetries, with comparison to accurate experimental measurements. For this project, we are collaborating with Fabien Bruneval (CEA, France). Preliminary results were presented at the 2015 APS March Meeting in San Antonio, TX.

Finally, we have started a new collaboration with the group of Leeor Kronik (Weizmann Institute, Israel) on investigating the electronic structure of copper-oxide clusters (Cu_xO_y, $x = 1$-2, y =1-4) using DFT, hybrid functionals as well as the GW method at various levels of theory. Preliminary results were presented at the 2015 APS March Meeting, San Antonio TX. These show that while DFT with hybrid functionals are better at predicting the binding energy of states with primarily *d*-character, PBE outperforms hybrid functionals at predicting the binding energy of peaks with more *p*-type character, and demonstrates the need for the more-transferable GW calculations.

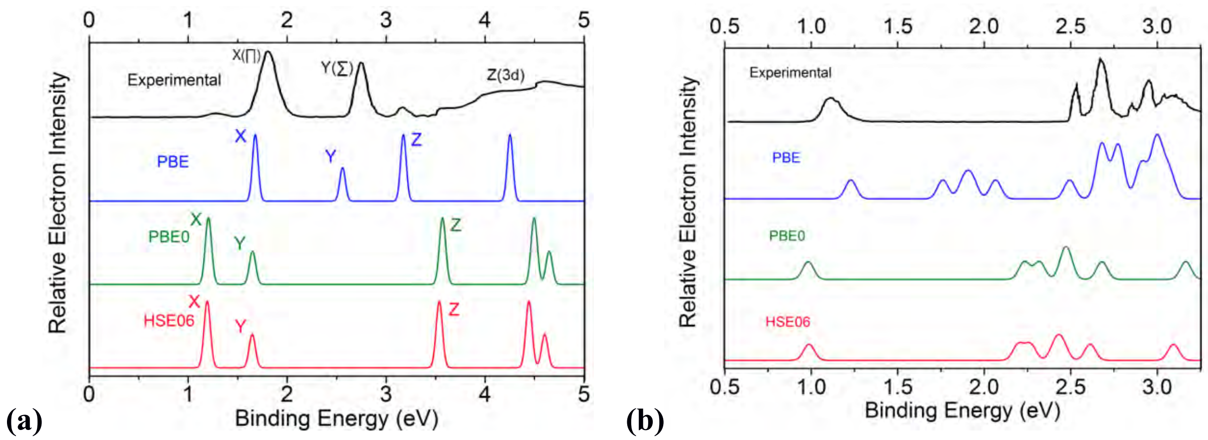

Fig. 3: (a) Calculated photoemission spectra for CuO using various exchange-correlation functionals (PBE, PBE0, and HSE06), with comparison to experiment. (b) Calculated photoemission spectra for CuO_2 using various exchange-correlation functionals (PBE, PBE0, and HSE06), with comparison to experiment.

FUTURE PLANS

Our ongoing research and future plans in first-principles investigations into the optical and electronic properties of transition-metal clusters and organic dyes also include:

- Deriving new approximate vertices for use with GW and GW-BSE (e.g., PBE)
- Modeling the optical properties of TiO_2-dye systems
- Modeling the optical and electronic properties of CuO_2-based nanocrystals
- GW-BSE optical properties of TiO_2-based nanocrystals
- Investigations into the optical properties of MOFs

PUBLICATIONS ACKNOWLEDGING THIS GRANT (2014)

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Fast Numerical Algorithms for Electronic Structure Calculation

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We highlight a number of new algorithmic developments resulting from the collaboration of applied mathematicians and materials and chemical scientists in the DOE SciDAC parternship projects that are funded jointly by DOE BES and ASCR. Part of the work is also supported by the Frameworks, Algorithms and Scalable Technologies for Mathematics (FASTMath) SciDAC institute.

1 Fast matrix diagonalization methods

Matrix diagonalization methods are used in many types of ground state and excited states electronic structure calculations. For planewave Kohn-Sham density functional theory (DFT) based ground state calculation, we have recently developed an algorithm called a projected preconditioned conjugate gradient (PPCG) method [9] that is efficient for computing a relatively large number of eigenpairs of a Kohn-Sham Hamiltonian. Compared to existing methods, PPCG performs fewer Rayleigh-Ritz (RR) calculations in which a dense subspace eigenvalue problem is solved. This is often the bottleneck on a distributed memory parallel computer when the number of electrons in the system is relatively large. PPCG constructs approximate solutions by solving k 3×3 small eigenvalue problems, instead of one $mk \times mk$ eigenvalue problem constructed in other iterative methods, where k is the number of eigenpairs to be computed and $m \geq 1$ is a small constant. The orthonormality constraint of the approximate solution is periodically enforced through a Cholesky QR factorization. A few RR calculations are used to deflate converged eigenvectors. We have implemented and tested the new solver in the Quantum Espresso and Qbox planewave codes. The new solver consistently and substantially outperforms the existing solvers.

For non-Hermitian eigenvalue problems that arise from coupled cluster equation of motion models and complex scaling configuration interaction calculation of meta stable states, we developed a new algorithm which is called *generalized preconditioned locally harmonic residual* (GPLHR) method [10], for computing a few eigenvalues in the interior of the spectrum. The method projects the non-Hermitian Hamiltonian matrix into a subspace spanned by the current approximation to the desired eigenvectors, a preconditioned residual associated with this approximation, and a number of auxiliary basis elements that can be viewed as the basis vectors of a subspace constructed to iteratively obtain approximate solutions to Newton correction equations associated with the desired eigenpairs. Instead of using the standard Ritz approximations, we perform a harmonic projection and extract harmonic Ritz values and vectors that are better approximations to interior eigenpairs. Our numerical experiments indicate that GPLHR can be more efficient and robust than the widely used generalized Davidson subspace diagonalization algorithm. The GPLHR solver has been integrated with the QChem software package.

The full Bethe–Salpeter equation (BSE) for describing optical absorption of materials is also a non-Hermitian eigenvalue problem. However, the problem has special structures that can be exploited in a diagonalization method. We recently developed a structure preserving diagonalization method for computing all eigenpairs of the BSE Hamiltonian [8]. The method preserves the positive and negative pairings of the computed eigenvalues. It uses real arithmetic and is relatively easy to parallelize. We have integrated the solver with the BerkeleyGW software package and shown that the new solver is more efficient than applying a general ScaLAPACK non-Hermitian eigensolver to the BSE problem.

2 Diagonalization-free methods

For some applications, it is sometimes not necessary to obtain the full set of eigenvalues and eigenvectors of a matrix operator. For instance, in the linear response time-dependent DFT analysis, one is interested in obtaining the absorption spectrum defined, up to a constant factor, as $\alpha(\omega) = \sum_{\mu} \mu^T \delta(H - \omega I)\mu$, where $\mu \in \{x, y, z\}$ is a dipole moment vector, and δ is the Dirac-δ function. Although we can calculate $\alpha(\omega)$ by diagonalizing H, a more efficient way to compute an approximation to $\alpha(\omega)$ is to use the Kernel Polynomial method (KPM) or the Lanczos algorithm to construct a polynomial approximation to $\alpha(\omega)$ directly [6]. This type of approach only requires a procedure to multiply H or subblocks of H with a number of vectors. We have shown that it is orders of magnitude faster than diagonalization based approach.

In Kohn-Sham DFT, diagonalization methods are often used to construct approximations to the electron density $\rho = \sum_j |\phi_j|^2$, where ϕ_j is the approximation to the jth Kohn-Sham eigenfunction. However, it is well known that ρ can be extracted from the diagonal of a matrix function $f(H - \mu I)$, where $f(t)$, often chosen as a Fermi-Dirac function, is an approximation to a step function that is zero when t is below the chemical potential μ and one when $t > \mu$. We developed an efficient algorithm which we call pole expansion and selected inversion (PEXSI) [3] to approximate selected elements of this matrix function required to evaluate the most important physical quantities such as the electron density, energy and atomic forces [3]. Our algorithm involves computing selected elements of the inverses of several shifted Hamiltonians, which can be implemented efficiently via sparse matrix techniques [7]. By exploiting the sparsity of the Hamiltonian, we reduced the complexity of the computation from $\mathcal{O}(N^3)$ in the diagonalization based approach to at most $\mathcal{O}(N^2)$ without loss of accuracy even for difficult metallic systems, where N is the number of atoms. We have implemented a parallel version of selected inversion that is highly scalable. Together with pole expansion, the PEXSI software, which is open-source (`http://www.pexsi.org`), and is scalable to more than 100,000 cores on DOE leadership computers. PEXSI has been integrated into SIESTA [4] and CP2K, two popular electronic structure packages based on atomic orbitals. We have recently used the SIESTA-PEXSI method to study the electronic structure of large scale graphene nanoflakes of unprecedented size (with more than 10,000 atoms) [2].

3 Methods that exploit sparsity

In addition to exploiting sparsity in DFT based methods, we have also examined ways to create and exploit sparsity in wavefunction methods. Recently, we developed an algorithm aiming at reducing the computational work involved in coupled cluster (CC) calculations by sparsifying the amplitude correction within a CC amplitude update procedure [1]. We provided a theoretical justification for this approach, which is based on the convergence theory of inexact Newton iterations. We demonstrated by numerical examples that, in the simplest case of the CCD equations, we could sparsify the amplitude correction by setting roughly 90% nonzero elements to zeros on average without affecting the convergence of the inexact Newton iteration.

4 New discretization method

Another area in which we have made significant progress in the SciDAC project is the development of a systematic adaptive local basis (ALB) expansion method for discretize the Kohn-Sham problem. The method is based on domain decomposition and discontinuous Galerkin (DG) techniques [5]. We have implemented this approach in a new KSDFT code which we call DGDFT. The use of ALB allows us to produce a compact representation of the KS Hamiltonian while maintaining the sparsity of the representation. We achieve this by partition the computational domain into a number of local elements, and solve the Kohn-Sham problem in each extended element that include both a local element and a buffer region to contruct basis functions that capture not only properties of atomic species within each local element, but also the chemical environment encoded in the buffer region. The solution of the local Kohn-Sham problem are restricted to each local element to produce basis functions. These basis functions are localized in the real space and discontinuous in the global domain. Approximations to the continuous Kohn-Sham orbitals and density are assembled from the discontinuous basis functions using the discontinuous Galerkin (DG) method. The use of domain decomposition and DG allows us improve the accuracy of the reprentation in a systematic fashion. We have recently used DGDFT to perform ab initio molecular dynamics simulation of 10,000-atom armchair edged phospherene nanoribbon (ACPNR). The simulation can scale to 50,000 cores on the Edison system at NERSC. It took roughly 25 seconds to perform each self-consistent field (SCF) cycle within each MD step. We were able to simulate a 2.5 picosecond trajectory (with a time step of 2 femtoseconds) that reveals edge reconstruction that had not been previously observed.

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Program Title: Theoretical Developments and Applications to Surface Science, Heterogeneous Catalysis, and Intermolecular Interactions

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Program Scope. Our research effort combines new theory and code developments with applications to a variety of problems in surface science and heterogeneous catalysis, as well as the investigation of intermolecular interactions, including solvent effects in ground and excited electronic states and the liquid-surface interface. Many of the surface science studies are in collaboration with Dr. James Evans. Much of the catalysis effort is in collaboration with Drs. Evans, Marek Pruski and Igor Slowing.

Recent Progress. A significant effort involves the development of efficient methods that can be applied to large systems, such as surfaces, nanoparticles and liquids. One such method is the effective fragment potential (EFP) method whose accuracy for intermolecular interactions rivals that of second order perturbation theory (MP2). The EFP method, which is a highly sophisticated model potential, can be combined with essentially any electronic structure method to, for example, provide insights about solvent effects and liquid behavior. Most recently, the EFP method has been combined with nonlinear time-dependent density functional theory to facilitate the investigation of solvent effects on nonlinear optical properties[10]. Because the EFP method is fully implemented only in the GAMESS program, we have used the common component architecture (CCA) approach to make the EFP method available to other codes, such as NWChem[5]. The EFP method has also been combined with our spin-flip TDDFT method to study solvent effects on the location and energy profile of conical intersections, which have a profound effect on excited states, photochemistry and photobiology.

Another (fully quantum) fragmentation approach is the fragment molecular orbital (FMO) method. The FMO method divides a large species into fragments to facilitate accurate QM calculations on very large systems. The FMO method can be used in concert with any electronic structure method in GAMESS. In order to optimize geometries using the FMO method, or to perform molecular dynamics (MD) simulations, it is necessary to derive and code fully analytic gradients for each method that is combined with the FMO method, such as Hartree-Fock (HF) or DFT. Fully analytic FMO/HF and FMO/DFT gradients have been derived and implemented in GAMESS, to enable geometry optimizations and MD simulations. We have shown that one can do FMO/HF MD simulations with periodic boundary conditions and that fully analytic gradients are absolutely essential[6]. We have therefore derived and implemented the fully analytic FMO/DFT gradient[13]. Most recently, we have derived and implemented analytic Hessians for DFT, FMO/DFT and FMO/HF[14]. The availability of Hessians enables the prediction of vibrational frequencies and infrared and Raman spectra for large molecular systems. Two invited reviews of fragmentation methods have appeared in high impact journals[1,11] The FMO method is also highly scalable, because the calculation for each fragment can be performed on a separate compute node. An alternative approach, the cluster in molecule (CIM) method developed by the Piecuch group, is based on localized molecular orbital (LMO) fragmentation. In principle, the CIM method is linear scaling, but the first step in the CIM procedure is to calculate the LMOs for the entire system of interest. This is a significant computational roadblock. We have solved this roadblock by developing a combined FMO-CIM method, in which the LMOs need only be calculated separately for each FMO fragment[15]. Advances have also been made in high performance computational chemistry. A prior INCITE grant has enabled us to have access to the BlueGene /P at Argonne, where we have demonstrated that the FMO method allows essentially perfect scaling to the petascale (more than 131,000 processors)[2]. The EFP and FMO methods have both been used to study problems related to biomass conversion to useful energy[4,8].

Another approach to making high-level electronic structure calculations is to use localized molecular orbitals (LMOs), because correlation is local. So, one can design LMO domains or subsystems and only perform the correlation calculation within those domains. Professor Carter (Princeton) has developed a multi-configurational (MR) configuration interaction (CI) code called TigerCI to perform such calculations. In collaboration with the Carter group, a preliminary parallel version of TigerCI code has been implemented[12]. The TigerCI code has now been incorporated into GAMESS. A manuscript that describes this effort is in preparation.

“Composite” methods refer to the use of multiple levels of theory to predict accurate thermodynamic properties of molecules. Most composite methods can predict very accurate thermochemistry, but are not reliable for the prediction of reaction mechanisms, barrier heights and (therefore) kinetics. We have recently developed a new composite method, called ccCA-CC(2,3), based on the Piecuch CR-CC(2,3) method, that can predict both thermodynamics and reaction mechanisms with very high accuracy. We have shown that the ccCA-CC(2,3) method correctly predicts complex mechanisms for important chemical reactions, whereas the usual single reference composite methods fail[3].

Mesoporous silica nanoparticles (MSN) have received increasing attention due to their catalytic capabilities. Because the MSN species are very important for their selective heterogeneous catalytic capability, we have an ongoing effort to model these complex species. Previously, we have implemented the ReaxFF force field into GAMESS. A combined ReaxFF/NMR study, in collaboration with the Pruski group, demonstrated that the ReaxFF method can produce structural data that are consistent with the temperature-dependent NMR data. Similarly, we have demonstrated that the FMO method is capable of studying reactions within MSN. Equally importantly, the HF-D method (HF combined with a dispersion correction) can provide energetics for a benzene molecule moving through a MSN with an accuracy that is comparable with that of MP2. The electronic structure theory calculations are also combined with the non-equilibrium statistical mechanics methods of the Evans group to provide mesoscale insights.

<u>Current and Future Plans</u>. The FMO-CIM/CR-CC(2,3) method will be applied to studies of phenomena on the Si(100) surface, such as more extensive studies of diffusion of Ga and In, and of the MSN systems. Preliminary FMO studies have been performed on model MSN species at the Hartree-Fock level of theory with a small basis set. The

agreement with the fully ab initio method is excellent, especially when one uses the HF-D method, so we will now apply FMO with higher levels of theory and reliable basis sets to processes that occur within the MSN. The EFP-QM exchange repulsion analytic gradients have been derived, and these will now be implemented so that any solvent can be studied.

The FMO method is being used to perform MD simulations on water and on aqueous solvation of ions such as hydronium ion and nitrate. It is apparent that three-body effects are critical for these simulations, so the derivation and implementation of the FMO3 fully analytic gradients is in progress. The more computationally efficient effective fragment molecular orbital (EFMO) method, a merging of EFP and FMO is very appealing for MD simulations that involve water. The derivation and implementation of the fully analytic EFMO gradients is underway.

An interface between the GAMESS electronic structure program and the FMS program from the Martinez group has been implemented. The combined GAMESS-FMS methodology will now be used to study excited state phenomena, such as conical intersections that are ubiquitous in photochemical processes. In order to fully analyze surface crossings and conical intersections, one needs the ability to calculate non-adiabatic coupling matrix elements (NACME) that couple multiple surfaces when they are in close proximity. For large systems, TDDFT and SF-TDDFT are the most efficient methods for exploring excited state phenomena, so the derivation and implementation of TDDFT and SF-TDDFT NACME are in progress.

A new INCITE grant will allow us to use the FMO and EFMO methods to study aqueous solvation of ions and ionic liquids, in collaboration with colleagues at Argonne National Laboratory, at a high level of electronic structure theory.

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Adsorption and Growth of Organic Materials on Metal Surfaces

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Program scope:

Density functional theory (DFT) has become a versatile, widely applied method to study the materials on the atomic scale. Its favorable scaling, good overall accuracy and easiness of usage have made the Kohn-Sham approach to DFT the method of choice in many application fields. The complications of the many-body interactions in the repulsion between the electrons have been collected into the exchange-correlation (XC) term, whose analytic form, unfortunately, has remained unknown until our days and several levels approximations to the XC energy functional have been proposed, tested. The increased numerical accuracy, and the larger and more complex systems reachable nowadays had made it apparent that there are several cases where the widely applied approximations to the XC fail. The expression of the exact exchange functional is indeed already known, but so long there is no appropriate correlation functional to couple with it is still advantageous to approximate both the exchange and correlation.

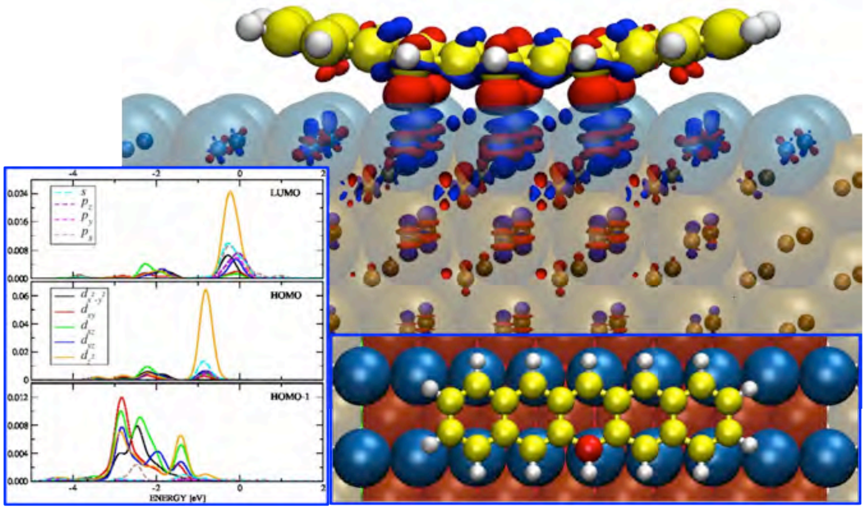
The awareness of the failure of the common approximations to XC to treat the London dispersion has risen in the last ten-or-so years, and has lead to several approximations to treat the problem. A severe complication is due to non-locality of the interaction: The potential felt by electrons in a system is modified due to well separated, another electron distribution, yielding a difficult many-body problem. Thus the models are either severely simplified, like in the semi-empirical models where the electronic structure is not taken into account at all but an additional potential is applied, or a correlation functional that includes the non-local dispersion are introduced. These "van der Waals density functionals" have appeared in several flavors in the last years, and thus lead to conceptually better description of the weak interactions between subsystems, but the results are not necessarily improved and there is no systematic way to do so. Another disturbing aspect is that sometimes the results depend more strongly on which approximation is chosen for the exchange functional and not the correlation functional used, even if the weak interactions are a result of the latter.

The scope of this program is to study the characteristics of the interface between organic materials and metal surfaces using DFT with and without the inclusion of the vdWs effects. These characteristics are determined using several functionals within the self-consistent implementation of the vdWs interactions into DFT (vdW-DF). As a result, within this program, we could screen and classify these functionals according to their performance.

Recent Progress:

1) Pentacene on Cu(110)[1,2]:

A detailed computational study of the atomic and electronic characteristics of the interface of a monolayer of pentacene (Pn) on Cu(110) revealed that Pn is bent upon adsorption. The adsorption of Pn introduces several changes: i) lowering of the workfunction, ii) a charge transfer from Cu(110) to Pn, and charge redistribution iii) appearance of an interface state, iv) a population of the LUMO. In the figure, we show the charge redistribution when Pn is adsorbed along with the projected densities of states showing the new interface state at 0.8 eV below the Fermi level, which has been observed using angle resolved photo-emission spectroscopy[1]. The adsorption of Pn on Cu(110) introduces also a buckling in the top few layers of the substrate; which has been observed lately using Surface X-Ray Diffraction[2].



Pentacene on Cu(110) adsorption geometry,
projected densities of states and charge redistribution

2) Adsorption of Benzene on (111) and (110) metal surfaces: screening vdWs[3,4]

Benzene adsorption on seven transition metal surfaces is studied to explore the performance of the vdW functionals within the self-consistent vdW-DF implementation. Our results reveal that vdW interactions are crucial for an accurate description of bonding on transition metal substrates. We find that the inclusion of vdW interactions increase substantially the adsorption energy on coinage metal surfaces (Au, Ag, Cu), while they lead to an increase in the adsorption energies on the reactive transition metal surfaces (Pd, Pt, Rh, Ni) when using three (optB86b, optB88 and optPBE) out of the five functionals tested, and a decrease in the binding energy for the remaining two (rPW86 and revPBE). Hence, our calculations reveal that changes in adsorption energies stemming from vdW functionals show significant variation, and can be grouped. Comparison between experimentally determined adsorption energies (averaged) and those computed suggests that optPBE and optB88 functionals show systematically good agreements.

3) Adsorption of Olympicene on Cu(111)[5]

Our computational study of the adsorption of an olympicene radical ($C_{19}H_{11}$) on Cu(111) with and without the inclusion of self-consistent van der Waals (vdW) interactions shows that for this system, the inclusion of the vdWs effects changes the adsorption character from week physisorption to strong chemisorption (0.24 eV for PBE vs 2.65 eV for optB86b). The inclusion of the vdWs interactions also induces other changes like appearance of an interface state, bending and tilting of the molecule, charge transfer and redistribution.

4) Adsorption of Sexithiophene on Ag(110)[6]

In good agreement with the experimental observation, we found that sexithiophene molecules adsorb, with similar adsorption energy, parallel and perpendicular to the Ag(110) channels. The inclusion of the vdWs interactions induced a substantial increase in the binding energy (0.8 eV for PBE vs 4.4 eV optB86b). We found an interface dipole of 0.6 eV in good agreement with the 0.7 eV experimentally reported.

5) Adsorption of a cyano-substituted triarylamine molecule on Au(111)[7]

This molecule has three CN ends (dipoles) and several adsorption geometries have been observed experimentally. For this system, the subtle interplay between molecule-molecule and molecule-substrate interactions play a crucial role in the self-assembly. We found, in collaboration with an experimental group, that the inclusion of the vdWs interactions is very important in determining accurately both molecule-molecule and molecule-substrate interactions. With the inclusion of the vdWs effects, the molecule adsorbs close to the surface with a bending that pulls the N ends towards the substrate, introducing a perpendicular (to the surface) component of the CN dipole. This has been shown to be very important in the anchoring of the molecule on the surface.

6) Adsorption of Silicene on Ag(111)[8,9]

Silicene is the silicon counterpart of graphene and it is attracting a lot of attention during the last few years. For silicene on Ag(111), several adsorption geometries have been identified by DFT calculations with and without the inclusion of the vdWs effects. These geometries have all been observed experimentally. For this system, the inclusion of vdWs effects was found to be marginal, which we expect to be important when silicene is adsorbed on insulating materials.

Future Plans:

As we have shown, the inclusion of the vdWs interactions is crucial for determining accurately the characteristics of the interface at the organic material and metal surface junction. However, the present implementations to DFT, though self-consistent, do not provide systematic good agreement with the experimental observations, when available. Improvements on the vdW-DF implementation have been reported that need to be tested. Since the computational cost of the vdW-DF type of calculations is very reasonable, we will continue to test the improvements on the vdW-DF and contribute in refining and sharpening this approach.

Another kind of approach to tackle the request for more accurate electronic structure calculations based on the density functional theory is the random phase approximation (RPA). What is characteristic for the RPA is that it includes the unoccupied states, or virtual orbitals, explicitly in its definition. This is lead to vast increase in the computing time and memory requirements as the number of electronic states that has to be treated is seriously increased. Due to the continuous increase in the computing resources and implementation of RPA in major electronic structure codes, RPA has recently gained popularity as a method to investigate fundamental interactions in weakly interacting systems.

We will apply the RPA to several systems. We will start in small, established systems where we can compare to existing literature and our own findings, and more easily test the various extensions and approximations to RPA. Eventually we wish to tackle systems that are at the frontiers of the present capabilities. These include adsorption of (small) molecules, such as benzene and thiophene, on metal surfaces. Despite the huge computational cost we expect these to be important pioneering calculations that will be a reference when new, computationally lighter approximations are derived. These approaches will then allow investigating systems where the calculations yield reliable predictions or are beyond the accuracy of modern experimental techniques. This opens a novel, exciting field or research direction.

Finally, we will continue to work in close collaboration with experimentalists and contribute in the fundamental understanding of the interface characteristics at the organic materials and metal surfaces junctions

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Surface Plasmon Enhanced Chemistry

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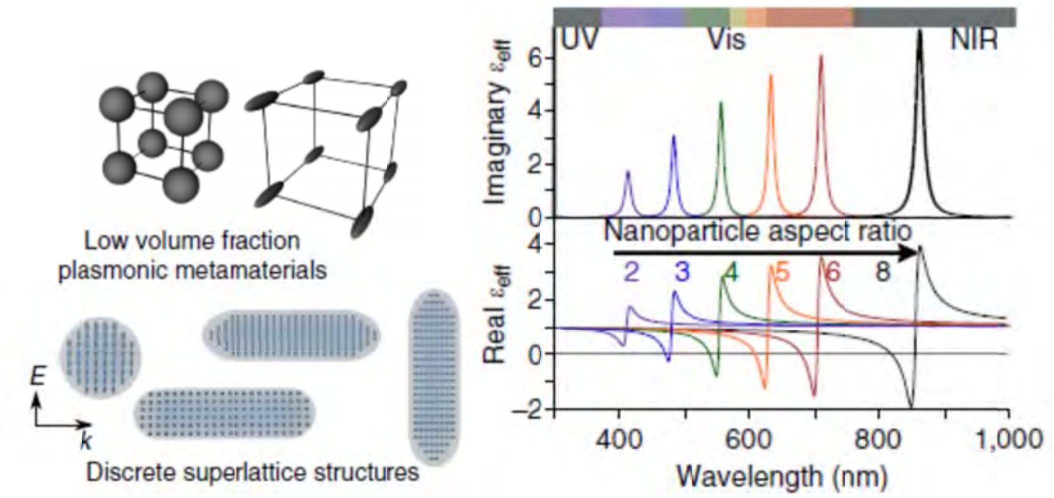
Program Scope

This project is concerned with the development of computational methods and new theory that enable one to describe plasmon excitation in metal nanoparticles, and the interaction of plasmon excited states with molecules and semiconductor nanoparticles that are nearby the metal nanoparticles. Plasmon excitation leads to dramatic modification of the optical and chemical properties of molecules or nanoparticles that are located near the surfaces of these particles, in some cases leading to enhancement in chemical reactivity or optical properties such as extinction, absorption, and Raman (SERS). Also of interest are the properties of lattices and arrays of plasmonic nanoparticles. The research program seeks to develop new electronic structure theories that can be coupled to continuum theories such as Maxwell's equations to describe the interaction of light with plasmonic metal particles leading to plasmonically enhanced chemistry and enhanced spectroscopic properties. In addition, the methods being developed will be used to model experiments being done by a number of collaborators.

Recent Progress

In a new initiative, we are developing theory methods that can describe arrays of plasmonic nanoparticles in three dimensions. This work takes advantage of a new class of DNA-linked nanoparticle superlattice materials that has been developed by the Mirkin group at Northwestern, in collaboration with Schatz. In our first purely theory paper on this topic, we demonstrated how the optical properties of arrays of silver particles can be modified by both the nanoscale properties of the particles and the mesoscale properties of the array.[1] Figure 1 shows a schematic of the array, as well as optical properties that we have generated by combining generalized Mie theory with an effective medium approximation. In this work we demonstrated that unlike gold nanoparticle superlattices, silver superlattices have a range of wavelengths for which the dielectric function (or permittivity) has a negative real part. This occurs for silver volume functions of a few percent, which means that it is possible to prepare films of this material that reflect light, but only over a narrow range of wavelengths (tens of nm). Experiments related to this discovery are just coming on-line.

Plasmon-exciton coupling is another new direction of this research program. Here we collaborated with Teri Odom on a project which demonstrated that it is possible to combine lattice plasmons (hybrid plasmonic-photonic optical modes associated with 2D lattices of gold nanoparticles) with laser dyes to enhance stimulated emission, and thereby produce a new class of subwavelength lasers.[2,3] In this work we developed a new theoretical method in which the laser photophysics, modelled with a four-level system for the dye molecule and including both stimulated and spontaneous emission (with Purcell effect included), is coupled to classical electrodynamics to describe the nanoparticle plasmonics and photonic modes. The modeling has proven crucial in guiding the choice of experimental parameters, particularly with respect to tuning of the lattice plasmon relative to the dye emission spectrum, and the selection of laser and particle densities.



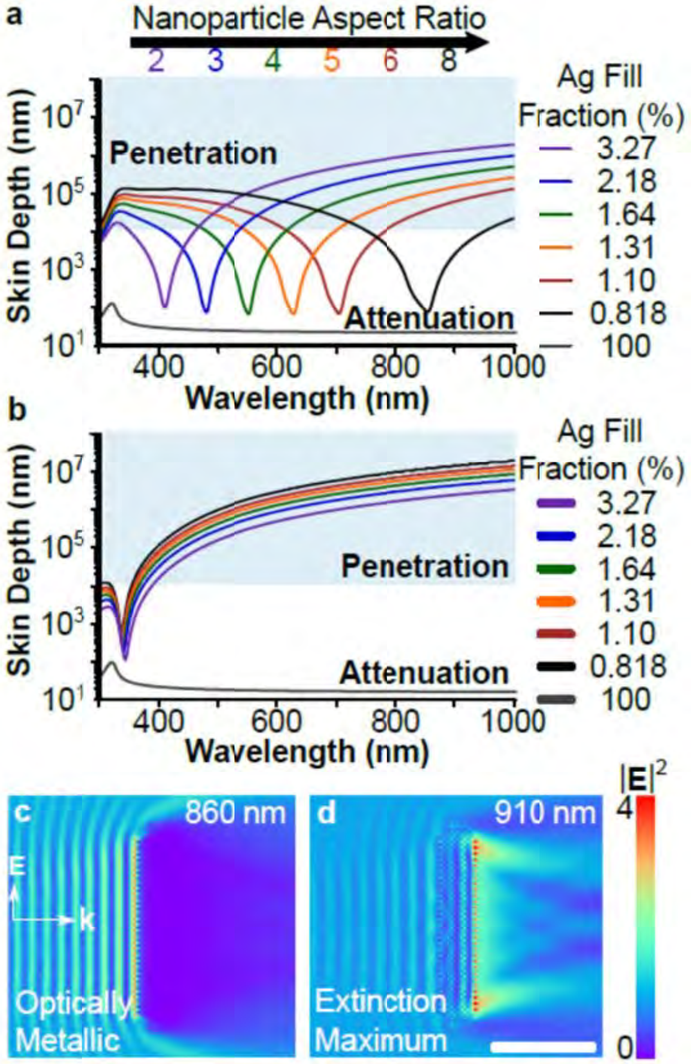


Figure 1. Studies of silver superlattice metamaterials from Ross, Blaber and Schatz [1]. Upper right shows how the lattices are constructed from individual nanoparticles, and then fabricated into mesoscale (micron) structures. Upper left shows effective medium dielectric functions for lattices composed of ellipsoid particles of aspect ratios varying from 2 to 8. Note that the real part of the dielectric function is negative over a narrow wavelength range that can be varied by changing aspect ratio. Panel on the left displays the skin depth predicted by the theory for the different aspect ratios, showing that metallic behavior (small skin depth) is achieved at wavelengths that can be tuned depending on polarization, with (a) showing longitudinal polarization and (b) transverse. Panel (c) shows the reflection of light from a mesoscale slab composed of the superlattice material, with 860 nm showing the metallic behavior and 910 nm the nonmetallic regime. Experiments to verify this behavior are underway.

In other work, a new theory for describing plasmon enhanced spectroscopic properties has been developed[4] which combines a previously developed DFT approach for calculating the chemical contribution to the SERS enhancement factor with a coupled QM/electrodynamics approach for determining electromagnetic enhancements. This is the most complete theory developed so far for SERS, and it is also quite practical, with applications possible for molecules with several dozen atoms. A number of applications of this approach have been done in collaboration with the Van Duyne group at Northwestern. We also performed further studies of our real-time TDDFT approach to photoinduced electron transfer.[5]

In other new theory work, we discovered that the plasmon width of Al nanoparticles is dominated by radiative effects,[6] which is fundamentally different from that for Ag and Au, providing new opportunities for Al that we will pursue in future work. Also we developed a new numerical approach for solving Maxwell's equations,[7] and a theory of refraction at metal-metal interfaces.[8]

We have collaborated with experimental groups to characterize plasmons for dimers of silver particles that are separated by less than 1 nm.[9] This demonstrated for gaps between gold and silver particles, that the plasmon resonances change character when the gaps are smaller than 1 nm, with conventional plasmons (which red-shift as the particles approach) being replaced by charge transfer plasmons (that blue shift). Also, we characterized plasmons for many rod segments that are pieced together with small gaps, [10] showing how resonances at gaps can be combined into collective modes when the gap spacings are chosen to match the plasmon-polariton wavelength. Several other applications to plasmonics, excitonics and plasmon/exciton coupling have been performed.

Future Plans

We will continue our work on metamaterials and laser modeling as the work so far has been limited by available theoretical methods, and the experimental work is getting more and more sophisticated. In the metamaterials direction, we are very interested in studying the transmission and backscattering properties of thin films of superlattice material, as the experimental technology for studying many classes of these materials is developing rapidly. While effective medium studies of these materials are easy to do, we find that effective medium approximations often fail, so our explicit particle codes need to be further developed. We will extend codes based on both generalized Mie theory and on the discrete dipole approximation, including codes in which calculations performed for several layers of material are linked together by matching boundary conditions. We will continue to pursue silver and gold lattices, but we also want to pursue lattices of a broader range of materials, including Al as mentioned earlier, and also pushing to mixed nanoparticle lattices.

Our work on subwavelength lasers will focus in developing more sophisticated models of the dye photophysics, going beyond the 4-level system description to an exciton Hamiltonian description, and pushing toward a Liouville equation description of the time evolution. In addition, we want to adapt these calculations to a modern generation of FDTD codes rather than using a home-written code as we have so far. We also hope to connect our laser modeling with broader applications to exciton-plasmon interactions, including studies of photoluminescence and the study of 3D lattices.

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List of students/postdocs supported (months, p=supported by government fellowship, only partial support from DOE):

1. Postdocs: Nicolas Large (10), Clotilde Lethiec (3), Jeffrey McMahon (3)
2. Students: Lindsey Madison (12,p), Adam Ashwell (12), Mike McAnally (3,p), Natalie Gruenke(3,p)

Statement about funds remaining: It is anticipated that all funds will be expended by June 1, 2015

Koblar A. Jackson

Using site-specific polarizabilities to probe the electric dipole response of metal atom clusters

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Presentation Abstract

We are using a method for decomposing the electric dipole polarizability into site-specific (*i.e.* atomic) contributions to study the response of atomic clusters to applied electric fields. The method further allows the partitioning of the response into charge transfer (metal-like) and local dipole (insulator-like) components. In a recent application to Na clusters (L. Ma *et al.*, Phys. Rev. B **89**, 035429 (2014)) we demonstrated that the charge transfer part of the polarizability reaches the per atom limit of the bulk metal at very small cluster sizes, and that the trends in both the charge transfer and dipole parts with the number of atoms in the cluster can be fit to a metal sphere model. This suggests that other metal atom clusters would behave in a similar way for small cluster sizes. In this talk we will present results for several other cluster systems (Mg_N, Al_N, K_N, Cu_N, and Zn_N) that confirm this hypothesis.

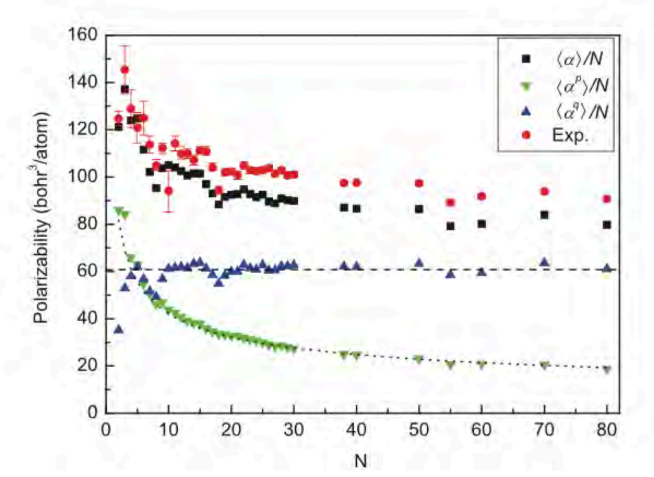
DOE DE-SC0001330: The Physics and Chemistry of Cluster-based Catalyst Systems

Postdoc: None.
Students: Ritaban Chowdhury; Kushanthe Withanage

RECENT PROGRESS

Investigating the metallic behavior of Na clusters using site-specific polarizabilities

We used a method for decomposing the cluster polarizability into site-specific contributions to study the response of Na clusters to an applied electric field. The method also allows the further partitioning of the polarizability into charge transfer (metallic-like) and local dipole (dielectric-like) components. We studied the behavior of clusters from N = 2 to N = 80. We find that the polarizability response as a function of N can be reproduced using a simple metal-sphere model. Furthermore, the charge transfer component of the polarizability reaches the per atom bulk value at

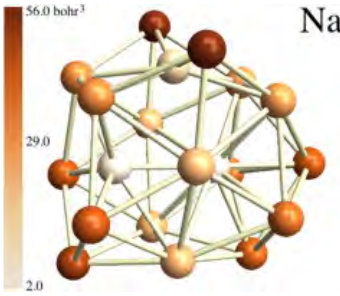


Size trends in the calculated polarizability for Na clusters, and its charge transfer and dipole components. The dashed line is the Na bulk limit.

very small sizes (N < 10), suggesting that clusters at these small sizes already display a metallic response to a static applied field.

Site-specific Polarizabilities from Analytic Linear-response Theory

We presented an implementation of the partitioning of the molecular polarizability tensor that explicitly employs the first-order electronic density from linear-response coupled-perturbed Kohn-Sham calculations. This new implementation provides a simple and robust tool to perform the partitioning analysis of the calculated electrostatic polarizability tensor at negligible additional computational effort. Comparison with numerical results for Si_3 and Na_{20}, and test calculations in all-trans-polyacetylene oligomeric chains up to 250 Å long show the potential of this methodology to analyze the response of large molecules and clusters to electric fields. This work was done in collaboration with J. E. Peralta (DE-FG02-10ER16203).



$$\alpha_{ij}^{A} = \int (r_i - R_i^{A})\, n_j^{(1)}(\boldsymbol{r}) w_A(\boldsymbol{r}) d^3 r$$

$$\alpha_{ij}^{CT} = \sum_{A} R_i^{A} \int n_j^{(1)}(\boldsymbol{r}) w_A(\boldsymbol{r}) d^3 r$$

$$\alpha_{ij} = \alpha_{ij}^{CT} + \sum_{A} \alpha_{ij}^{A}$$

H_2 Saturation on Pd_N clusters

Following up on earlier work that demonstrated that H_2 adsorbates bind dissociatively to small Pd_N clusters, we investigated the case of multiple H_2 adsorbates, addressing how many H_2 can bind stably to Pd_N as a function of cluster size and temperature. For N =2, 3 and 4, one H_2 unit dissociates, and saturation coverage at T = 0 K corresponds to two molecular H_2 units attached to each atop site on the Pd_N core. At T = 300 K, saturation corresponds to one molecular H_2 per atop site, in addition to the one dissociated unit. Saturation for the N = 7 cluster involves two dissociated H_2 units and 11 and 6 molecular H_2 units at T = 0 and 300 K, respectively. For N = 13, we find that 8 H_2 units dissociate and at least one unit binds molecularly at T = 0 K. At T = 300 K, only the dissociated H atoms remain stably attached to the cluster. The presence of molecularly adsorbed H_2 units on atop sites affects the migration of dissociated H atoms across the cluster surface.

FUTURE PLANS

1. Investigate the reactivity of Cu_NPd_M clusters to H_2. This is a cluster analogue to “single atom alloy” systems that have been studied for bulk surfaces. The goal is to determine whether mixed metal cluster systems with a small fraction of Pd atoms are effective in splitting H_2.
2. Continue the work on site-specific polarizabilities, investigating the trends with size of other types of clusters (Si_N and alkali-halides) to probe the evolution of semiconductor and insulator properties. We will also study the use of alternate techniques for partitioning the cluster charge density into atomic contributions, including a self-consistent Hirshfield approach. We currently use a Voronoi decomposition for homonuclear systems. Another area of interest is to apply the site-specific method for time-dependent polarizabilities. Finally, we are

interested in the Fermi-orbital approach of partitioning the electronic charge density. This would allow us to re-cast our methodology for site-specific polarizabilities into orbital-specific polarizabilities.

Publications Acknowledging this Grant in 2013-2015

1. *H_2 reactions on Palladium clusters.* A. Pelzer, K. A. Jackson, and J. Jellinek, J. Phys. Chem. A **117**, 10407 (2013).
2. *Site-specific Polarizabilities from Analytic Linear-response Theory*. J.E. Peralta, V. Barone, and K. A. Jackson, Chem. Phys. Lett., **608**, 24 **(**2014).
3. *Investigating the metallic behavior of Na clusters using site-specific polarizabilities.* L. Ma, K. A. Jackson, J. Wang, M. Horoi, and J. Jellinek, Phys. Rev. B **89**, 035429 (2014).
4. *H_2 Saturation on Palladium Clusters*. A. W. Pelzer, J. Jellinek, and K. A. Jackson. Submitted to J. Phys. Chem., Feb. 2015.

Interactions, Phase Equilibria and Self-Assembly in Ionic Systems

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Presentation Abstract

In this presentation, I plan to review key recent results from my group's work supported by the Computational and Theoretical Chemistry program of the Office of Basic Energy Sciences, DOE. In particular, I will present a recently developed computational methodology that allows for accurate determination of chemical potentials and activity coefficients for molecular, explicit-solvent models of electrolyte solutions. Despite the importance of such systems for fossil fuel production, desalination, separations, and electrochemical processes, the strong interactions present in these solutions makes these computations quite challenging. Our initial results for a series of popular fixed-point-charge models of water and common salts suggest that the activity coefficients are not well represented by existing models over the concentration and temperature ranges of technological interest. Moreover, models that perform adequately for the activity coefficients tend to significantly underestimate the solubilities. Interestingly, simulation-based determinations of critical micelle concentrations (cmc's) for ionic surfactants using the same force fields indicate that the predicted cmc's are also significantly underestimated relative to experimental data. These results point to the need for improved water and ion models, with the most promising path being the inclusion of polarizability.

DE-SC0002128: Interactions, Phase Equilibria and Self-Assembly in Ionic Systems

PI: Athanassios Z. Panagiotopoulos

Postdocs (past 3 years): Dr. Stephen Barr (PhD from U. Illinois, now with Air Force Research Laboratory); Dr. Hao Jiang (PhD, U. of Wyoming); Dr. Zoltan Mester (PhD, U.C. Santa Barbara);

PhD Students (past 3 years): Kevin Daly (graduated in Nov. 2014, now with ExxonMobil); Yang Liu (graduated in the fall of 2012, now with Air Products); Andrew Santos (current student, Hispanic-American, B.S. from N. Carolina State).

1 PROGRAM SCOPE

This project focuses on developing methods for the accurate determination of activity and osmotic coefficients in salt solutions using atomistic, molecular-based models, and on self-assembly in surfactant solutions. Atomistic models that can be used in a fully predictive mode offer distinct advantages over previously available phenomenological and implicit-solvent models; their performance at elevated temperatures, which are important for separation and CO_2 geophysical sequestration applications, has not been previously determined. For calculations of free energies in electrolyte solutions, we are developing thermodynamic integration and staged insertion algorithms that can be used in turn for obtaining improved intermolecular potential models. In the area of ionic surfactant self-assembly, we are investigating the effects of added salt on the cmc, aggregation number, and aggregate morphology, the effects of temperature, the dynamics of surfactant exchange between micelles and free solution and of micelle breakup and reformation, and the relationship between grand canonical Monte Carlo methods for determining critical micellar concentrations and the methods based on extrapolation with respect to total surfactant loading.

2 Recent Progress

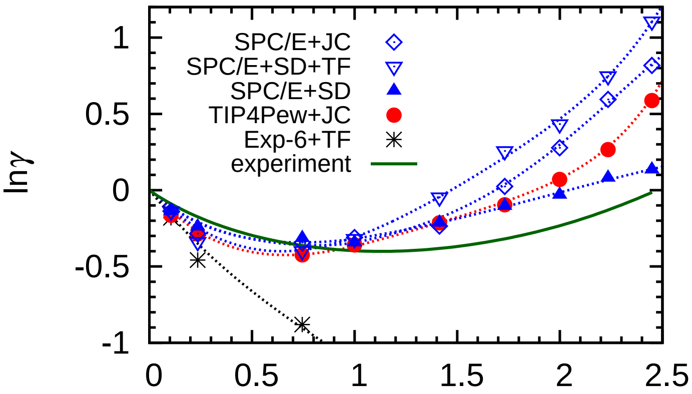

Fig. 1. Natural logarithm of the mean activity coefficient ln γ of NaCl *versus* salt molality at 298.15 K and 1 bar [1].

In the past year, a major area of work under the project has been the development of efficient methods for obtaining activity and osmotic coefficients in electrolyte solutions [reference 15 in the Publications List]. We used gradually insertions of an ion pair and water molecule into the solution to obtain the activity and osmotic coefficients, respectively. Gibbs-Duhem equation calculations were used to confirm the thermodynamic consistency of the coefficients. Several common non-polarizable water and ion models have been examined in the simulations. While the majority of model combinations predict the correct trends in mean ionic activity coefficients, they overestimate their values at high salt concentrations, as seen in Fig. 1. The solubility predictions also suffer from inaccuracies, with all models underpredicting the experimental values, some by large factors.

Thermodynamic and transport properties of aqueous NaCl solutions such as the vapor pressure, surface tension, and viscosity were obtained in [14]. Specifically, Molecular dynamics and Monte Carlo simulations have been carried out at temperatures from T = 298 to 473 K. Several previously proposed fixed point-charge models that include either Lennard-Jones (LJ) 12-6 or exponential-6 (Exp6) functional forms to describe non-Coulombic interactions were studied. None of the model combinations are able to reproduce simultaneously all target properties, which strongly suggests that there is a need for further ion and water model development.

Atomistic molecular dynamics simulations were performed to obtain a better understanding of the water transport through Nafion, a perfluorosulfonic acid membrane [12] and its mechanical properties [13]. Water mass transfer near the vapor interface was shown to be much slower than at any other point within the membrane, in qualitative agreement with permeation experiments. Membrane viscosity was shown to increase by up to 4 orders of magnitude in response to composition changes of as little as 2 % (by weight) of the system. Counterion type was shown to strongly influence the morphology. The simulations are able to reproduce some important experimental trends without crystalline domains or high-MW effects like entanglements, providing a simplified understanding of the mechanical properties of Nafion.

3 FUTURE PLANS

We plan to continue studies of activity coefficients in aqueous electrolyte solutions, following the methodology developed in [1] and anticipate the completion of studies for alkali and alkali earth halides (such as KF, NaI, $CaCl_2$), over a range of temperatures. Existing force fields for the salts and water will be tested, as previously done for NaCl at room temperature. Given the shortcomings of fixed-point-charge models identified in our current work and by other prior studies, of particular interest in future is the use of polarizable force fields, such as BK3 [P. T. Kiss and A. Baranyai, "A systematic development of a polarizable potential of water," *J. Chem. Phys.*, **138**, 204507 (2013)]. In the area of ionic surfactant self-assembly, we plan to investigate methods for reliable extrapolation of the free surfactant concentration observed at loadings much greater than the critical micelle concentration (cmc), so that the cmc can be obtained, and to use the method for force field development that addresses limitations of existing models seen in our earlier work.

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John M. Herbert

Efficient Methods for Computing High-Accuracy Non-Covalent Interaction Energies in Clusters, Liquids, and Molecular Crystals

Department of Chemistry & Biochemistry, The Ohio State University

Presentation Abstract

A variety of fragment-based approaches for accurate yet efficient quantum chemistry calculations of non-covalent interaction energies are presented. The fragment-based nature of the methods makes them even faster than traditional density functional theory, and amenable to large-scale distributed computing so that large non-covalent assemblies with numerous fragments can be treated. At the same time, care has been taken to develop methods whose accuracy is within ~1 kcal/mol of the best available quantum chemistry benchmarks. Preliminary attemps to develop a fragment-based method amenable to macromolecular systems will also be presented.

DE-SC0008550: Development of accurate and affordable electronic structure methods for the condensed phase

Students: Ryan M. Richard, Ka Un Lao, Adrian F. Morrison, Kuan-Yu Liu

RECENT PROGRESS

Program Scope

This project aims to develop, implement, and test new algorithms for accurate yet efficient calculation of non-covalent interactions in large systems. Target accuracy is ~1 kcal/mol with respect to the best available correlated wavefunction benchmarks for small systems, but based on a fragmentation approach that is inherently scalable to large non-covalent assemblies (crystals and liquids). Accuracy is assessed based on benchmark comparisons, while efficiency can be judged based on timings and scalability plots with respect to traditional (supersystem) quantum chemistry methods.

Recent Progress

We have taken a two-pronged approach to the quantum chemistry of non-covalent interactions: (1) development of an "extended" version of symmetry-adapted perturbation theory (XSAPT) in which monomer-based self-consistent field calculations are combined with a perturbative (and embarrassingly parallelizable) description of intermolecular interactions; and (2) many-body expansions that decompose the total energy into a sum of monomer, dimer, trimer… energies of small fragments, that can again be computed in an embarrassingly parallelizable manner.

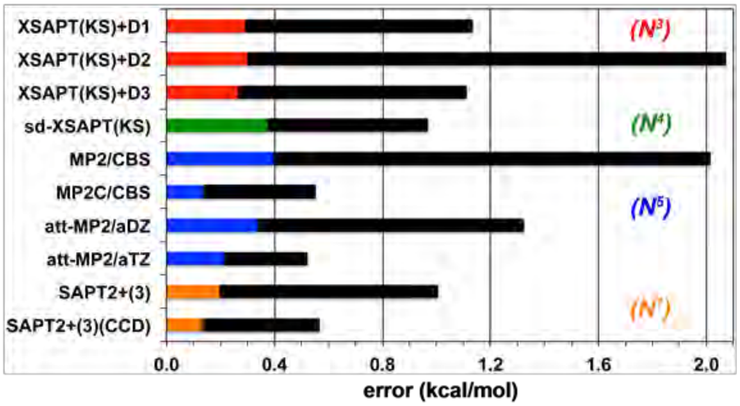

Figure 1. Error statistics (vs. CCSD(T)/CBS results for S66) for a variety of quantum chemistry methods. Shown are the mean absolute errors (colored bars, color-code according to how cost scales with system size) as well as the maximum errors (black bars).

On the XSAPT front, we have made significant progress on a method called XSAPT(KS)+D, which combines Kohn-Sham DFT for the monomers with SAPT for the intermolecular interactions, but with empirical atom–atom potentials for dispersion (+D). This is in recognition of the fact that second-order perturbation theory does not afford benchmark-quality results for systems where dispersion is significant. Dispersion potentials can be parameterized in a fully *ab initio* way by using high-order SAPT to extract *ab initio* dispersion potentials for a training set of dimers. Results in Fig. 1 show that our third-generation version of this method, XSAPT(KS)+D3, affords a mean accuracy of 0.3 kcal/mol with respect to CCSD(T)/CBS benchmarks, and a maximum error of about 1 kcal/mol. These are gas-phase, T=0 calculations, but in collaboration with Dan Chipman at Notre Dame we are benchmarking these methods against experimentally-measured, room-temperature solution-phase binding affinities (using continuum treatments of the solvent development by Chipman) and, separately, against gas-phase binding free energies that are inferred from cluster ion spectroscopy. Preliminary results suggest that sub-kcal/mol mean accuracy is preserved, using simple continuum and monomer-based DFT treatments of the entropic contribution to ΔG.

With regard to the many-body expansion, our recent results have pointed to some key challenges associated with this widely-used technique, which forms the basis, for example, of the popular Fragment Molecular Orbital method. Specifically, it is not entirely clear that the many-body expansion is convergent, a fact that has been overlooked in most previous studies because (prior to our work) there has been no effort to systematically benchmark this method in *large* systems, using against *high-accuracy* benchmarks (preferably CCSD(T)/CBS). For systems that are much larger than those used in previous benchmark studies, four- and even five-body terms remain significant and are not substantially diminished by popular electrostatic embedding approaches; this leads to serious loss-of-precision problems due to the staggering number of fragment calculations that are required, and is only feasible in pilot studies even when parallelized over hundreds of cores. Results obtained with large basis sets and/or many-body counterpoise corrections (both of which are unusual in most applications of the many-body expansion) suggest that much of this behavior is an artifact of basis set superposition error, and we are currently pursuing ways to avoid this.

Future Plans

On the XSAPT front, we are currently working to establish the accuracy and utility of this methodology in realistic applications, in particular the binding of small ligands to macromolecules and molecular scaffolds. This is a collaborative effort with Profs. Lee Woodcock and Brian Space at the University of South Florida, in which enhanced sampling techniques based on Bennett's Acceptance Ratio, developed by the Woodcock group and driven by MD simulations with a low-level method (force field), are combined with accurate, high-level energetics from XSAPT. With Prof. Space's group, we are interested in applying this methodology to metal-organic frameworks, as a means to assist in force field development. This will be facilitated by an implementation of the (X)SAPT method in the atomic orbital (as opposed to molecular orbital) basis, currently underway in the PI's group, which will significantly reduce the memory requirements for calculations involving large fragments, as may be necessary in materials science applications. We are also exploring alternatives to the empirical +D dispersion potentials. Such alternatives include the Tkatchenko-Scheffler method for computing on-the-fly, *ab initio* C_6 coefficients, and also methods that compute the dispersion energy based on frequency-dependent polarizabilities for the individual fragments. (The latter approach is what is done in the so-called SAPT-DFT and "coupled MP2" methods.)

In the context of the many-body expansion, we are in the process of obtaining a set of relative energy benchmarks, extrapolated to the basis-set limit, for large molecular clusters. This will enable a more incisive examination of the effects of basis set superposition error. Recognizing that many-body terms beyond trimers may be necessary to achieve benchmark accuracy, we are testing a variety of low-cost, on-the-fly screening procedure that will allow us to throw out many insignificant fragment calculations *a priori*; preliminary tests on water clusters suggest that as many as 85% of the four-body calculations can be eliminated in this way, without loss of accuracy. Analytic gradients for simulations have already been formulated (as have analytic Hessians for vibrational frequencies), and implementation of periodic boundary conditions is planned. An alternative formulation of the many-body expansion that relies on overlapping fragments (*i.e.*, an overlapping tessellation of the supersystem), developed in our group in a manner that generalizes several related approaches, shows promising accuracy at the *two-body* level, which sidesteps many of the problems with four- and higher-order expansions, although the number of dimers is significantly larger when overlapping fragments are employed. We are working to benchmark this approach in large systems in the way that we have done for the non-overlapping apporach, and to implement thresholds.

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Novel Modeling Approaches to Multiphase Electrolytes

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Presentation Abstract

Permeation of nanopores by electrolytes is important in numerous processes in energy and materials technologies. Commonly, the confined electrolyte maintains equilibrium with the surrounding bulk phase. A liquid-to-vapor transition may take place in narrow hydrophobic confinements. Permeation can be enhanced by external stimuli, including electric field. We study pore thermodynamics and equilibrium partitioning between the pore and the bulk phase in the Extended Grand Canonical Ensemble Monte Carlo simulation, where we overcome prohibitively low acceptances of ion exchanges through incremental changes in particle (de)couplings. We discuss novel and counterintuitive salt effects on interfacial properties of NaCl solution in the absence or presence of external field. In a refined Molecular Dynamics approach, suitable for thinner *and* laterally restricted pores inside a pressure-buffered electrolyte reservoir, we address dynamic transitions between confined liquid and vapor phases controlled by electric field across the pore. Reversible response to the changes in the field, observed in a narrow window of nanopore geometries, suggests a variety of applications relying on transient control of liquid/vapor competition in the pores.

DOE Award DE-SC-0004406 - Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

Postdoc(s): Shadrack Jabes

RECENT PROGRESS

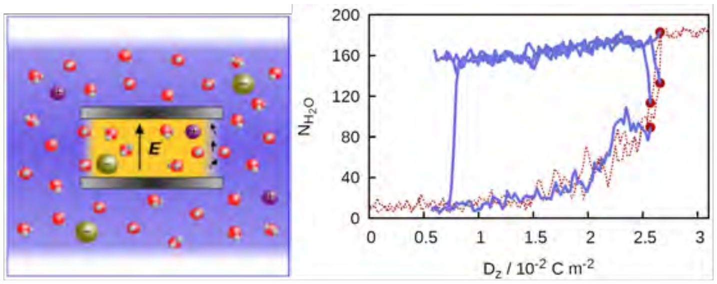
1) *Electrolytes in Nanoporous Media: Insights from Expanded Ensemble GCMC simulations*

1.1 **Field-free systems.** The development of Grand Canonical Monte Carlo (GCMC) approach with fractional couplings of ion pairs analogous to the expanded osmotic ensemble method, but augmented by fractional exchanges of water molecules enabled us to study ion and water partitioning between laterally extended confinements and electrolyte environment. This computationally intense method overcomes the problem of insufficient exchange acceptances for charged species and avoids the limitations of quasi/grand canonical Molecular Dynamics (MD) approaches. Anisotropic pore conditions also prompted the development of a novel iterative algorithm for a self-consistent correction of interaction cut-off effects. We show the concentration of the salt is depleted in narrow slits but shows oscillatory depletion/enhancement width dependence in wider pores, in accord with nonuniform capacitance of nanoscale supercapacitors. The structuring of ion layers increases the range of inter-wall surface forces with superimposed repulsive contribution growing with salt concentration in the bath. The long-range repulsion contrasts the enhanced short-ranged attraction revealed in MD studies of laterally restricted nanoparticles. A striking consequence of the varying sign of excess salt concentration at different pore widths is that the wetting free energy of the confining walls can be either increased or decreased due to the presence of the salt.

1.2 **Nanopores under electric field.** Field-enhanced nanopore wetting by electrolytes underlies diverse applications from surface energy storage to hydrophobic valves and the control of membrane permeability. Using an extension of the GCMC methodology discussed above and further augmented to include the incremental coupling to external field, we studied thermodynamic effects of the field spanning semi-infinite pores in implicit equilibrium with electrolyte bath. At up to 0.7 V potential drop across the pore, the field consistently enhances the packing of absorbed solution. It also leads to a moderate increase in salt molality. The presence of up to 6 molal salt shows moderate effects on the field-induced confinement pressure and reduction in the wetting free energy. According to our preliminary results, both quantities present an asymptotically quadratic dependence on the strength of applied field in analogy to dielectrics. The method provides estimates of the materials capacitance (per unit volume), confirming a rapid increase with the porosity but unexpectedly weak dependence on salt concentration, with only ~30% capacitance increase at the solubility limit of the salt.

2) ***Dynamic Control of Nanopore Infiltration by Salt Solution***.

We demonstrate the possibility of field-induced uptake and release of solution for channel gating or surface energy absorption. Our mean-field analyses show that a two-way control requires a pore width sufficient for infiltration at experimentally relevant voltages, yet below kinetic threshold of spontaneous expulsion in the absence of the field. Molecular insights are necessary to identify the narrow window of pore geometries and fields satisfying both requirements. We developed a self-consistent MD simulation approach to study dynamic, field-controlled transitions between nanoconfined liquid and vapor phases in contact with an unperturbed bath. Local electric field enhances the uptake of water and ions in the confinement and can reverse capillary evaporation occurring in the absence of the field. The simulation uncovers the positions and the field-dependence of both, the activation barrier to fluid expulsion, and a lower barrier to infiltration. For alternating displacement field, we identify the conditions where O(ns) responses of the infiltration/expulsion cycle can be secured for experimentally realizable field strengths, porosity, and salinity of the solution.



Detection of the wetting/expulsion activation barrier in 1.2 nm pore under varied electric displacement field D_z. N_{H2O} is the number of molecules in the pore. Trajectories initiated beyond the barrier continue to fill despite subsequent weakening of the field.

3) ***Wetting Transparency of Carbon Nanostructures.***

Characterizations of nanoporous substrates have to account for changes in the apparent material's affinity to the solvent due to solvent-solvent correlations across confinement walls. Using mean field arguments, we predicted up to ten degrees reduction in water contact angle at a graphene plane wetted from both sides rather than on a single side alone. We confirm this prediction by full-atom simulations. Water absorption in, as well as evaporation from a graphene based nanoporous material will therefore proceed in a strongly cooperative manner. Computations on alkyl-substituted graphane show the effect is readily suppressed by wall-thickening functionalization.

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Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis

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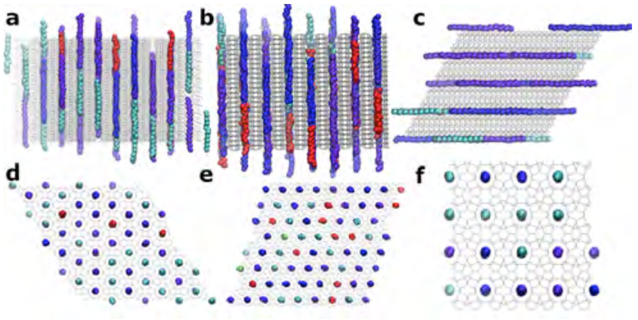
Project Scope

The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including **metal-organic frameworks** (MOFs), **zeolites**, and **porous polymer networks**. These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. The NMGC develops state-of-the-art predictive modeling tools, databases, and web-based repositories, and employs them to increase the pace of materials discovery. The goals of the NMGC are advanced by a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups with experience in molecular simulation, electronic structure calculations, and theory. The majority of the completed projects resulted from iterative feedback where computational modeling was instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis.

Technical Progress

The NMGC research efforts have already led to more than 45 publications. In this presentation, we highlight the key achievements of five application projects and one web tool that are central to the goals of the NMGC. (a) Experimentally refined crystal structures for MOFs often include solvent molecules and partially occupied or disordered atoms. This creates a major impediment to applying high-throughput computational screening to MOFs. To address this problem, we construct a database of MOF structures that are derived from experimental data but are immediately suitable for molecular simulations.[1] The computation-ready, experimental (CoRE) MOF database contains ~5000 porous structures with important physical and chemical properties including the surface area and pore dimensions. To demonstrate the utility of the database, we compute the adsorption of methane and of the five hexane isomers on all CoRE MOF structures, and investigate the structural properties governing methane storage capacity and selectivities for specific hexane isomers. (b) MOFs are actively being explored as potential adsorbed natural gas storage materials for small vehicles. Experimental exploration of potential materials is limited by the throughput of synthetic chemistry. To complement and guide these experimental efforts, we develop a computational methodology using known chemical transformations *in silico* to identify MOFs with high methane deliverable capacity. We efficiently search the composition and conformation space of organic linkers for nine MOF networks, finding 48 materials with higher predicted deliverable capacity (at 65 bar storage, 5.8 bar depletion, and 298 K) than MOF-5.[2] (c) Screening sorbents and catalysts for complex mixtures composed of large, articulated molecules, where advanced algorithms are required for sampling the distribution of thousands of conformers, or polar, hydrogen-bonding molecules, where an accurate description of electrostatics and the resulting mixture non-idealities are of paramount importance, has so far been an intractable problem.

Enabled by a multistep screening workflow, efficient sampling algorithms, accurate force fields, and a two-level parallel execution hierarchy utilizing up to 131,072 compute cores on Mira, a leadership-class supercomputer at Argonne National Laboratory, we perform high-throughput screening for two energy-related applications and identify zeolites with exceptional selectivities for ethanol purification from aqueous solution and the transformation of alkanes with 18-30 carbon atoms.[3] (d) Enzymatic heme and non-heme high-valent iron-oxos are known to activate very strong C–H bonds with relative ease, yet duplicating this impressive reactivity in a synthetic system has been a formidable challenge. We demonstrate that a MOF featuring site-isolated iron centers in a weak-field ligand environment can convert ethane into ethanol and acetaldehyde using nitrous oxide as the terminal oxidant. Using electronic structure calculations we show that the active oxidant is a high-spin, $S = 2$ single-state iron(IV)-oxo acting via a σ -pathway and elucidate all steps in the mechanism.[4] (e) Quantum mechanical computations can provide useful guidance in prioritizing the synthesis of optimal materials for a given gas separation; we use such computations to identify a new MOF with open vanadium sites that is of potential utility for the separation of dinitrogen from other light gases, such as methane or dioxygen. The differential adsorption energy $\Delta E = E_{ads}(N_2) - E_{ads}(CH_4)$ is larger for V-MOF-74 compared to analogous M-MOF-74 materials with other metals. Orbital analysis reveals that two types of interactions, the σ donation and π^* backbonding, are responsible for the strong V-N_2 bond.[31]



Snapshots of alkanes inside ATO (a,d), MTW (b,e), and PCOD-8113534 (c,f) with adsorption occurring from a liquid phase containing an equimolar mixture (linear C18, C24, C30, and branched C18 isomers in cyan, purple, blue, and red, respectively) at $T = 573$ K and $P = 3$ MPa.

In collaboration with the Materials Project, the NMGC has developed the *Nanoporous Materials Explorer*. This openly accessible web-based tool aids materials discovery and also serves as repository for computational and experimental data generated by the NMGC.

Future Plans

The NMGC team will continue its collaborative endeavors to discover nanoporous materials with optimal gas storage, separation, and catalytic abilities and to use an integrated computational/experimental approach for unraveling structure/chemistry/function relationships. Two provisional patent applications resulting from NMGC discoveries have been filed, and the NMGC will further develop these and other nanoporous materials. The collaborative NMGC activities have also strengthened the training of a large number of postdoctoral associates and of graduate, undergraduate, and high school students.

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Spin-dependent potentials for separations in metal organic frameworks

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The incorporation of open-shell metal centers such as Fe(II) and Co(II) into metal-organic frameworks (MOFs) results in frameworks that can display spin-crossover (SCO) behavior. For example, in octahedral coordination environments (such as those usually found in MOFs), the d orbital manifold of open-shell metals splits into two sets of orbitals, the non-bonding t_{2g} and the anti-bonding e_g sets. Depending on the energy gap between the two sets of orbitals, the corresponding MOF can thus exist in two possible spin states, the low-spin (LS) and the high-spin (HS) state. If the energy gap between the t_{2g} and e_g sets is comparable to the pairing energy, spin crossover can occur in response to external perturbations driven by temperature gradients, pressure fluctuations, or light irradiation. Importantly, SCO transitions in MOFs are accompanied by distinct changes in the physicochemical properties of the frameworks, including changes in color, magnetism, and structure. The combination of large surface areas and high framework tunability thus makes spin-crossover MOFs (or SCOFs) promising multifunctional materials for potential applications in gas separation, sensors, and nanoscale memory devices.

Although a weak correlation between the SCO transition and the dielectric constant of the guest molecules can be found, the modulation of the SCO behavior of MOFs upon guest adsorption remains poorly understood. Over the last year, we have focused our efforts on the development and implementation of a novel theoretical/computational approach that enables direct simulation of spin-crossover in MOFs as described below.

We have developed a novel hybrid Monte Carlo / molecular dynamics (MC/MD) method that builds upon the ligand field molecular mechanics (LFMM) model and enables modeling of SCO properties in bulk materials, including MOFs. Within the LFMM model, conventional molecular mechanics (MM) energy expressions are supplemented with an additional term that effectively represents the ligand field stabilization energy (LFSE) arising from the splitting and different occupation of the d orbitals of the metal centers. LFMM thus explicitly includes energy contributions that depend on both the instantaneous coordination geometry and the electronic structure of the metal centers.

Briefly, the LFMM method is based on the angular overlap model (AOM) that approximates the total ligand field potential, V^{LF}, of a generic ML_n complex (M = metal and L = ligand) with a sum of localized contributions associated with each M-L bond. As a result, the ML_n complex is effectively treated as *n* M-L diatomic molecules, each with its own σ- and π-bonding properties. V^{LF} includes radial contributions that are specific to the chemical nature of each M–L bond and angular contributions that depend on the geometry of the ML_n complex. To enable direct simulations of the SCO properties in bulk materials, including MOFs, we have combined the original LFMM model with a Monte Carlo scheme based on the Metropolis acceptance/rejection criterion that is used to model the transitions between different spin states. The resulting hybrid MC/MD scheme has then been extended to systems with multiple metal centers in periodic boundary conditions. Our MC/MD approach, implemented in a modified version of the publicly-available DL_POLY Classic software, is designed to describe SCO materials with an arbitrary number of different metal centers, each with its own set of possible spin states.

We first assessed the accuracy of our hybrid MC/MD method through the characterization of a series of $[MCl_4]^{2-}$ complexes (with M = Co, Ni, and Cu). These complexes, in which the metal centers differ in both number of d electrons and spin states, represent a comprehensive test for the accuracy of our simulation method and offer a systematic approach to its validation. Our results are in excellent agreement with those reported in the literature. We then carried out hybrid MC/MD simulations for the $[Fe(pz)_2Pt(CN)_4]$ MOF, which was found experimentally to display bidirectional chemo-switching of spin state upon adsorption of different guest molecules. Interestingly, it was also shown that the [Fe(pz)$_2$Pt(CN)$_4$] MOF exhibits “memory” response, being able to retain a given spin state upon guest desorption. The magnetization curve of the SCOF material obtained with our hybrid MC/MD approach using our own ab initio-based LFMM parameterization correctly reproduces the sharp transition between the LS and HS state observed experimentally, which is attributed to the collective nature of the framework vibrations (Figure 1). The hybrid MC/MD simulations for the SCOF material predict a transition temperature between 400 K and 475 K, which is in good agreement with the corresponding experimental value.

Our hybrid MC/MD approach along with the results obtained for the [Fe(pz)$_2$Pt(CN)$_4$] MOF are reported in Ref. 2. To the best of our knowledge, our hybrid MC/MD method is the first approach that enables direct simulation of spin crossover in bulk materials, effectively capturing electronic-driven processes within a physically-based computational framework. We are currently investigating the effects of guest molecules (e.g., C_6H_6, H_2O, and CS_2) on the spin-crossover transition in the Fe(pz)$_2$Pt(CN)$_4$] MOF for which experimental measurements are available.

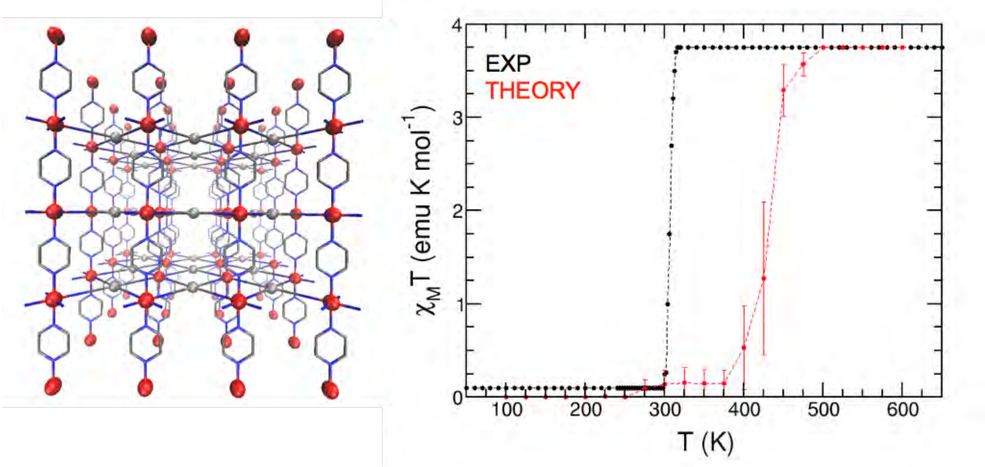

Figure 1. *Left: Three-dimensional model of the [Fe(pz)$_2$Pt(CN)$_4$] MOF. Right: Comparison between the experimental (black) and calculated (red) c_MT values for the [Fe(pz)$_2$Pt(CN)$_4$] MOF.*

In parallel with the development of our hybrid MC/MD approach, we are extending our “first principles” many-body (MB) potentials, which we developed for water, to guest molecules of interest for storage and separation in MOFs (e.g., alkanes, CO_2, and H_2). The implementation of these MB potentials within our hybrid MC/MD approach will enable fully polarizable, “first principles” simulations of adsorption, diffusion, and separation processes in MOFs, explicitly taking account framework flexibility.

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Theoretical Studies of Spin Crossover Metal-Organic Frameworks

Postdocs: Jordi Cirera, A. Götz
Students: Pushp Bajaj, Kevin Bao

Publications Acknowledging this Grant in 2013-2015

Cirera, J.; Babin, V.; Paesani, F. Theoretical Modeling of Spin Crossover in Metal–Organic Frameworks: [Fe(pz)$_2$Pt(CN)$_4$] as a Case Study. *Inorg. Chem.* **2014**, *53*, 11020-11028

Design of Lewis Pair Functionalized Metal Organic Frameworks for CO_2 Reduction

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Presentation Abstract

Metal organic frameworks (MOFs) are highly versatile nanoporous materials because of their structural and functional tailorability. We use density functional theory (DFT) methods to design functionalized MOFs that are capable of chemically binding and hydrogenating CO_2. We employ UiO-66 as our starting base material because it is a MOF that has chemical and thermal stability, is highly selective toward CO_2 and can be functionalized post-synthetically. We design functional moieties for CO_2 hydrogenation based on frustrated Lewis pairs because these organic molecules have been shown to be very active for chemisorption of CO_2 and the heterolytic dissociation of H_2. We have developed a family of Lewis pair functional groups for inclusion in UiO-66 all based on 1-(difluoroboranyl)-4-methyl-1H-pyrazole, denoted as P-BF_2, by replacing the -BF_2 group of P-BF_2 with the following moieties: -$B(CH_3)_2$, -BH_2, -BCl_2, -BBr_2, -$B(CN)_2$, -$B(CF_3)_2$ and -$B(NO_2)_2$. We investigated the reactivity of these materials for CO_2 hydrogenation to produce formic acid. We found a linear relationship between the H_2 adsorption energies and activation energies for CO_2 hydrogenation. Furthermore, the adsorption energies of H_2 were observed to scale linearly with the acidity of functional groups.

DE-FG02-10ER16165: Design of Stratified Functional Nanoporous Materials for CO_2 Capture and Conversion

Postdoc: Jingyun Ye
Affiliation: University of Pittsburgh

Recent Progress

The objective of this project is to develop novel nanoporous materials for CO_2 capture and conversion. As the initial step in this project we have studied the reduction of CO_2 to formic acid through catalytic hydrogenation within a nanoporous material. We have used van der Waals corrected periodic density functional theory, non-periodic density functional theory, and post-Hartree-Fock wavefunction methods to design and screen catalytic functional groups for CO_2 reduction that can be incorporated into the pores of metal organic frameworks (MOFs). We use Lewis pairs (LPs) that can both bind CO_2 and heterolytically dissociate H_2 as the catalytic moieties within the MOFs for CO_2 reduction. We have chosen UiO-66 as a candidate MOF for LP functionalization because it is chemically and thermally stable, highly selective toward CO_2 adsorption, and can be readily functionalized via various approaches. We have screened a total of eight different functional groups for their ability to hydrolytically dissociate H_2, chemically bind CO_2, and catalyze the hydrogenation of CO_2. Each functional group was based on 1-(difluoroboranyl)-4-methyl-1H-pyrazole, denoted as P-BF_2, shown in Fig. 1(a) attached to the BDC linker in Fig. 1(b) where the R groups are F atoms. The eight different structures were generated using R = H, F, Cl, Br, CN, CH_3, CF_3, and NO_2. These groups were chosen to span a range of electron withdrawing potentials and steric effects. We computed dissociation energies for H_2 chemisorption, H_2 dissociation pathways, CO_2 binding energies and chemisorption

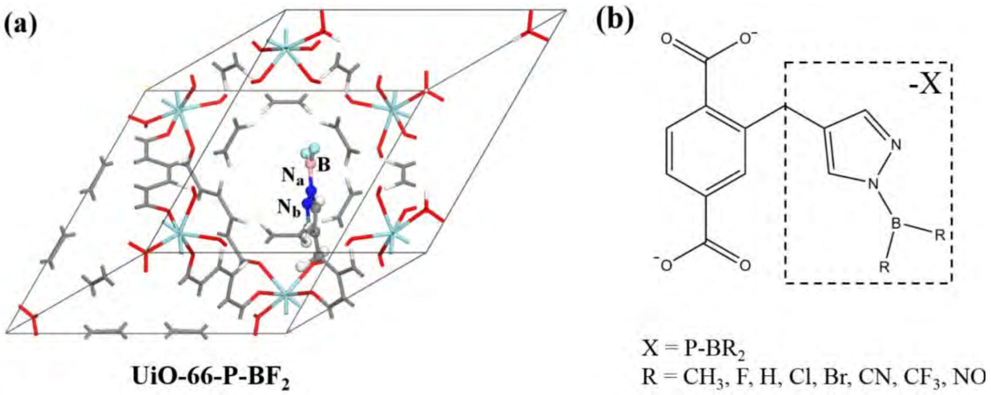

Fig. 1. Lewis Pair functionalized UiO-66 (UiO-66-X): (a) Primitive cell of UiO-66-P-BF$_2$, (b) BDC linker with Lewis pair functional group, where X represents the Lewis pair with different R substituents.

barriers, and barriers for CO_2 hydrogenation starting from CO_2 physisorbed in the pore with dissociated H_2 chemisorbed on the functional group. The reaction pathways and barriers were generated using the climbing image nudged elastic band (CI-NEB) method. The full reaction pathways for CO_2 hydrogenation to HCOOH on each of the materials have been computed. Each proceeds by heterolytic dissociation of H_2 resulting in a protic hydrogen bound to the N_b site shown in Fig. 1(a) and the hydridic hydrogen bound to the B site in Fig. 1(a) followed by hydrogenation of CO_2 in a single step with the protic H adding to an oxygen and the hydridic H adding to the carbon via a single-step concerted mechanism. The eight different functional groups have transition state energy barriers for H_2 dissociation ranging from 0.48 to 1.09 eV and CO_2 hydrogenation barriers ranging from 0.28 to 1.79 eV. This wide range of values clearly shows the need to optimize the R groups to obtain the best overall performance. We have identified a Brønsted-Evans-Polanyi (BEP) relationship between the H_2 chemisorption energies and the CO_2 hydrogenation reaction barriers. A plot of the reaction barrier as a function of the adsorption energy is given in Fig. 2. A linear fit to the data gives a coefficient of determination of $R^2 = 0.978$. Thus far we have only considered a single functional group per pore. On-going work includes studying multiple functional groups per pore to bind both H_2 and CO_2 in order to identify lower barrier pathways for CO_2 reduction. We are also screening additional functional groups to identify better catalysts for reducing the H_2 dissociation barrier and binding energy, along with a different functional group to reduce the CO_2 reduction barrier.

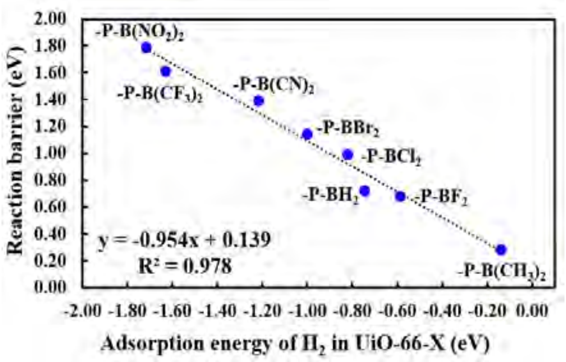

Fig. 2 BEP relationship between the chemisorption energy of H_2 and the reaction barrier for CO_2 hydrogenation

Publications Resulting from the Grant

Ye, J; Johnson, J. K. Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO_2 Hydrogenation, *ACS Catalysis*, **2015**, accepted.

Non-equilibrium statistical mechanical modeling and coarse-grained mesoscale modeling of catalytic reaction-diffusion processes

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Presentation Abstract

A key goal for CTC is development of realistic molecular-level models for overall catalytic reaction-diffusion processes, e.g., predicting reaction yield in flow- or batch-reactors. Such modeling will apply when the traditional mean-field rate or reaction-diffusion equations of chemical kinetics fail due to strong spatial correlations between reactants. Such correlations can be induced by either strong interactions or by inhibited transport or mobility. In addition, it is instructive to develop reliable coarse-grained models to describe behavior such as mesoscale concentration variations and fluctuations. Motivated by catalysis efforts at Ames Laboratory, we have modeled conversion reactions in catalytically-functionalized nanoporous materials where a single-file-diffusion regime may exist for narrow pores. KMC simulations of a spatially-discrete molecular-level reaction model reveal localization of the reactant near pore openings with anomalous scaling of penetration depth and reactivity, features reflecting the complex interplay between inhibited transport and reaction. A coarse-grained generalized hydrodynamic treatment captures this behavior which is impacted by both fluctuations in adsorption-desorption at pore openings and by anomalous transport. Separate Langevin dynamics and Fokker-Planck equation analyses assess the passing propensity of reactants and products in narrow pores, providing a key input parameter for modeling. Finally, we note that mean-field chemical kinetics also breaks down for catalytic reactions on extended surfaces at low-pressure (P) due to interactions and ordering of reactants, and at high-P due to inhibited mobility. KMC simulation of detailed and realistic stochastic multisite lattice-gas (msLG) models elucidates this behavior.

DOE Grant DE-AC02-07CH11358: Ames Laboratory Chemical Physics Program; and Theoretical/Computational Tools for Energy-Relevant Catalysis Project

Lead PIs: James W. Evans, Mark S. Gordon.
Staff Scientist: Da-Jiang Liu. Student: Andres Garcia (summer support).

PROGRAM SCOPE

This theoretical Chemical Physics and CTC projects at Ames Laboratory pursue molecular-level and coarse-grained modeling of **heterogeneous catalysis and other complex reaction phenomena** at surfaces and in mesoporous materials. The effort incorporates: *electronic structure analysis; non-equilibrium statistical mechanics; and meso- or multi-scale modeling*.

RECENT PROGRESS

Catalytic Reactions in Functionalized Nanoporous Materials

Recent efforts have considered catalytic conversion reactions occurring inside linear nanopores of zeolites or functionalized mesoporous silica nanospheres (MSN) with inhibited passing of reactants and products within pores.[3,4,11,13,15,19,22] These studies are motivated by experiments at Ames Laboratory, e.g., on conversion of PNB to an aldol compound and on esterification reactions in MSN.[15,22] Extensive previous analyses of such systems, mostly for catalysis in zeolites, had produced only partial understanding of such basic issues such as limited reactant penetration into pores (resulting in low reactivity). We showed that mean-field reaction-diffusion equation (RDE) treatments fail to describe behavior, as do "hydrodynamic" treatments.[3,4] For similar mobility of reactants and products, we developed a successful "generalized hydrodynamic" treatment incorporating fluctuation effects near pore openings.[13] This theory exploited: (i) a relation between chemical diffusion fluxes appearing in the RDE and tracer diffusivity; and (ii) a generalized tracer diffusion coefficient, D_{tr} which is enhanced near pore openings. We have continued analysis of the strong spatial correlations generated by reaction subject to single-file diffusion, noting that these can impact reaction kinetics. We are exploring extensions of the theory to unequal mobilities of reactants and products, and alternative analyses of the generalized D_{tr} from concentration profiles for so-called counter-diffusion modes.

Reactivity increases strongly with the propensity, P, of reactants and products to pass each other inside narrow pores. Only one previous study analyzed P based on the effective free energy versus separation along the pore, applying transition state theory (TST). We performed detailed Langevin simulations of reactant-product pairs, and characterized the vanishing of P approaching pore diameter where passing is blocked by steric effects. TST fails in this case.[19] Actual behavior was explained by analysis of the appropriate Fokker-Planck Equation (FPE), a diffusion equation in high dimension. Judicious approximation reduced the FPE to a 2D diffusion equation where conformal mapping ideas further elucidated behavior.[19]

Chemisorption and Catalysis on Extended Surfaces

Detailed and predictive msLG models and efficient KMC simulation algorithms were developed to describe oxidation reactions on unreconstructed metal surfaces. Reactive steady-states are impacted not only by adlayer thermodynamics, but also by kinetics.[16] Thus, guided by DFT analysis, we have developed more realistic models for dissociative adsorption of oxygen on mixed reactant adlayers on metal(100) surfaces. These studies revealed the shortcomings of the traditional Langmuir and refined Brundle-Behm-Barker pictures of O_2 dissociation.[17,18] We also developed realistic CO-adsorption models including steering and funneling. Extensive DFT analysis has been performed to determine adspecies interactions for CO+O on unreconstructed (100) surfaces of Pd, Rh, Ir, and Pt.[16] These interactions, together with the above refined adsorption models, were incorporated into msLG CO-oxidation models.[16] These models refined our previous models for Pd and Rh, and constituted the first detailed models for Ir and Pt (with distinct O-ordering). The models were used to assess: sticking, adsorption energetics, TPD for separately for CO and O; bifurcations of reactive steady-states, titration and TPR kinetics. Extensive comparison was made with experimental data for all of the above features.[16]

In related but more general statistical mechanical studies, we have pursued the BESAC scientific grand challenge related to development of a fundamental understanding of discontinuous non-equilibrium phase transitions (e.g., catalytic poisoning transitions in surface reaction models), specifically attempting to describe associated metastability and nucleation phenomena.[5,9,10,16] We have also recently explored models for catalysis on oxide surfaces at high-P where inhibited mobility due to high reactant coverages induces strong spatial correlations in reactant distributions which impact reaction kinetics. We are developing appropriate formulations to describe these strong spatial correlations.

Detailed and precise characterization of chemisorption processes is key for modeling of catalytic reactions, e.g., to describe reactant ordering, possible chemisorption-induced restructuring and dynamics of metal surfaces, and poisoning and/or promotion by impurities such as sulfur (S). Our previous DFT analyses explored formation of Ag-S complexes on Ag surfaces and related enhanced decay of Ag nanoclusters.[2,7,8,14] These studies were extended to Cu (and also Au) surfaces confirming the existence of a stable Cu_2S_3 complex on Cu(111).[23] Recently, and extensive DFT analysis was also performed to assess viable structure models for S-induced reconstructions on Cu(111) terraces,[21] and also a variety of complex structures at step edges.

FUTURE PLANS

Future research efforts will focus on developments in CTC in the following areas. (i) Development of more detailed system-specific models for catalysis in nano- and meso-porous materials. These studies should account for different mobilities of reactants and products, the details of rotational diffusion in controlling passing propensities of molecules in pores, solvent-mediated interactions, etc. (ii) Development of more realistic predictive models for catalytic reactions on metal surfaces addressing limitations of DFT predictions for energetics, and incorporating the local-environment dependence of barriers for reactions and of the dynamics of dissociative adsorption, etc. (iii) Development of theoretical framework to understand non-equilibrium poisoning transitions and related phenomena in these systems. (iv) Development of appropriate theoretical framework to reliably describe strong correlations due to inhibited mobility in surface reactions at high-P. (v) Further analysis of complex dynamics of metal surfaces in the presence of additive and poisons, and more generally under reaction conditions.

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Theoretical modeling of spin-forbidden channels in combustion reactions

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1 Scope of the project

The goal of our research is to develop predictive theoretical methods, which can provide crucial quantitative data (e.g., rate constants, branching ratios, heats of formation), identify new channels and refine reaction mechanisms. Specifically, we are developing tools for computational studies of spin-forbidden and non-adiabatic pathways of reactions relevant to combustion, and applying these tools to study electronic structure, reactions, and spectroscopy of open-shell and electronically excited species involved in these processes.

We are also involved in a collaborative Scidac effort "Simulating the generation, evolution and fate of electronic excitations in molecular and nanoscale materials with first principles methods" lead by Martin Head-Gordon. Within this project, we develop new algorithms and computer codes for efficient implementation of advanced many-body theories. The two directions are synergistic — the infrastructure developments conducted within Scidac effort facilitate efficient implementations of the new theoretical approaches developed for multiple interacting states.

2 Summary of recent major accomplishments

During the past year, we conducted several computational studies of open-shell and electronically excited species. The common theme in these studies is interactions between states of different character and intersections between the corresponding potential energy surfaces. We also continued to develop and benchmark computational methods for modeling electronic structure and spectroscopy of open-shell species. Particular emphasis was placed on determining spectroscopic signatures of transient species, to facilitate comparisons with experimental data. In 2014-2015, the DOE support was acknowledged in two papers.[1,2] Two manuscripts are in the final stage of preparation. The Scidac support has been acknowledged in four papers;[3–6] one more paper has been submitted for publication. Some of the recent results are highlighted below.

2.1 Formalism and computer codes for calculating spin-orbit couplings for EOM-CC wave functions

We have developed a formalism and an implementation for calculating spin-orbit couplings (SOCs) within EOM-CCSD (equation-of-motion coupled-cluster methods with single and double substitutions) for the following variants of EOM-CCSD: EOM-CC for excitation energies (EOM-EE), EOM-CC with spin-flip (EOM-SF), EOM-CC for ionization potentials (EOM-IP) and electron attachment (EOM-EA). We employ a perturbative approach in which SOCs are computed as matrix elements of the respective part of the Breit-Pauli Hamiltonian using zero-order non-relativistic wave functions. We follow the expectation-value approach rater than the response theory formulation for property calculations. Both the full two-electron treatment and the mean-field approximation (a partial account of the two-electron contributions) have been implemented and benchmarked using several small molecules containing elements up to the fourth row of the periodic table. The benchmark results illustrate excellent performance of the perturbative treatment and the mean-field approximation (see Table 1). When used with an appropriate basis set, the errors against experiment are below 5%. The findings regarding basis set requirements are in agreement with previous studies. The impact of different correlation treatment in zero-order wave functions was analyzed. Overall, EOM-IP-CCSD, EOM-EA-CCSD, EOM-EE-CCSD, and EOM-SF-CCSD wave functions yield SOCs which agree well with each other (and with the experimental values when available). Using an EOM approach that yields a more balanced description of the target states yields more accurate results. The manuscript presenting this work is finalized for publication. The code will be released in the upcoming 4.3 release of Q-Chem.

Table 1: Spin-orbit splittings (cm^{-1}) in selected doublet radicals computed by various EOM-CCSD methods using cc-pCVTZ.

System	Exp.[a]	EOM-EA	EOM-IP[b]		EOM-EE[b]		
		1el+2el	SOMF	1el+2el	SOMF	1el+2el	SOMF
CF	77.1	76.28	74.93	78.66	79.32	77.00	76.48
O_2^+	200.3	204.17	201.37	194.86	195.60	195.13	193.70
NO	123.1	124.16	122.12	122.11	122.74	121.85	120.90
PO	224.0	232.97	232.21	215.96	216.52	223.87	223.76
NS	222.9	227.93	226.84	242.28	242.85	231.46	231.09
PS	321.9	330.44	330.01	327.76	328.35	327.92	328.11

[a] Experimental values are taken from Klein and Gauss, J. Chem. Phys. **129** 194106 (2008).
[b] ROHF reference.

2.2 Multiple potential energy surfaces and conical intersections

Accurate description of conical intersections is a challenging task for electronic structure methods as it requires balanced description of interacting states. Using a simple model system, PSB3, we investigated the performance of various approaches in the vicinity of a conical intersection,[1,7] see Fig. 1 (left). We considered multi-reference methods, such as CASSCF, MR-CI with and without Davidson correction, various flavors of MR-PT, as well as spin-flip methods. We found that a balanced description of dynamical and non-dynamical correlation is essential for reproducing the location and energy of conical intersections. As illustrated in Fig. 1 (right), dynamical correlation stabilizes the S_1 state along the entire path and, also, stabilizes the S_0 energy of all structures relative to the equilibrium cis and trans structures. While it is not surprising that the CASSCF surfaces are quite far from the reference MR-CISD(Q), the discrepancies between various MR-PT methods are disconcerting. Overall, the performance of XMCQDPT2 is solid, whereas the CASPT2 methods exhibit artifacts in the regions of exact degeneracies. EOM-SF-CCSD provides a qualitatively accurate description of the two PES, however, the triples correction (dT) is needed for quantitatively accurate profiles that are in good agreement with MRCISD+Q.

2.2.1 Eigenvalue solvers

In collaboration with mathematicians (Chao, Vecheryanski, LBNL), we developed new algorithms for iterative diagonalization procedures solving for a small set of interior eigen-states of a large

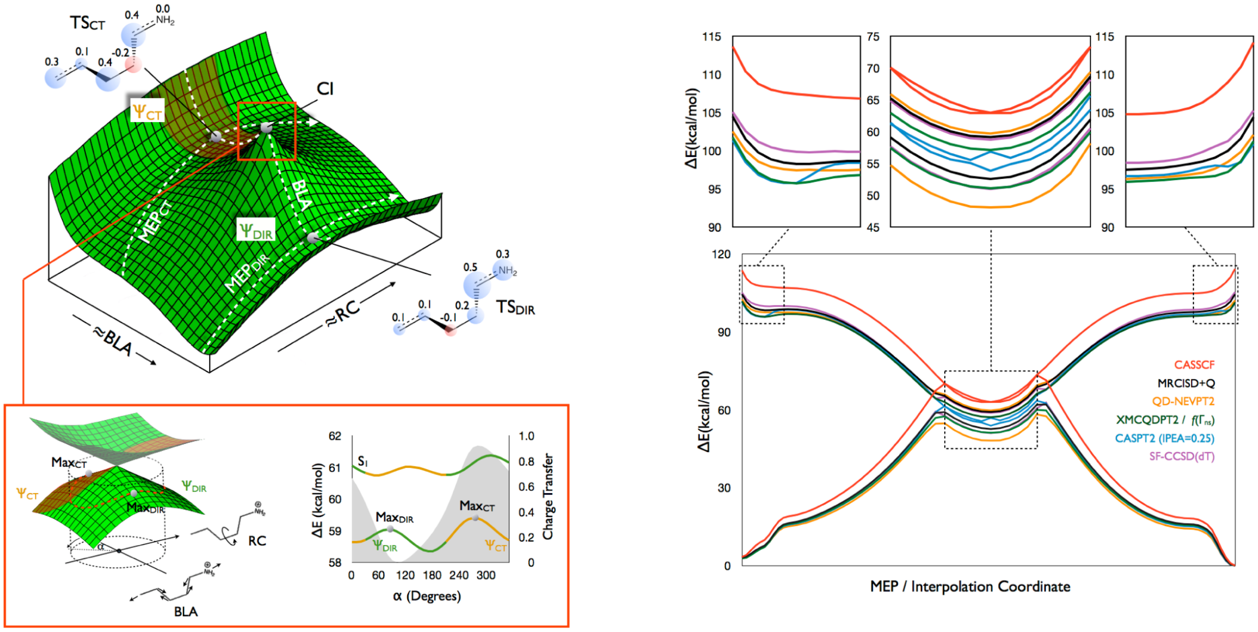

Figure 1: Left: Schematic two-dimensional cut of the ground-state potential energy surface of PSB3. The two coordinates can be described as bond length alternation (BLA) and the C2-C3 twisting reaction coordinate (RC). Around the intersection, the wave function changes its character from charge-transfer (brown) to diradical (green). Three different paths around the intersection (dashed lines) are shown by the dashed lines on the surface. Right: CASSCF (red), MRCISD+Q (black), QD-NEVPT2 (orange), XMCQDPT2 (green), CASPT2 (blue), and SF-CCSD(dT) (violet) energy profiles along the composite CASSCF path comprising MEP$_{CIS}$, CI seam, and MEP$_{TRANS}$. The insets show an expansion of the 10 points nearest to each of the cis- and trans-PSB3 structures and of the CI seam.

matrix. The new algorithms have been implemented within the EOM-CC suite of methods in Q-Chem and have been publicly released.[6]

Many electronic structure methods involve finding a few eigenstates of large matrices. The new algorithms enable solving for highly excited states which are not accessible by standard techniques. Specifically, the Davidson method was extended to solve for several states around specified energy or for a state of a given character. A new solver called Generalized Preconditioned Locally Harmonic Residual (GPLHR) method was introduced; it has more robust convergence behavior for highly excited states.

New solvers allow one to solve for highly excited states that would be inaccessible by the standard method, which is designed to find only a few lowest energy transitions. Moreover, these methods lead to computational savings for low-lying roots.

3 Current developments and future plans

Currently, we are improving the methodology for calculating cross sections from Dyson orbitals and conducting extensive benchmarking of total cross sections and angular distributions. This is conducted in collaboration with the experimental groups (Kaiser, Osborn) and theoreticians (Stanton). Other projects include computational studies of several radicals relevant to combustion and spin-forbidden channels in the reactions of oxygen with unsaturated hydrocarbons. We are also improving numeric stability of analytic gradients for non-collinear SF-TDDFT.

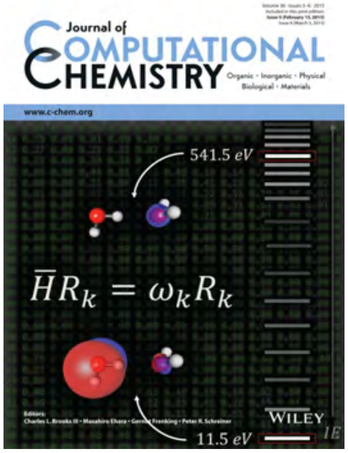

Figure 2: New iterative diagonalization algorithms targeting interior eigenstates of large matrices enable calculations of highly excited states within equation-of-motion coupled-cluster framework. For example, the core-ionized states that are embedded deeply in the spectrum (shown on the cover are core-ionized states of water that lie around 500 eV) can now be computed in the same number of iterations (and with the same storage requirements) as valence ionized states.

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Applications of noncollinear spin DFT

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Presentation Abstract

Spin density functional theory (SDFT) with noncollinear spin magnetization is a powerful tool that can be used beyond the identification of low-energy spin frustrated states. Examples are the self-consistent inclusion of spin-orbit, or the treatment of spin-flip excitations. Here I will review our recent efforts related to the calculation of the spin-orbit coupling at the minimum energy crossing point in spin-forbidden chemical reactions, the evaluation of magnetic exchange couplings, and real-time dynamics simulations based on time-dependent SDFT.

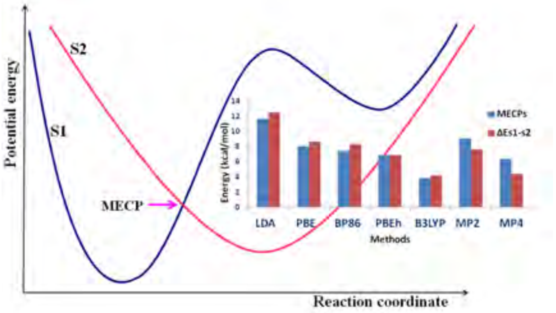
DOE DE-FG02-10ER16203: Spin-forbidden Chemical Reactions from First Principles

Postdoc: None.
Student: Bayileyegn A. Abate.

RECENT PROGRESS

The Performance of Density Functional Approximations for the Structures and Relative Energies of Minimum Energy Crossing Points

The structural parameters and relative energies of the minimum-energy crossing points (MECPs) of eight small molecules are calculated using five different representative density functional theory approximations as well as MP2, MP4, and CCSD(T) as a reference. Compared to wave function methods, the main structural features of the MECPs of these small molecules are reproduced reasonably well by density functional approximations, in agreement with previous works. Our results show that when wave function methods are computationally prohibitive, density functional approximations offer a good alternative for locating and characterizing the MECP in spin-forbidden chemical reactions.

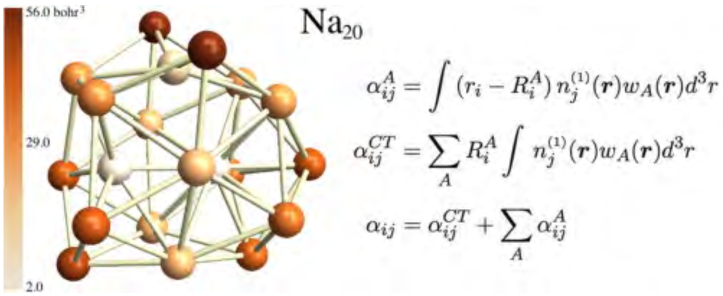


Gradient Copolymers of Thiophene and Pyrrole for Photovoltaics

The electronic properties of copolymers can be tuned by controlling their monomer ratio, and therefore can potentially be used to improve charge separation in organic photovoltaic devices. Here we show evidence based on density functional theory calculations that it is possible to control the electronic structure of π-conjugated copolymers of thiophene and pyrrole to obtain a gradient in the band gap and both conduction and valence crystal orbital band levels by controlling their composition. Our calculations predict and optimal thiophene monomer fraction range between zero and 40% is needed in order to obtain the largest electronic structure gradients.

Site-specific Polarizabilities from Analytic Linear-response Theory

We presented an implementation of the partitioning of the molecular polarizability tensor that explicitly employs the first-order electronic density from linear-response coupled-perturbed Kohn-Sham calculations. This new implementation provides a simple and robust tool to perform the partitioning analysis of the calculated electrostatic polarizability tensor at negligible additional computational effort. Comparison with numerical results for Si_3 and Na_{20}, and test calculations in all-trans-polyacetylene oligomeric chains up to 250 Å long show the potential of this methodology to analyze the response of large molecules and clusters to electric fields. This work was done in collaboration with K. A. Jackson (DE-SC0001330).



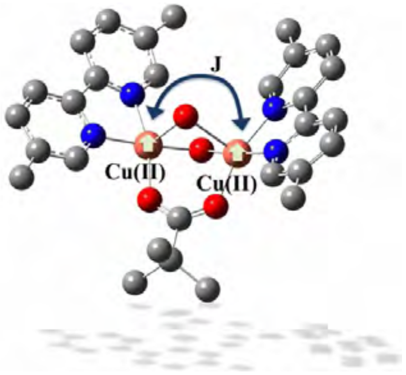
$$\alpha_{ij}^{A} = \int (r_i - R_i^A)\, n_j^{(1)}(\boldsymbol{r}) w_A(\boldsymbol{r}) d^3r$$

$$\alpha_{ij}^{CT} = \sum_A R_i^A \int n_j^{(1)}(\boldsymbol{r}) w_A(\boldsymbol{r}) d^3r$$

$$\alpha_{ij} = \alpha_{ij}^{CT} + \sum_A \alpha_{ij}^{A}$$

Magnetic Exchange Couplings from Noncollinear Perturbation Theory: Dinuclear Cu^{II} Complexes

We benchmarked the performance of a new method based on noncollinear coupled-perturbed density functional theory. To this end we calculated the magnetic exchange couplings in a series of triply bridged ferromagnetic dinuclear Cu^{II} complexes that have been recently synthesized. We find that for any basis-set the couplings from our noncollinear coupled-perturbed methodology are practically identical to those of spin-projected energy-differences when a hybrid density functional approximation is employed. This demonstrates that our methodology properly recovers a Heisenberg description for these systems, and is robust in its predictive power of magnetic couplings.



FUTURE PLANS

1. Assess the impact of the choice of different spin-orbit approximations on the coupling between diabatic spin surfaces, including different flavors of all-electron Pauli and Douglas-Kroll-Hess operators, and spin-orbit pseudopotentials.
2. Benchmark the performance of DFT for the spin-orbit coupling, energetics and location of the MECP against multi-reference wave function methods.

Publications Acknowledging this Grant in 2011-2014

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Predicting Spin-Forbidden Reaction Rates in Combustion Chemistry

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Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL

Presentation Abstract

Many key reactions in combustion involve prominent spin-forbidden steps. For example, the oxidation of an unsaturated singlet species by atomic or molecular oxygen often initially results in a weakly bound triplet adduct. Fragmentation and isomerization of these adducts on the triplet surface may compete with intersystem crossing to a lower-energy singlet surface with different sets of intermediates and fragmentation channels. Similarly, radical-radical reactions may give rise to both singlet and triplet intermediates, which may be connected via energetically accessible crossing seams. Here, we consider the accuracy of statistical theories for predicting microcanonical intersystem crossing rates and for use in master equation calculations for predicting pressure-dependent thermal rates and product branching. Results obtained using statistical theories are compared with those from multistate trajectory calculations and experiment. The statistical approach is shown to be very accurate so long as models for electronic decoherence and multidimensional nonadiabatic transitions are included. The following systems are considered: ^{3}O + CO, ^{3}O + C_2H_4, and H + NCO.

AITSTME: An Expert Ab Initio Transition-State-Theory-Based Master Equation Code, Part of the Predictive Theory and Modeling Component of the Materials Genome Initiative

Co-PIs: Judit Zador and James A. Miller
Postdoc: Xiaohu Li

RECENT PROGRESS

Software

Our general-purpose AITSTME software package, which is termed PAPER (Predictive Automated Phenomenological Elementary Rates), implements a new formulation of the master equation for complex-forming chemical reactions with multiple wells and multiple bimolecular products. The reformulation of the master equation provides compact expressions for the phenomenological rate coefficients describing all chemical processes, i.e., internal isomerization reactions, bimolecular-to-bimolecular reactions, isomer-to-bimolecular reactions, and bimolecular-to-isomer reactions and helps understand the relation between various earlier master equation derivations. The PAPER code, which is now finding widespread use within our team and in external research efforts, incorporates a variety of advances beyond other existing codes, including: automated merging of species as their equilibration rates exceed collisional stabilization rates, automatic consideration of all reactions on a given potential energy surface, generation of modified Arrhenius fits for all channels, multidimensional quantum and semiclassical treatments of torsions, anharmonic treatment of umbrella modes, threaded parallelization of the diagonalization step, a procedure for reducing the matrix dimension through energy dependent species merging, a perturbative procedure that yields more stable results for low temperature, and a procedure for properly modeling the separation into thermal and direct kinetics for hot initial distributions.

Pressure dependence

We have developed a method for making accurate a priori predictions of pressure-dependent kinetics. This work required the solution of a two-dimensional master equation in energy *E* and angular momentum *J*, as well as accurate trajectory-based calculations of collision induced *E* and *J* transfer rates.

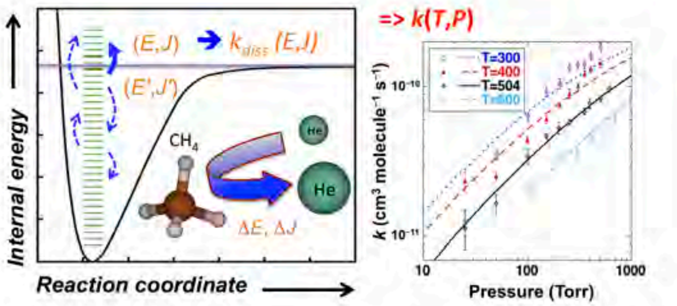

Figure caption. "Third-body" collisions activate unimolecular reactants, stabilize energized intermediates, and generally give rise to pressure dependence in chemical kinetics. Here, CH_4 + He collisions are shown schematically exchanging energy and angular momentum among the ladder of internal states (*E*,*J*) of methane. Collisions that activate methane above its dissociation threshold promote reaction. The mathematical treatment of these processes yields a priori predictions for the thermal rate coefficients that agree quantitatively with the experimental data.

Publications Acknowledging this Grant in 2011-2014

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ABSTRACT

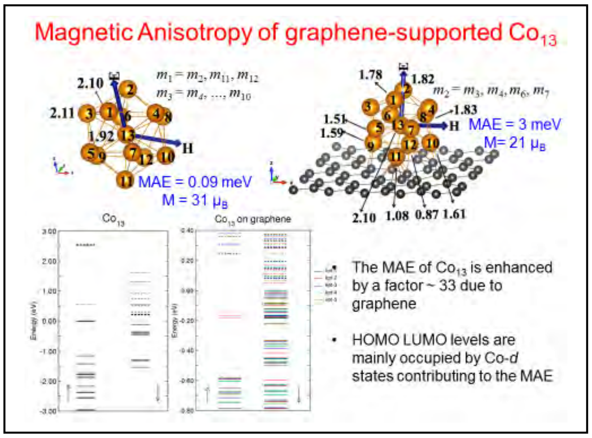
- **Program Title**: Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies.
- **Principal Investigator**: Khanna, Shiv
- **Mailing Address**: Physics Department, Virginia Commonwealth University, Box-2000, Richmond, VA 23284-2000, USA
- **Email**: snkhanna@vcu.edu
- **Program Scope**: An exciting development in nanoscience is the formation of materials whereby nanoscale clusters serve as building blocks. Since the properties of clusters change with size and composition, cluster assemblies offer the attractive proposition of forming materials with novel combination of properties; it is often referred to as the "next frontier" in the field of nanoscience. The proposed work is directed towards developing cluster materials with magnetic building blocks. For ordinary magnets, the reduction in size leads to a decrease in magnetic anisotropy and the magnetic moment undergoes fluctuations in direction under ordinary conditions. Identifying motifs with larger magnetic anisotropy is critical to applications as they require stable magnetic moments.

  We propose to undertake a comprehensive program starting from electronic structure calculations and magnetic properties of free and supported clusters for identifying stable magnetic motifs with large magnetic anisotropy energy and of varying band gaps, to the investigation of the transport properties of molecules of such motifs and efforts towards synthesis and properties of assemblies of such motifs. The requested program will involve four interrelated areas of study, namely: A) motivated by our recent preliminary findings of high anisotropy, we shall investigate magnetic properties of free TM_nC_m/TM_nSi_m (TM=Cr, Mn, Fe, Co, Ni) clusters and TM_n clusters supported on graphene to identify potential magnetic building blocks.; B) carry out studies of metal chalcogenide superatoms and Si_nTM_m (TM= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Pd) clusters to identify potential semiconducting magnetic building blocks.; C) carry out studies of ligated cluster assemblies and supported ligated clusters to explore magnetic assemblies with tunable band gaps.; and D) develop computational codes to carry out electronic transport studies that incorporate the effect of excess charge, spin ordering and anisotropy. The theoretical studies on free clusters will be carried out in close collaboration with experimental groups. Thereafter, we plan to build on our recent success in synthesizing nano-assemblies using synthetic chemical methods in collaboration with experimental groups to form similar assemblies of magnetic motifs.

- **Recent Progress:** Our recent work has proceeded along three different directions.

  (1) The reduction in size leads to a decrease in magnetic anisotropy energy (MAE) and the magnetic order in small clusters/nanoparticles is thermally unstable as the direction of the magnetic moment can fluctuate exhibiting superparamagnetic relaxations. The first step towards any spintronics applications is to have thermally stable magnetic order. Finding novel ways to enhance MAE is thus the key to potential applications. In small sizes, the MAE is mainly due to magnetocrystalline anisotropy that arises due to spin orbit coupling. Our first objective has been to identify free TM_nC_n clusters that offer high MAE to have thermally stable magnetic order. We showed that the magnetic anisotropy energy (MAE) in cobalt clusters can be significantly enhanced by doping them with group IV elements. Our first-principles electronic structure

calculations show that Co_4C_2 and $Co_{12}C_4$ clusters have MAEs of 25 K and 61 K, respectively. The large MAE is due to controlled mixing between Co d- and C p-states and can be further tuned by replacing C by Si. Larger assemblies of such primitive units are shown to be stable with MAEs exceeding 100 K in units as small as 1.2 nm, in agreement with the recent observation of large coercivity in nanoparticles. We have also found a large enhancement in MAE of a Co_{13} cluster supported on graphene. These findings are being written for publication and may pave the way for the use of nano-clusters in high density magnetic memory devices or in spintronics applications.



Magnetic Anisotropy of graphene-supported Co_{13}

- The MAE of Co_{13} is enhanced by a factor ~ 33 due to graphene
- HOMO LUMO levels are mainly occupied by Co-*d* states contributing to the MAE

In addition to MAE, we also found that the easy axis can be controlled by charging offering a new approach to control the orientation of magnetization that is of central importance for the application of nanoparticles in spintronics. Conventionally, magnetization is controlled directly by an external magnetic field or by an electric field via spin-orbit coupling. Here, we demonstrated a different approach to control magnetization in small clusters. We first showed that the low magnetic anisotropy of a Co_5 cluster can be substantially enhanced by attaching benzene molecules due to the mixing between p states of C and the d states of Co sites. We then show that the direction of magnetization vector of Co_5 sandwiched between two benzene molecules rotates by 90 degrees when an electron is added or removed from the system. An experimental set up to realize such effect is also suggested.

(2) Metal silicon clusters have attracted a great deal of interest because the incorporation of large quantities of transition metal atoms into bulk silicon is difficult and overcoming this limitation could offer new materials for the microelectronics industry. Assembling solids using metal silicon clusters would alleviate this difficulty, and this started a vigorous search for stable metal silicon magic clusters almost 20 years ago. One of the areas of potential interest has been silicon cages encapsulating metal atoms. The bonding between the silicon and the transition-metal dopant stabilizes the cage. Previous experimental studies by Hiura et al. identified WSi_{12} to be a highly stable species and argued that the stability could also be attributed to the 18-electron rule assuming that each Si atom contributes one valence electron while the W contributes six electrons. The ground-state structure of WSi_{12} is a hexagonal prism with an endohedral W atom. Each Si is bonded to three other Si atoms and the central W atom, so by assuming electron-precise bonding, each Si donates 1 e^- to the W atom that has 6 valence electrons leading to a total count of 18 electrons. Furthermore, these clusters were thought to be analogous to transition-

metal aromatic complexes that are most stable when the central atom has 18 effective valence electrons. These findings sparked a flurry of activities in MSi_n clusters and, in particular, on the congener cluster $CrSi_{12}$. Numerous works examined the stability of $CrSi_n$ clusters and showed that the energy gained in adding a Si atom to the $CrSi_n$ clusters does peak at $CrSi_{12}$, and debated the utility of the 18-electron rule in predicting the stability of the clusters; however, determining if the 18-electron rule actually applies to $CrSi_{12}$ has not been examined.

We recently critically examined the bonding and nature of stability of $CrSi_{12}$ and showed that its electronic structure does not conform to the 18-electron rule. Through theoretical studies, we showed that $CrSi_{12}$, has 16 effective valence electrons assigned to the Cr atom and an unoccupied $3d_z^2$ orbital. We demonstrated that the cluster's apparent stability is rooted in a crystal field-like splitting of the 3d orbitals analogous to that of square planar complexes. $CrSi_{14}$ was shown to follow the 18-electron rule and exhibits all conventional markers characteristic of a magic cluster. These findings are critical to develop guiding principles that could enable identification of the stable metal silicon clusters for cluster assembled materials.

(3) We have also examined the electrical transport across magnetic superatoms and assemblies connected to gold leads to determine new features offered by such devices. Our studies focused on electronic transport across a $FeMg_8$ magnetic superatom and its dimer using a density functional theory combined with Keldysh nonequilibrium Green's-function formalism. For a single cluster, our studies for the cluster supported in various orientations on a Au(100) surface showed that the transport is sensitive to the contact geometry. Investigations covering the cases where the axes of Mg square antiprism are 45 degrees, perpendicular, and parallel to the transport direction, showed that the equilibrium conductance, transferred charge, and current polarizations can all change significantly with orientation. Our studies on the transport across a magnetic superatom dimer $FeMg_8$-$FeMg_8$ focused on the effect of electrode contact distance and the support. The calculated I-V curves show negative differential resistance behavior at larger electrode-cluster contact distances. Further, the equilibrium conductance in ferromagnetic state showed an unusually high spin polarization that was about 81.48% for specific contact distance, and a large magnetoresistance ratio exceeding 500% was also found. The results showed that the superatom assemblies can provide unusual transport characteristics, and that the spin polarization and magnetoresistance can be controlled via the contact geometry.

- **Future Plans**:

We are proceeding along several directions to identify potential magnetic building blocks and properties of their assemblies. We are currently exploring the MAE of nickel clusters to see if the enhancement observed for cobalt can be extended to other metals. We are also examining cobalt clusters supported on pristine and defected graphene flakes and have some exciting findings. We are extending our studies to ligated chalcogenide superatom clusters where it has been recently possible to synthesize cluster assembled materials using C_{60} and iron oxide cluster counter ions and investigate their magnetic properties. These assemblies offer a unique example of collective behavior of magnetic nanoparticles and we have some interesting preliminary theoretical results.

We are continuing our work on metal silicon clusters using iron and other transition metal atoms. Our key objective is to develop guiding rules that could allow identification of new building blocks that are magnetic. The next issue is the collective response of an assembly of such units. It is hoped that these findings could open the path towards magnetic silicon.

Finally, we are continuing our studies of transport across clusters and cluster molecules to identify the unique features offered by such units.

- **Selected Publications:**

1. ”Stable magnetic order and charge induced rotation of magnetization in nano-clusters.” M.F. Islam and S.N. Khanna App. Phys. Lett. **105**, 152409 (2014).
2. “Does the 18-Electron Rule Apply to $CrSi_{12}$?” M.B. Abreu, A.C. Reber, and S.N. Khanna J. Phys. Chem. Lett. **5**, 3492-3496 (2014).
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First-Principles Spin-Dependent Many-Electron Dynamics: Dielectric Response and Dirac Formalism

Principle Investigator:
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Program Scope:

The research activities in this funding period (Nov 2014 – Nov 2107) can be broadly defined in two themes of method development:

(1) We will develop an explicit time-dependent dielectric response formalism that couples to the real-time many-electron time-dependent method. Initially, we will develop a time-dependent linear response function that can be propagated in time to describe the dynamics of the dielectric medium. In the context of the spin-dependent many-electron dynamics, such a time-dependent dielectric response method will allow us to study spin-dephasing dynamics, and offer important insights into the dynamical interplay between spin-dependent many-electron system and dielectric medium (e.g. solvent and semiconductor lattice).

(2) We will introduce spin-dependent formalisms into the time-dependent framework with a hierarchical approach. We will first develop the time-dependent generalized Hartree-Fock and the time-dependent generalized Kohn-Sham (given the availability of non-collinear DFT kernel) methods that allow electron spin to take on a non-collinear pathway – a crucial requirement for spin magnetization dynamics. We will continue to develop a time-dependent two-component relativistic Dirac-Fock/Dirac-Kohn-Sham method that includes spin couplings (spin-spin, spin-orbit and spin-other-orbit). Within the two-component relativistic Dirac formalism, we will develop time-dependent Dirac-Coulomb and Dirac-Coulomb-Breit methods that account for spin couplings at different levels. As part of the hierarchical approach and our futuristic mindset, we also aim for a development of the time-dependent configuration interaction Dirac method that is beyond the next funding period.

Recent Progress:

We have formulated an *ab initio* time-dependent two-component spinor (TD2C) theory, to study the non-collinear spin dynamics of many-electron systems in response to an external magnetic field.[1] We employed a direct integration of the time-dependent non-relativistic two-component Hartree-Fock equation using atom-centered basis functions and a unitary propagation approach with a modified midpoint algorithm. An analysis tool based on the Hirshfeld partitioning scheme has been developed to analyze the time-dependent spin magnetization. For the simple one-electron system of the hydrogen atom and collinear multi-electron system of the lithium atom, the real-time two-component Hartree-Fock simulations yield the same results as the analytical Larmor precessions. As an important application of our methodology, we have simulated spin dynamics of a non-collinear Li_3 trimer in response to an external magnetic field (Fig. 1). The switching of the magnetization at each lattice node was observed during the dynamical simulation.

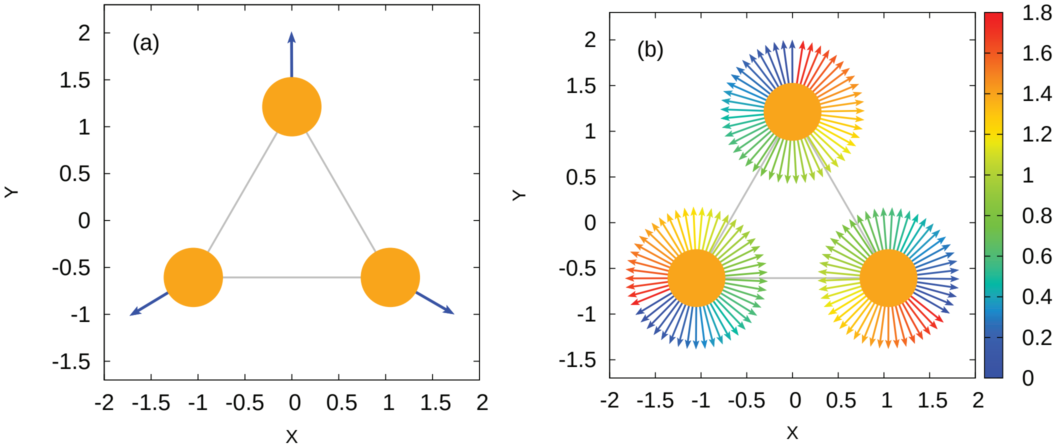

Figure 1. (a) the initial magnetization (in the unit of Bohr magneton) of Li_3 at $t = 0$, and (b) the time evolution of the spin magnetization (in the unit of Bohr magneton) in a uniform magnetic field applied perpendicular to the xy plane (the time-evolution is represented as the progression of coloration in the unit of picosecond).

Future Plans:

The new TD2C framework can be viewed as the bridge that connects the non-relativistic Schrödinger equation and the fully relativistic Dirac equation. The "spin-relaxed" approximation in the generalized equations is a step towards relativistic electronic structure theory, as the relativistic two-component methods can be formulated in the same way as the equation derived in this work. This framework provides us with a unique opportunity to study spin dynamics from the first-principles perspective. As illustrated in this work, the coupling between a many-spin system and a homogenous magnetic field can be introduced into this framework as a perturbation by taking the non-relativistic limit of the Dirac equation. Although including this coupling term in the time-dependent non-relativistic two-component spinor model does not offer much more than what can be learned from the parameterized models (e.g. Heisenberg Hamiltonian), the test cases presented in this work calibrate the robustness of the numerical implementation. The time-dependent non-relativistic two-component spinor formalism introduced herein lacks electron correlation, a problem inherited from the HF formalism. In a following work, we will examine the correlated non-relativistic two-component method using non-collinear DFT functionals.

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Two-Dimensional Plasmonic Nanosurface for Photovoltaics

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Presentation Abstract

We investigate a two-dimensional corrugated plasmonic nanosurface for efficient light trapping in a photovoltaic cell. The design was chosen to minimize light polarization effects and generate robust optical properties for unpolarized sources. It consists of two, perpendicular gratings in the silver film that intersect to yield cross-shaped nano-elements. A thin, silicon film then covers all of this surface structure. An additional degree of freedom can be introduced into the design by interrupting the grid in both directions. We show that this extra spacing between the array elements can be used to tune the absorption properties of the nanosurface. We demonstrate how this two-dimensional configuration is more efficient than its one-dimensional counterpart in terms of the short circuit photocurrent density. We also briefly discuss possible extensions of this structure design, which can further enhance the solar cell performance. Time permitting, we will discuss how light absorption in a plasmonic grating nanosurface can be calculated by means of a simple, analytical model based on a transmission line equivalent circuit. We will also show the utility of the circuit theory for understanding how the peaks in the absorption coefficient are related to the resonances of the equivalent transmission model as well as how this can help in designing more efficient structures.

DE-SC0010212 (previously DE-SC0006922): Plasmon Enhanced Photovoltaics: Modeling Energy and Charge Transfer in Solar Nanoassemblies

PI: Kevin L. Shuford
Postdocs: Alessia Polemi, Chengyong Xu, Olga Samoylova
Students: Andrew Smith

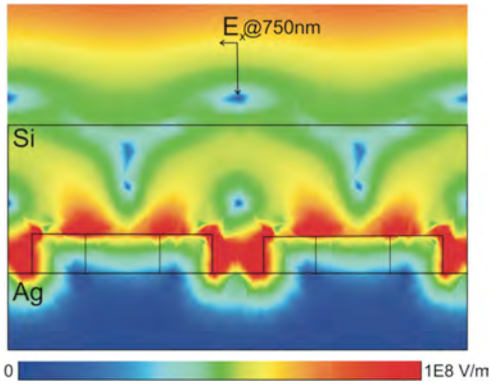
Program Scope

The overarching goal of the project is to better understand how energy and charge move through assemblies of nanomaterials such as wide bandgap semiconductors, strongly absorbing dye molecules, and plasmonic nanoparticles. The former two are highly relevant for current photovoltaic devices and the latter are known to have unique optical properties resulting from surface plasmon excitations. The impetus for the project is the high cost and relatively low efficiency of current solar devices. We want to determine if the highly tunable plasmon modes supported by the metal particle – and the sizeable electromagnetic fields generated upon exciting them – can be utilized to enhance the chemical and physical processes associated with photovoltaic devices.

RECENT PROGRESS

Light Trapping in Photovoltaic Cells

Our group has developed models and methodologies to compute the optical properties of metal nanostructures in a classical electrodynamics framework. Using these, we have demonstrated that noble metal components can function as light antennas that efficiently attract and redirect incident electromagnetic energy into thin semiconductor layers, thereby effectively trapping light in photovoltaic active layers and increasing photon absorption. Current designs require materials to be optically thick (~200 microns) to effectively absorb incident sunlight, whereas our studies show this layer can be decreased to tens of nanometers by incorporating plasmonic components, which may increase efficiency and/or decrease cost.



Electric field trapped within a thin silicon layer by a silver grating.

Modeling Metal Nanoparticle/Molecule Systems

We have examined electromagnetic interactions between a molecule and a metal nanoparticle. We find that the molecular absorption and emission processes are drastically altered by the presence of a metal nanoparticle and the degree of inter-nanoparticle coupling. When a molecule is placed within the gap of a strongly coupled nanoparticle dimer, the radiative decay rate is enhanced notably more than the non-radiative channels for the dimer compared to the single nanoparticle. The result is a suppression of quenching in the dimer case until the molecule is in very close proximity to the metal surface (~2 nm); single nanoparticles quench the emission readily for a metal/molecule distance inside of 15 nm. We have carried out similar investigations on coated nanoparticles and find that quenching can also be avoided by providing a physical barrier around the nanoparticle without drastically affecting the molecular relaxation. These studies demonstrate that the plasmon fields from nanostructures can be utilized to effectively facilitate energy transfer to molecules without detrimental losses to the metal.

Properties of Nanomaterials

We have begun studying the electronic, optical, and transport properties of titania and low dimensional nanomaterials such as graphene and MoS_2. In particular, we have just completed studies on the electronic and structural properties of pnictogen-doped graphene and multilayer graphene interacting with halogens. Plane wave DFT was used to compute equilibrium geometries and band structures. These calculations are a first step towards the late stage goals of the project examining molecule/surface interactions and interfacial charge transfer of photovoltaic nanoassemblies within a quantum mechanical framework. Concurrently with the periodic calculations, we are also performing quantum chemical calculations on common Ru dyes, porphyrins, and organic donor-acceptor molecules. Future work will attach these to semiconductor clusters to elucidate the effects of surface binding as well as system size.

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Interfacial Electrocatalysis from First Principles

DOE-BES-CTC Early Career Award

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Program scope and definition

We are exploring the fundamental principles of electrocatalysis and electrocatalytic reaction mechanisms at electrified solid/liquid interfaces using periodic Density Functional Theory methodologies. The effort seeks to identify and exploit efficient methods to generate pH/potential-dependent phase diagrams of multifunctional interfaces in aqueous environments, elucidate complex electrocatalytic reaction mechanisms under realistic in-situ conditions, estimate the thermodynamics and kinetics of charge transfer at interfaces, and reduce the impact of electronic structure self-interaction errors on the calculated energetics.

Recent Progress

We are currently exploring two primary themes that focus on structural and mechanistic analysis of electrified interfaces; a few subsidiary themes are also being pursued but will not be discussed in this abstract. First, we are investigating the structure, chemistry, and physics of thin, base metal (Ni, Co, Fe,…), oxyhydroxide films on crystalline precious metal substrates. These films have been shown by our collaborators in the group of Nenad Markovic (Argonne National Laboratory) to possess remarkable properties for fundamental electrocatalytic processes in alkaline electrochemical environments; such environments are, in turn, among the most promising research areas in the field of electrocatalysis. While the experimental results are compelling, atomistic knowledge of the films' structure and properties is almost entirely absent. Successful prediction of films' structure and physical/chemical properties, in turn, represents a significant theoretical challenge, given the multitude of structural and electronic features that can affect these features. In particular, we have identified, and are seeking to address, four classes of problems that are relevant to the determination of the films' electrocatalytic properties. First, standard GGA-based periodic DFT calculations often have insufficient accuracy to treat the multiple oxidation states of the base metal films that naturally result from to changes in the electrochemical potential. Second, identification of low energy structures for the films requires consideration of a large and complex configurational space. Third, the actual catalysis on these structures occurs not on the films themselves, but on so-called three phase boundaries (TPB's) between the film, the precious metal substrate, and the surrounding environment, and the structure and properties of these TPB's must be elucidated to ultimately understand the catalysis. Finally, the effect of explicit water molecules on the kinetics and thermodynamics of the films, and the associated catalytic processes, is often non-trivial and must be addressed if a fully comprehensive description of the reaction chemistries is to be obtained.

We have made progress in addressing the above challenges during the current award cycle. Recently, we have developed a simple extension of the well-known Hubbard U-based methods for correction of self-interaction errors that accurately describes the thermodynamics of oxyhydroxide phase transformations in aqueous electrochemical environments. The approach employs a careful choice of bulk reference state (related to liquid water), a self-consistent van der Waals-corrected functional, and U fitting to bulk oxyhydroxide reaction energies, and it is able to describe bulk reaction energies with an average error of less than 0.05 eV per formula unit. Importantly, the strategy also preserves accurate descriptions of bulk gas phase reaction energies, such as oxygen reduction, that must be properly described to permit reliable description of catalytic reactions. We have applied this approach to the description of thin oxyhydroxide base metal films on Pt(111) and Au(111) substrates, where we have performed a comprehensive search for different film/substrate epitaxies to ensure minimal lattice strain in the adsorbed films. The resulting film geometries, which possess a rich spectrum of local structures and oxidation states, can be incorporated into a phase diagram which describes the most thermodynamically stable structures as a function of the pH and electrode potential on the reversible hydrogen scale (Figure 1). The films' phase behavior is substantially different from that of the bulk metals, a result that we have very recently traced to a delicate balance between the films' strain and their interaction with the substrate. Using these complete film structures as a starting point, we are now elucidating the edge structures of the films, again as a function of potential and pH. We have identified several edge terminations that are thermodynamically stable at low electrochemical potentials, and we are in the process of developing explicit models of water structure around these edges and understanding the impact of water on catalytic processes at such edges. Preliminary results from analysis of the hydrogen evolution reaction, a central reaction in alkaline electrolyzer chemistry, imply that hydrogen bonding of surrounding water molecules significantly lowers the barrier to dissociation of water near the oxyhydroxide/metal three phase boundary. This behavior, in turn, may be responsible for acceleration of alkaline HER in these multifunctional systems.

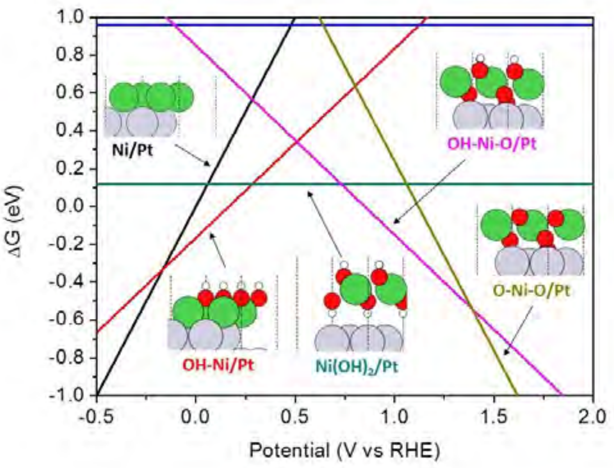

Figure 1. First principles phase diagram of monolayer nickel oxyhydroxide films on Pt(111) at pH=13.

In parallel work, we are developing a comprehensive electrocatalytic reaction mechanism for selected nitrogen-cycle electrochemical processes on both low-index and defected platinum surfaces. Nitrogen cycle electrochemistry lies at the heart of electrochemical treatments of ammonia- and nitrate-contaminated wastewater streams and has also received attention as a possible means of low-temperature ammonia production. We are systematically investigating the reaction mechanisms for electrochemical NO and nitrate reduction on Pt(111), Pt(100), and Pt(211), which constitute common models of low-index transition metal surfaces. Thermodynamics and barriers are placed on an appropriate electrochemical reference scale through Nernstian-type thermodynamic corrections, and solvation corrections to the energetics are obtained through ab-initio molecular dynamics simulations. Key recent results include the identification of several highly active pathways for NO conversion to ammonia, as well as the discovery of a very uncommon solution phase mediated-mechanism for the formation of N_2O dimers.

Future Plans

We seek to generalize the thin film, three-phase boundary studies to other metal and alloy systems, with a view to both establishing reactivity trends and, ultimately, identifying novel catalysts for the alkaline hydrogen evolution reaction. We are additionally extending these analyses to other chemistries that play a central role in fuel cell and electrolyzer operation, including carbon monoxide oxidation and oxygen reduction, and we are seeking to apply the developed models to other processes of interest in thin film science. On the methological side, we will explore the performance of periodic hybrid functionals as a possible alternative to Hubbard U analyses, and we will additionally probe the applicability of metadynamics- and potential of mean force-based techniques to better understand the impact of solvation on near-surface reaction events. Insights gleaned from these methodological studies will be applied to the mechanistic work in the nitrogen-cycle electrocatalysis, where we are also developing strategies to rapidly and efficiently extrapolate the predicted kinetics of NO and nitrate reduction from one metal surface to the next.

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In Search of Natural Design Principles for Efficient and Robust Energy Transfer in LH2 of Purple Bacteria

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Department of Chemistry and Biochemistry

Presentation Abstract

Photosynthetic organisms can achieve near perfect quantum efficiency under optimal condition. This is remarkable considering that electronic excitations should travel about 100 nm or larger distances through rugged, fragile, and dynamic membrane protein environments. There are various structural motifs and arrangements of pigment-protein complexes adopted by different organisms, but the exact molecular and organizational factors enabling their superb capability to relay excitation energy have not been well understood. This is true even for one of the most well characterized systems, the photosynthetic unit (PSU) of purple bacteria, which has only two types of antenna complexes called light harvesting 1 (LH1) and light harvesting 2 (LH2) with known crystal structures. Of these, the LH2 serves as the major initiator and carrier of the excitation energy. This presentation reports comprehensive series of classical simulations and quantum calculations so as to understand the relation between natural sizes of LH2s and their functionality, while considering realistic molecular details and the disorder. The analysis of computational results leads to a convincing scenario that natural sizes of LH2s are outcomes of the interplay between structural constraints of hydrogen bonding and the need to optimize their energy transfer capability against the disorder.

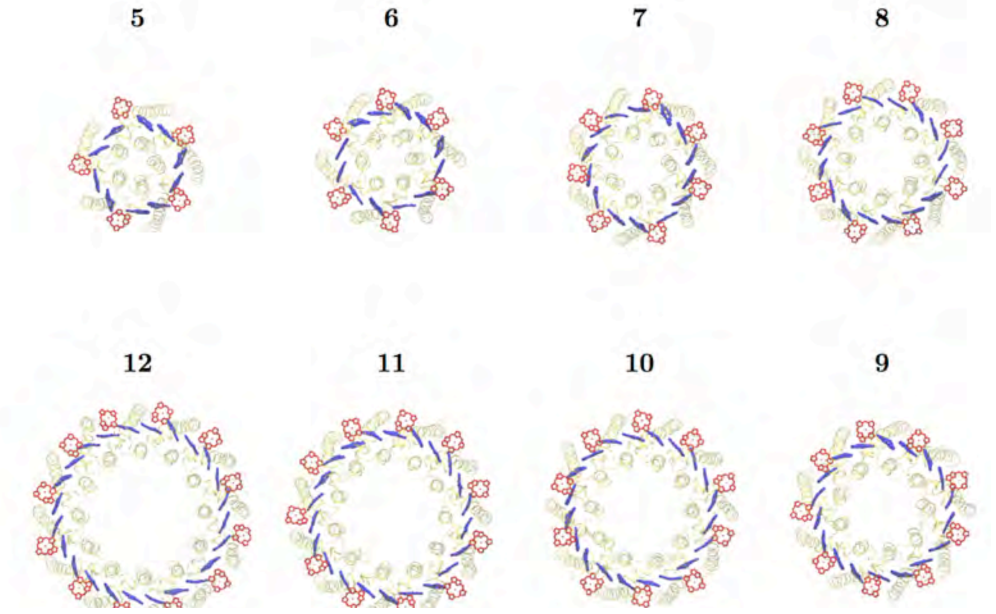
DE-SC0001393: Elucidating Positive Quantum Effects for Efficient Energy and Charge Transfer Dynamics in Soft Solar Energy Conversion Systems

Postdocs: Eva Rivera and Daniel Montemayor

RECENT PROGRESS

Generalized Master Equation for Modular Exciton Density (GME-MED)

This project was conducted in collaboration with Profs. G. Fleming and K. B. Whaley. The GME-MED allows efficient calculation of long range resonance energy transfer dynamics for large scale systems while including the effects of non-Markovian dynamics and realistic effects of disorder. An application of this theory to a subset of Fenna-Matthews-Olson (FMO) complex demonstrated that the accuracy of GME-MED, when proper lineshape function is used, can be made comparable to that of the hierarchical equations of motion (HEOM) approach, which is considered to be almost exact. Application of the GME-MED to the energy transfer between two light harvesting 2 (LH2) antenna complexes of purple bacteria demonstrated its practical utility.



Elucidation of Molecular Level Design Principle behind Optimal Sizes of LH2 Complex

This project was conducted with major contributions from the two postdoctoral researchers, Eva Rivera and Daniel Montemayor. The natural LH2 complexes are known to have mostly 9-fold symmetry with some having 8 or 10 fold symmetries. To examine why this is the case, we constructed *in silico* models of both natural LH2 and its non-natural analogues. All atomistic model of the natural LH2 (symmetry number *N=9*) was constructed employing the X-ray crystal structure of *Rps. acidophila*. Using the protomer of this as a building block, we have also succeeded in building and stabilizing atomistic models with *N=5-8* and *10-12*, in appropriate membrane environments. Molecular dynamics (MD) simulations were conducted, and it was confirmed that all complexes remained stable during MD simulations for about 10 ns. However, distinctively different features were observable for different sizes in their final structures as can be seen in the figure above. Close examination of bonding characteristics of each complex revealed that the main source of such difference is the variation in the pattern of the hydrogen bonding (HB) between bacteriochlorophylls (BChls) of LH2 and protein residues. For small complexes (*N=5-7*), angle strains make the formation of HB unfavorable. For larger complexes (*N=11-12*), a new kind of competing HB becomes available, which introduces new source of frustration and disorder. Based on time dependent density functional theory (TD-DFT) calculations of BChls including their protein residues in close proximity and experimental data on mutants, we confirmed that breaking of HB results in blue shift of excitation energy by about *0.06* eV. As a result, stable formation of HB is important not only for structural stability but also for reducing the disorder in the excitation energies of BChls. The exciton dynamics between two LH2s were simulated employing the GME-MED approach. When all the effects of the structure and variation of the disorder due to different HB patterns were taken into consideration, the results demonstrated that the inter-LH2 exciton transfer rates are near maximum for *N=9,10*. These results suggest that natural sizes of LH2 have indeed been optimized for the maximum inter-LH2 exciton transfer rate, and have also revealed the natural design principle of LH2 to minimize the negative effect of the disorder through a stable HB formation as well as the quantum delocalization of exciton.

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Program Title: **EARLY CAREER RESEARCH PROGRAM: Modeling of Photoexcited Process at the Interfaces of Functionalized Quantum Dots**
Principal Investigator: **Svetlana Kilina**
Address: 1355, Elm Circ. N, Fargo, ND 58102; e-mail: Svetlana.kilina@ndsu.edu

Simulating Phonon-Induced Photoexcited Dynamics in Ligated and Core/Shell Quantum Dots

In many respects, colloidal QDs are near-ideal materials for solar energy conversion and lighting technologies. However, the electronic and optical properties of QDs exhibit extreme sensitivity to surface passivation and chemical environment. As such, surface chemistry plays a crucial role in defining the work functions of QDs critical for technological applications. Our research aims to fill the gap in the understanding of the role played by QD surfaces in light-driven processes. Several important steps have been already fulfilled toward this goal.

We have continued to develop non-adiabatic (NA) dynamics and validated the approximations we used in this methodology when it applied to phonon-mediated dynamics in pristine, ligated, core/shell, and doped QDs [1, 2]. Our NA time-domain DFT approach treats phonons semi-classically, which allows us to explicitly incorporate quantum decoherence effects within the electronic subsystem. We revealed the role of surface defects and decoherence in the ultrafast loss of photoexcitation to heat in QDs and established a connection between the slow energy relaxation — the phonon bottleneck — and Zeno effect. Quantum confinement can significantly slow down electron-phonon relaxation in QDs; known as the phonon-bottleneck the effect remains elusive. Our simulations confirm that the bottleneck, in CdSe QDs occurs under quantum Zeno conditions: To achieve the bottleneck, elastic electron-phonon scattering (decoherence) must be faster than the coherent electronic transition [1]. The calculated electron-phonon relaxation time shows excellent agreement with the experimental data. Our study also shows that defects in the shell in CdSe/ZnS QDs can destroy the electron-hole decoupling allowing for faster relaxation. The established relationship between the phonon-bottleneck and the quantum Zeno effect together with the atomistic details obtained from our simulations, provide the understanding of the conditions necessary to achieve and control the phonon-bottleneck via synthetic manipulations of the QD's shells, dopants, ligands, packing, etc.

Combining NA time-domain DFT with the time-dependent density matrix technique, we have extended our approach to identify conditions affecting radiative and nonradiative pathways of the exciton cooling and obtained, for the first time, the time-resolved emission spectra of co-doped Si QDs [2]. Our extensive analysis of extracted relaxation rates revealed ultrafast electron-phonon dynamics that is enhanced by a presence of a doping in 1-1.5 nm Si QDs. Provided computational insights into pathways and mechanisms of relaxation dynamics in silicon nanostructures could be useful in specifying ways of controlling both radiative and non-radiative process and might help in rational design of Si-derived novel nanomaterials. Within DFT simulations, we also determined which form – QD arrays or nanowires – maximizes the absorption and emission of Si and how that efficiency is affected by the interaction between QDs and their structural disorder [3]. Surprisingly, the structural disorder in the amorphous QD arrays results in better light absorption at the lowest energies compared to crystalline-based nanomaterials. Our new focus is on the question how the interaction between different QDs impacts their photodynamics. It was experimentally found that close packing of Si QDs at distances of ~ 1 nm significantly increases 'on' time of blinking. We hypothesize that fast energy transfer between an excited QD to the nearest one provides additional channel for occupation of semi-dark and dark trap states in neighboring QDs forcing the emission to happen from higher laying optically bright states and thus increasing 'on' blinking time in clusters of interacting Si QDs.

Calculating energy transfer rates from transition density matrixes obtained from linear-response time-dependent DFT (TDDFT), we predicted times of energy transfer between a donor and an accepter Si_{29} and Si_{35} QDs with ideal surface passivation, surface defects, and charges being at the range of 5-15 ns. This is much faster than the photo-luminescence time (~100-1000 ns) in these systems and supports our ideas regarding occupation of trap states via energy transfer channel. Our NA dynamics simulations will provide more details on photodynamics in interacting Si QDs.

We are currently studying charge and energy transfer mechanisms in QDs functionalized by metal-organic dyes. New photovoltaic and photocatalysis applications have been recently proposed based on these hybrid systems. The charge transfer from the photoexcited QD to the dye or backward is the key process in these applications. However, the exact mechanism and ways of controlling the charge transfer in QD-dye composites are still under debates. Our DFT simulations of the morphology, electronic structure, and optical response of chemically functionalized QDs led us to predictions of the thermo-dynamic conditions that govern the direction of charge transfer in these systems [4,5]. Independent on the attachment and the QD type (CdSe, PbSe, or ZnO), all Ru(II)-dyes with neutral ligands, like bipyridines, introduce additional states at the edge of the QD conduction band, governing the direction of electron transfer in these systems [4]. Change in a transition metal of the complex insignificantly affects the alignment of the electronic levels of the dye versus the QD's states. In contrast, negatively charged ligands and less polar solvents significantly destabilize the dye's occupied orbitals shifting them toward the very edge of the valence band, thus, providing favorite conditions for the hole transfer, as illustrated in Figure 1. Compared to the energy offsets of the isolated QD and the dye, QD-dye interactions strongly stabilize dye orbitals with respect to the QD states, while the surface chemistry of the QD has a minor effect on the energy offsets [5]. As such, the energy offsets in the QD/dye composites does not represent a simple difference of the isolated Ru(II) complexes and the QDs, which should be accounted for in experimental studies. Overall, our calculations demonstrate that variations in the dye's ligands, specifically in their charge, are instrumental in adjustments of the electronic structure of QD/dye assemblies [5]. We also closely work with the NDSU experimental group of Prof. W. Sun on studying optical properties of various Ru(II), Ir(III) and Pt(II) complexes with the goal to establish the relationship between photophysics and molecular structure and enabling a systematic design procedure for this important class of optical materials. Our calculations complement experiments by providing insights on characters of optical transitions and their changes upon ligand modification [6-9]. Careful comparison of the experimental and calculated results allows for quantifying the range of applicability of our simulation techniques in predicting both linear and non-linear (two photon absorption) properties of pristine dyes and ligated CdSe QDs [10]. Our close collaboration with experimentalists helps for practical realizations of DFT predictions and finding synthetic conditions for destabilizing the HOMO level of the dye in order to facilitate the hole transfer from the photoexcited QD. In the nearest feature, we plan to apply our NA dynamics techniques to simulate charge transfer process in QDs functionalized by metal-organic dyes and obtain charge transfer rates that can be directly compared to experimental data.

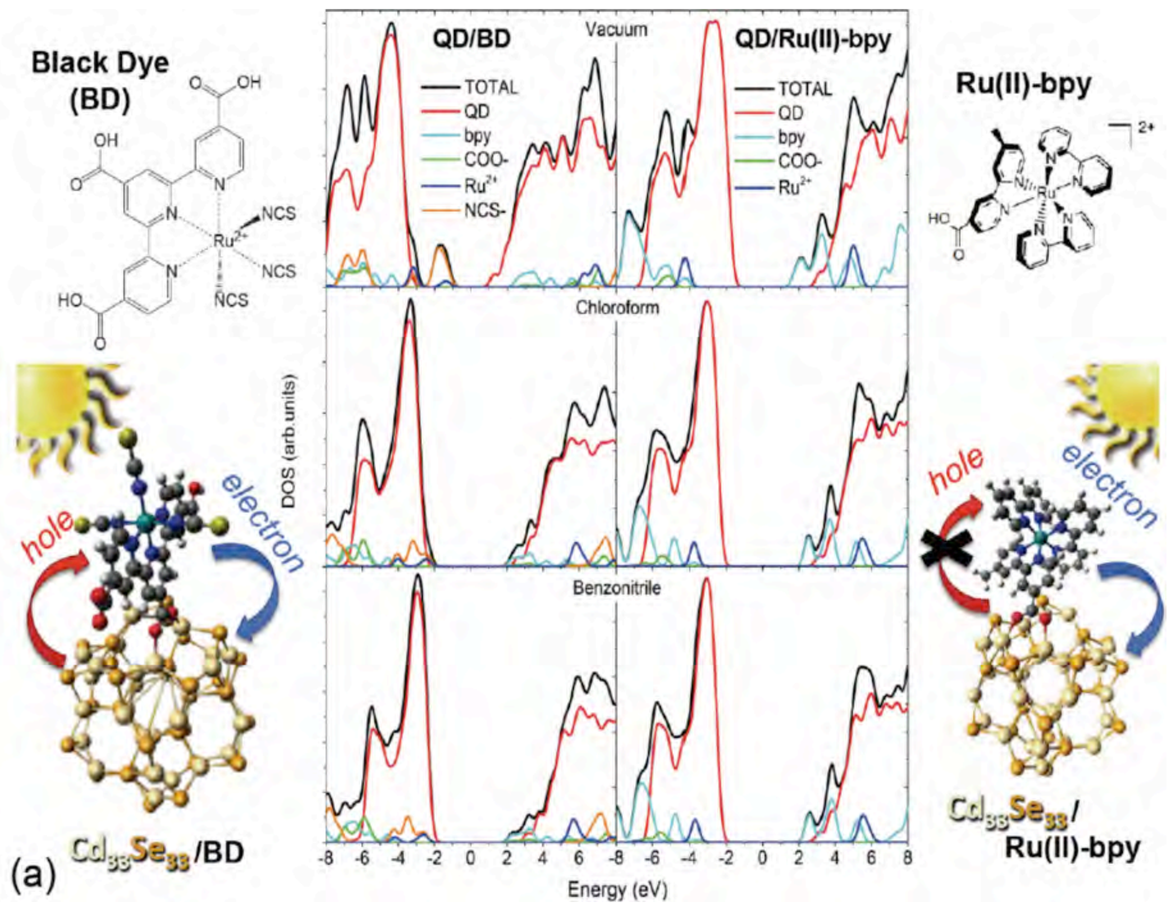

Figure 1: *Calculated projected density of states of the $Cd_{33}Se_{33}$ QD functionalized by the black dye (left) and the Ru(II)-bypiridine (right) dyes. NCS- groups are responsible for alignment of dye's orbitals at the edge of the valence band of the QD providing favorable thermodynamic conditions for the hole transfer from the photoexcited QD to the dye, especially in nonpolar solvents [5].*

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Presentation Title: Excited states with real-time TDDFT: Molecular complexes, doped metal oxides, core excitations and non-Hermitian dynamics

Presenter: Niri Govind (PNNL), niri.govind@pnnl.gov

Project Title: Charge Transfer and Charge Transport in Photoactivated Systems

Investigators: Christopher Cramer (Project Director, University of Minnesota, cramer@unm.edu), Niri Govind (PNNL), Esmond Ng (LBNL), Laura Gagliardi (University of Minnesota), Don Truhlar (University of Minnesota), Ilja Siepmann (University of Minnesota), Wibe A. de Jong (LBNL), Chao Yang (LBNL), Leonid Oliker (LBNL)

Project Scope: A suite of new theoretical methods is being *developed* and *implemented* in the *NWChem* computational chemistry software suite in order to provide *improved* capabilities for excited-state dynamics in the gas phase and to *add* the capability to perform electronically excited-state dynamics in solution. Successful implementation will be transformative for the study of photochemical reactions with levels of accuracy similar to those commonly available for ground-state thermal reactions. Developed methods will have a broad impact as they will be implemented in a robust, widely available, actively supported software environment. The implementation will benefit from the expertise of the *NWChem* development team and infrastructure at the Environmental Molecular Science Laboratory and from dedicated "guinea pig" end users. It will also benefit from the expertise of people at the SciDAC Institute for Frameworks, Algorithms, and Scalable Technologies for Mathematics (FASTMATH) and at the SciDAC Institute for Sustained Performance, Energy, and Resilience (SUPER) who will ensure the robustness of employed algorithms and programming approaches for various hardware architectures. The scope of the overall research effort integrates and spans the missions of BES and ASCR within DOE.

Note: Since this is a very large collaboration involving several investigators, only recent developments relevant to the presentation title will be covered in this abstract. For recent progress and future plans for the entire project, please refer to the complete project report (Please contact: Christopher Cramer or Mark Pederson)

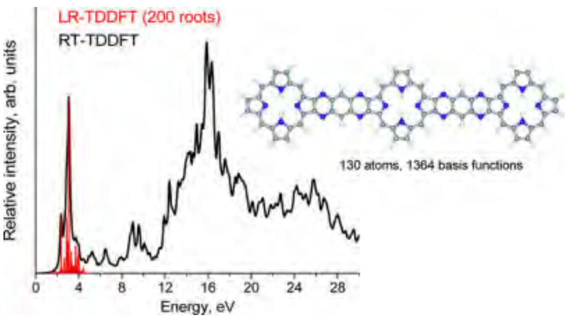
Development and application of real-time (RT) TDDFT in NWChem

Probing electron dynamics in the sub-femtosecond time regime offers unparalleled insight into the underlying mechanisms charge transfer and optical absorption to name a few. As part of the SciDAC project we have optimized our RT-TDDFT implementation and have made it compatible with all exchange-correlation functionals implemented in NWChem including the Minnesota functionals. The functionality has been full integrated in NWChem and was made available to the broader community in NWChem 6.3 with further enhancements released in NWChem 6.5 (the current release).

Comparison of Real-Time and Linear-Response Time-Dependent Density Functional Theories for Molecular Chromophores Ranging from Sparse to High Densities of States

We have assessed the performance of real-time time-dependent density functional theory (RT-TDDFT) for the calculation of absorption spectra of large organic dye molecules relevant to photovoltaics and dye sensitized solar cells with 8 exchange-correlation functionals (3 traditional, 3 global hybrids, and 2 range-separated hybrids). We compared the calculations with traditional linear-response (LR) TDDFT and experimental spectra (the figure at right compares the two as a function of simulation time for the RT variant). In addition, we demonstrated the efficacy of the RT-

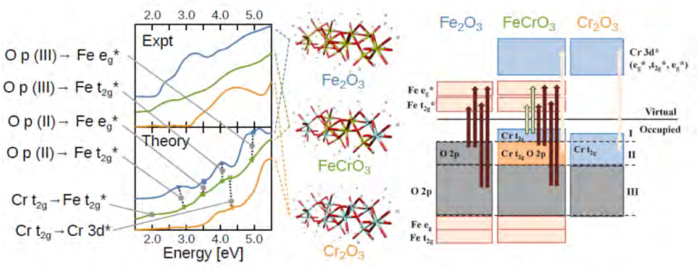
TDDFT approach to calculate wide absorption spectra of two large chromophores relevant to photovoltaics and molecular switches. In general, RT-TDDFT requires longer simulation times compared with LR-TDDFT for absorption spectra of small systems. However, it becomes more effective for the calculation of wide absorption spectra of large molecular complexes and systems with very high densities of states, and our future plans look to couple the real-time character of the model with nuclear dynamics in order to model both the electronic *and* nuclear evolution of excited states in complex (large) systems.



Optical Absorption in α-$(Fe_{1-x}Cr_x)_2O_3$ Solid-Solution Thin Films using LR and RT-TDDFT

Harvesting solar energy for photochemical production of hydrogen and photovoltaics are promising and sustainable ways to tackle the increasing global demand for energy. Materials that have an optical band gap of about 1.3-1.4 eV and are at the same time inexpensive, environmentally friendly, and also have tunable electronic properties are highly desirable. It is expected that the photo-absorption characteristics of α-Fe_2O_3–Cr_2O_3 system can be tuned without dramatically affecting its structural and redox properties. A recent experimental study by Chambers et al. at PNNL reported that the band-gap of $(Fe_{1-x}Cr_x)_2O_3$ mixtures can be reduced to ~1.6 eV, which is smaller than that of both α-Cr_2O_3 (3.4 eV) and α-Fe_2O_3 (2.0 eV) and close to the optimum value for highly efficient solar optical absorption.

We have used both linear-response (LR) and real-time (RT) TDDFT in conjunction with a suitable embedding models to perform the first detailed theoretical analysis of the optical excitations of bulk $(Fe_{1-x}Cr_x)_2O_3$ solid solutions. Excited-state response calculations were performed to assign the optical absorption bands for x = 0.0, 0.5 and 1.0 and photon energies up to 5.5 eV. Consistent with recent experimental data, a band gap reduction of as much as 0.7 eV with respect to that of pure α-Fe_2O_3 was found. Our calculations demonstrate that Fe−Cr mixing gives rise to a new spin-allowed optical transition from Cr t_{2g} to Fe t_{2g}* and Fe e_g*, which in turn results in a lowering of the optical band gap. Thus, forming solid solutions of materials with offset valence and/or conduction band edges is a plausible approach to tuning the optical gap. Finally, we note that our assignment of the low energy part of the α-Cr_2O_3 absorption spectrum differs from that in earlier studies. In particular, the broad shoulder at 3.4 eV was assigned to O 2p → Cr 3d* charge-transfer transitions. In our calculations this part of the spectrum is dominated by Cr t_{2g}→ Cr 3d* excitations, while the O 2p → Cr 3d* transitions appear at excitation energies above 5 eV.



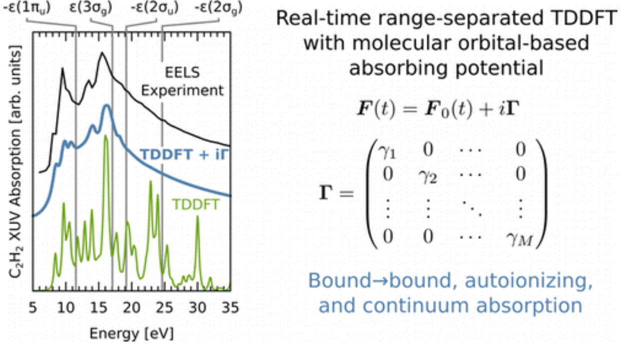
► Optical band gap in $FeCrO_3$ (~ 2 eV): Cr t_{2g} → Fe t_{2g}*

Experimental and calculated real-time TDDFT optical absorption spectra and schematics of the optical transition types. The dark arrows are transitions to the unoccupied Fe T2g* and Eg* states. The light arrows are the transitions to the unoccupied Cr 3d states. The light arrows with dark outlines are transitions from occupied top Cr T2g to unoccupied Fe T2g* and Eg* states. The occupied states are separated as indicated by black dashed lines into three regions: I, II, and III. Note that the widths of regions I and II are not to scale.

In LR-TDDFT calculations of the excited states, due to the close proximity of several electronic states in the valence band, a large number of states are involved in, for example, the optical absorption spectra of $(Fe_{1-x}Cr_x)_2O_3$ solid solutions. This requires the calculation of an extremely large number of roots with Davidson solvers, which is computationally expensive. The RT-TDDFT approach shines in this regard as one can excite the system with a resonant laser pulse or a Gaussian-enveloped pulse that can excite a band of excitations and the approach also allows one to visualize the rich excitation structure in this system. Figure 2 shows the excitation spectra for pure α-Fe_2O_3, pure α-Cr_2O_3 and $(Fe_{1-x}Cr_x)_2O_3$ mixtures as calculated using RT-TDDFT and the respective embedded clusters.

Near and Above Ionization Electronic Excitations with Non-Hermetian RT-TDDFT

Light-induced molecular excitations near and above the ionization threshold are of fundamental importance to a range of processes such as X-ray spectroscopy, the photodamage of biomolecules, superexcited states, and autoionization. Moreover, the mechanisms of, and downstream chemical dynamics resulting from, these types of excitations are now accessible to cutting-edge ultrafast experiments; however, many issues remain. Metastable states are of particular interest, where electronic excitations to above the ionization limit persist for a finite lifetime before autoionizing. Broadly speaking, these autoionizing states can be broken into two classes: shape resonances, where the singly excited state of molecule A is above the energy of an electron-detatched (A+ + e−) state; and Feshbach resonances, where the excited state is below its own continuum but above another ionization threshold.

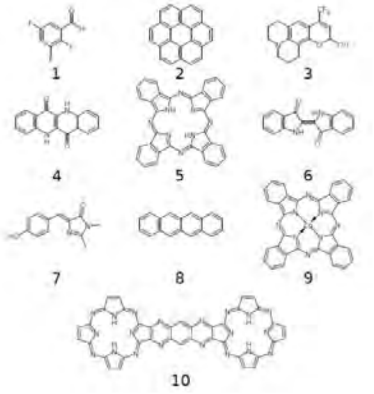


RT-TDDFT computed extreme UV absorption spectrum of gas-phase acetylene with (blue) and without (green) an imaginary potential (iΓ), along with DFT Koopmans' IPs (gray). EELS data are shown in black.

Using TDDFT for these excitations, however, is problematic, because the states are highly diffuse (i.e., Rydberg) or even continuum-like (planewaves), which not only makes significant demands on atom-centered basis sets (e.g., Gaussians, Slaters, etc.) but also brings the validity of the DFT exchange-correlation functional into question. Moreover, since the picture of discrete eigenstates breaks down in the continuum, traditional frequency-domain TDDFT approaches such as Davidson solvers become problematic. In the TDDFT literature, these are often applied in a grid-based representation to describe the wave function distant from the atoms. However, atom-centered functions are often the preferred basis for molecular calculations for efficiency and implementation reasons, and also for processes involving core electrons (e.g., X-ray absorption) where grids and planewaves have difficulty describing the wave function near the nucleus. Finally, from a first-principles dynamics standpoint, a real-time TDDFT approach is a natural starting point.

We have developed an atom-centered basis RT-TDDFT prescription for capturing excitations ranging from low-lying valence to post-ionization (e.g. resonance) states. The approach involves three ingredients: first-principles tuned range-separation to calculate the ionization potentials and high-lying states reliably, a simple phenomenological molecular orbital-based imaginary absorbing potential to mimic coupling to the continuum, and non-Hermitian time propagation of the density matrix. Our approach yields spectra consistent with EELS experiments over a broad range (0-50 eV) for gas phase C_2H_2, H_2O and CF_2Cl_2, including autoionizing resonance states. The crucial role of the imaginary potential is to "filter out" the spurious virtual states, which should lie in the continuum but are artificially bound as a consequence of the finite basis. This not only removes artifacts from the spectral response, but also purifies high-energy bound excitations which would otherwise include significant contributionsfrom these nonphysical states. By constructing the potential directly in the molecular orbital space, no extra computational cost is incurred, with significant savings over a traditional spatial absorbing boundary, which in a finite basis requires numerous extra “ghost” basis functions to properly function. The main drawback to this approach, however, is that one must carefully pick the form of the absorbing potential.

Implementation of analytic linear-response (LR) TDDFT gradients in NWChem



In order to be able to perform optimizations on excited-state surfaces, we have developed a new framework for analytic LR-TDDFT gradients within NWChem. Our parallel implementation is based on the Lagrangian approach of Furche and Ahlrichs. Analytic LR-TDDFT optimizations can be performed for a range of exchange-correlation (XC) functionals (LDA, BP86, PBE, BLYP, B3LYP, PBE0, BHLYP, CAM-B3LYP, LC-PBE, LC-PBE0, BNL, LC-wPBE, LC-wPBEh, LC-BLYP). Both closed and open shell systems can be handled. We have validated our implementation with calculations of the Stokes shifts (excited-state optimizations) for a range of organic dye molecules (see Figure) and vibronic effects (collaboration with Lasse Jensen at PSU) in one-photon absorption (OPA) and resonance Raman scattering (RRS).

This framework has enabled the implementation of the vertical excitation model (VEM) for solvatochromatic studies in collaboration with the groups of Don Truhlar and Chris Cramer (Minnesota). These developments have been released in NWChem 6.5. Future developments will include excited-state and non-adiabatic dynamics capabilities.

Other applications include applications of RT-TDDFT to core-level X-ray spectroscopies where we have compared the real-time approach with linear-response TDDFT core-level near-edge X-ray absorption.

Relevant Publications

1. K. Lopata, N. Govind, “Modeling Fast Electron Dynamics with Real-Time Time-Dependent Density Functional Theory: Application to Small Molecules and Chromophores”, *J. Chem. Theory Comput*, 2011**,** 7 (5), pp 1344-1355
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4. K. Lopata, N. Govind, “Near and Above Ionization Electronic Excitations with Non-Hermitian Real-Time Time-Dependent Density Functional Theory”, *J. Chem. Theory Comput*, 2013**,** 9 (11), pp 4939-4946 DOI: 10.1021/ct400569s
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6. S. Tussupbayev, N. Govind, K. Lopata, C. J. Cramer, “Comparison of Real-Time and Linear-Response Time-Dependent Density Functional Theories for Molecular Chromophores Ranging from Sparse to High Densities of States”, *J. Chem. Theory Comput*, 2015**,** 11 (3), pp 1102-1109
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Capturing Correlated Electron and Ion Dynamics After Photoexcitation

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Department of Physics and Astronomy, Hunter College CUNY

Predictive modeling of solar cell processes requires an accurate treatment of correlated electron dynamics as well as coupled electron-ion motion. Time-dependent density functional theory is a good candidate by which to computationally study electron dynamics after photoexcitation. Although it has had much success in the linear response regime for calculations of excitation spectra and response, its reliability in the fully non-perturbative regime, as relevant for the transfer of charge from one region in space to another, is less clear. By studying some exactly-solvable models of charge-transfer dynamics we find that the exact correlation potential develops stark features in time that are missed by the currently available approximations. We discuss these features and their implications for charge-transfer dynamics and for time-resolved spectroscopy. We then broaden our focus to the description of coupled electron-ion motion. When the coupling to quantum nuclear dynamics is accounted for, we find additional terms in the potential acting on the electronic subsystem, that fully account for electron-nuclear correlation, and that can yield significant differences to the traditional potentials used when computing coupled electron-ion dynamics. We study such potentials for the phenomena of field-induced electron localization, and charge-resonance enhanced ionization, within the exact-factorization approach to coupled electron-ion dynamics.

Award DE- SC0008623
Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

PI: Neepa T. Maitra
Postdocs: Dr. Johanna Fuks (Fall 2013-present), Dr Ali Abedi (Fall 2014), Dr. Elham Khosravi (Fall 2014)
Students: (Kai Luo, Ernesto Sandoval (but neither supported by DOE))

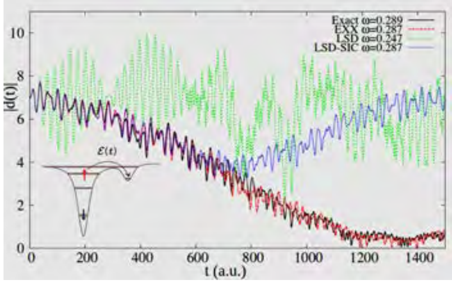
RECENT PROGRESS

The Time-Dependent Exchange-Correlation Potential

On the electronic side, we found new step features in the exact correlation potential that do not appear in calculations of spectra, but appear in simulating non-perturbative dynamics, as in solar cells. A step structure associated with the transfer of charge develops, as well as an oscillatory step with a faster time-scale, both of which require non-adiabatic and spatially non-local density-dependence. Lack of these structures in approximations resulted in their failure to transfer charge in a model system, and likely leads to incomplete transfer in realistic systems, explaining recent results of Nest et al. on small molecules. We derived a decomposition of the potential into a component that depends on the interaction via the exchange-correlation hole, and a component that is kinetic in origin. Although both contribute to the non-adiabatic step, the contribution is often larger in the kinetic term.

We asked whether propagating with the best possible adiabatic approximation, i.e. the exact ground-state functional ("adiabatically-exact") is good enough to model charge transfer. We found that, despite sometimes capturing charge-transfer excitations and ground-state step features in dissociation accurately, adiabatically-exact propagation fails to transfer charge across a model long-range molecule. Full charge-transfer *dynamics* is harder for functionals than calculating charge-transfer energies.

Still, ALDA was shown to predict charge-transfer reasonably well (although not fully) in the light-harvesting carotenoid-porphyrin-C60 triad of Rozzi and co-workers, leading us to investigate when the calculation *begins in a photo-excited state*. If the initial Kohn-Sham state is also chosen excited, no charge-transfer step should appear (although an oscillatory step probably remains), so approximations might perform better. Indeed we found that the simple EXX achieved resonant full transfer on a two-electron model. Other functionals however failed, and understanding this led us to uncover a new exact condition on the functional with general implications for time-resolved spectroscopy. A fundamental property is that when a field driving the system is turned off, the system response frequencies are independent of the time at which the field is turned off. The Kohn-Sham potential typically continues evolving, yielding time-dependent Kohn-Sham frequencies. The exchange-correlation kernel must cancel this time-dependence, yielding an exact condition. The condition is typically violated, but we showed that the success of the EXX mentioned earlier is due to its satisfaction.



Dipole moments under weak resonant driving under the respective resonant frequencies, where the amount of transferred charge is inversely related to the degree of violation of our new exact condition.

Electron-Ion Dynamics via Exact Factorization Approach

In earlier work with collaborators from MPI-Halle, we had derived a new formalism for coupled electron-ion dynamics where the exact molecular wavefunction can be factored into a nuclear wavefunction and an electronic wavefunction conditionally dependent on the nuclear coordinates. The nuclear wavefunction satisfies a Schroedinger equation with a scalar potential, called the time-dependent potential energy surface (TDPES) that contains all the coupling to external fields as well as to the electronic degrees of freedom exactly, and a vector potential containing possible Berry phase effects. In exploring features of this TDPES, we found that quasiclassical propagation of an ensemble of nuclear trajectories on the exact TDPES is accurate in describing branching of a nuclear wavepacket in a model non-adiabatic charge-transfer event in the Shin-Metiu model. This suggests that it is the correct starting point for mixed quantum-classical methods. Further, we related features of the exact surface to aspects of surface-hopping, like velocity renormalization. We also see hints of a force-induced decoherence, but more care is needed to fully analyze this aspect. We then used the exact factorization to define the exact potential acting instead on the electronic system, and compared this to traditional potentials used to study laser-induced electron localization, a technique developed for attosecond control of electrons. Errors in the localization asymmetries predicted by the traditional potential can be explained by features in our exact potential missing in the former. This exact electronic potential also allows for a fully time-dependent analysis of the problem of charge-resonance enhanced ionization, for which only largely quasistatic analyses have been done so far. Of course, finding these exact potentials is impossible for any realistic system, but the insights we are gaining as to the role the different components play will be put to use in developing a mixed quantum-semiclassical propagation scheme that should ameliorate the short-comings current mixed quantum-classical or semiclassical schemes such as Ehrenfest and surface-hopping have.

Publications Acknowledging this Grant in 2011-2014

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John P. Perdew

SCAN: Strongly Constrained and Appropriately Normed Semilocal Density Functional

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Presentation Abstract

The ground-state energy, electron density, and related properties of atoms, molecules, condensed matter, and surfaces can be computed efficiently when the exchange-correlation energy as a functional of the density is approximated semilocally. We propose the first meta-generalized gradient that is fully constrained (obeying all 17 known exact constraints that a meta-GGA can). It is also exact for a set of “appropriate norms” (not only the electron gas and the H atom, but also rare-gas atoms and nonbonded interactions). This nonempirical SCAN meta-GGA can achieve remarkable accuracy when the exact exchange-correlation hole is localized near its electron, and especially for lattice constants and weak interactions. (Supported in part by NSF-DMR 1305135, and to be used in the DOE EFRC Center for the Computational Design of Functional Layered Materials)

Evaluation of Force Field Performance for High-Throughput Screening of Gas Uptake in Metal–Organic Frameworks

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Presentation Abstract

High-throughput computational screening is an increasingly useful approach to identify promising nanoporous materials for gas separation and adsorption applications. The reliability of the screening hinges on the accuracy of the underlying force fields, which is often difficult to access systematically. To probe the accuracy of common force fields and to assess the sensitivity of the screening results to this accuracy, we have computed CO_2 and CH_4 gas adsorption isotherms in 424 metal–organic frameworks using ab initio force fields and evaluated the contribution of electrostatic, van der Waals, and polarization interactions on the predicted gas uptake and the adsorption site probability distributions. While there are significant quantitative differences between gas uptake predicted by standard (generic) force fields (such as UFF) and ab initio force fields, the force fields predict similar ranking of the MOFs, supporting the further use of generic force fields in high-throughput screening studies. However, we also find that isotherm predictions of standard force fields may benefit from significant error cancellation resulting from overestimation of dispersion and neglect of polarization; as such, caution is warranted, as this error cancellation may vary among different classes of materials.

Enabling high-throughput computational screenings of nano-porous materials via transferable, physically-motivated force fields and novel simulation methodologies

Postdocs: Jesse G. McDaniel
Students: Mary Van Vleet, Tingting Weng

RECENT PROGESS

Overview

The objective of this research program is to develop and apply the theoretical framework necessary to generate transferable "physically-motivated" classical force fields for complex systems, with an emphasis on nano-porous materials for gas separation applications. The overarching goal is to develop models which include, by construction, the right balance of all of the relevant "physics" of inter-molecular interactions, with the physical properties of interest emerging as a natural consequence. We make use of symmetry-adapted perturbation theory calculations, exploiting the resultant energy decomposition to parameterize force fields which enforce the right balance of exchange, electrostatics, polarization, and dispersion, thus generating robust and transferable force fields that yield the right answer, for the right reason. We have applied this basic methodology to a variety of complex systems, but with a particular emphasis on the development of transferable force fields for nano-porous metal-organic framework (MOF) materials. We have extended the approach outlined above to generate physically-motivated force fields for adsorbate-MOF interactions and a comprehensive "library" of functional group and metal parameters that covers a sizable fraction of all known (or potentially synthesizable) MOFs.

More recently, emphasizing the generality of this approach, we showed that the methodology can also generate accurate and transferable models for a wide range of systems ranging from gases, to bulk organics, to strongly interacting ionic liquids.

Evaluate of force fields for high-throughput screening

A significant output of our work over the past several years is a "library" of accurate and transferable force field parameters for MOFs, which can be utilized to screen MOFs for their gas adsorption and separation properties using computational approaches. Recently, in collaboration with Randy Snurr (Northwestern), we examined the sensitivity of such high-throughput screenings with respect to the quality of the force field, contrasting our force fields with simpler "standard" models (which have not been optimized for MOFs). Interestingly, we find that although quantitative results may differ substantially (by 100+%!), the *correlation* between predictions accurate and "standard" models is strong, thus suggesting that *pre-screening* with efficient standard force fields is a feasible strategy.

Force fields of ionic liquids

Significantly, we also established the generality of our force field development methodology well beyond MOFs. In collaboration with Arun Yethiraj (Wisconsin), we showed that, by including appropriate three-body dispersion interactions, our "physically motivated" methodology yields accurate results even for bulk liquids even in absence of empirical refinement. We also showed that we can even extend the approach to strongly interacting ionic liquids (ILs). Here, we developed, for the first time, an entirely first-principles based model for the prototypical [BMIM][BF_4] system which yields essentially quantitative accuracy with a wide range of physical properties. We are now extending this work for a wide variety of popular ionic liquids, for applications to separations and beyond.

Anisotropy and charge penetration

In collaboration with Anthony Stone and Alston Misquitta (Cambridge), we are working on simple methodologies to further increase the accuracy and transferability of our approach (while maintaining simplicity), by introducing targeted treatments of atomic anisotropy and charge penetration. These effects are important particularly for hydrogen bonding species, or atoms containing "lone pairs".

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Accurate Excited States via Symmetry Projection Approaches

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Overall research goals: The methodological development and computational implementation of symmetry breaking and restoration methods for the accurate calculation of electronic structure, ground and excited states, and properties of molecules and solids.

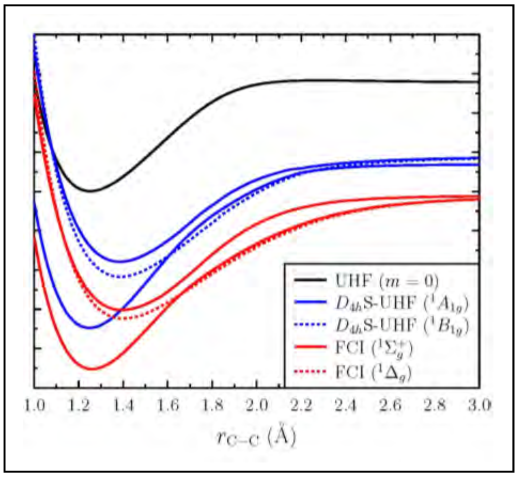
Recent Progress:

Highlights include the following theoretical, computational, and applications oriented projects:

- The calculation of excited states for the one-dimensional Hubbard model with different quantum numbers (spin, space group), which can be compared to exact results (Paper 1).
- The calculation of singlet-triplet energy splittings with projected Hartree-Fock on challenging cases (Paper 5).
- The development of a multi-component symmetry projected approach (Paper 6).
- The evaluation of excited states on an extremely difficult proof-of-principle system like C_2 (Paper 7) ---see Figure below.
- A stability study of using PHF methods (Paper 8).
- Studies on the 2D Hubbard model using PHF (Papers 10 and 15).
- Analytic energy gradients for PHF (Paper 11).

Future Plans:

For the rest of the duration of this grant ending in 2015, we will continue examining the accuracy of symmetry breaking and restoration techniques, now well developed in our group, for problems of interest to the overall community, including energy related processes, on both ground and excited states.



Excited states of the C_2 molecule: this plot compares energies obtained from symmetry broken and restored wave functions with exact FCI results. Point group (***D_{4h}***) and spin (S-UHF) projections are carried out on the singlet ground state and first singlet excited state. While the projection methods (**blue**) are far from being quantitatively correct, they qualitatively reproduce the exact results (**red**), and they do so at mean-field computational cost, providing substantial savings over the combinatorial FCI cost.

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COMPUTATIONAL AND THEORETICAL CHEMISTRY PROGRAM

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The construction of quasi-diabatic representations of adiabatic potential energy surfaces coupled by conical intersections, for both bound (used in our treatments of nonadiabatic photoelectron spectroscopy) and dissociative systems (used to treat nonadiabatic photodissociation and nonadiabatic chemical reactions) is a key aspect of our research effort. The focus of this abstract is our work on global, full dimensional representations of adiabatic potential energy surfaces (PESs) coupled by conical intersections using quasi diabatic Hamilonians, $\mathbf{H}^d$.

Representing Adiabatic Potential Energy Surfaces coupled by conical intersections

As part of other funded research,[1] we developed new algorithms to construct coupled diabatic states representations of global adiabatic PESs coupled by conical intersections. The method is a generalization of the approach we originally developed to treat the coupled bound states encountered in nonadiabatic photoelectron spectroscopy. The resulting quasi diabatic representations of coupled adiabatic PESs will enable accurate dynamics studies, avoiding the accuracy limitations inherent in the dynamics on the fly approach usually used. The following aspects of our approach are key:

(i) The representation is based on electronic structure data, energies, energy gradients and derivative couplings. Currently these data are obtained from multireference configuration interaction single and double excitation (MRCISD) wave functions. The use of MRCISD wave functions is not essential but is convenient given that energy gradients and derivative couplings are readily obtained using analytic gradient techniques.

(ii) The incorporation of energy gradient data dramatically reduces the number of geometries at which data is required enabling the treatment of molecules with ~ 10-15 atoms.

(iii) the use of derivative coupling data allows us to construct demonstrably quasi-daibatic representations and provides for an accurate representation of the neighborhood of a conical intersection seam. $\mathbf{H}^d$ can describe seams of conical intersections of two or three states.

(iv) The electronic structure data are calculated at points determined by quasi classical surface hopping trajectories (QCT) obtained using Truhlar's ANT program. This allows us to construct global representations by which we mean the electronic structure is well reproduced in all regions sampled by the nuclear dynamics.

(v) We use Nuclear Permutation Inversion symmetry rather than point group symmetry. This facilitates incorporation of proper permutational symmetry in the evaluation of off-diagonal matrix elements in the quasi-diabatic Hamiltonian.

(vi) $\mathbf{H}^d$ can smooth the irregularities in the electronic energies attributable to the orbital changes in the active space that are inherent to nonadiabatic processes.

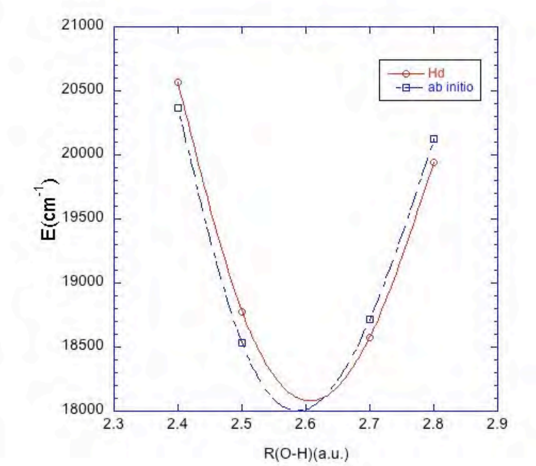
WORK COMPLETED.

The projects discussed in this report were made possible by a generous grant of computer time from NERSC.

A Multichannel PESs coupled by conical intersections: The photodissociation $CH_2OH(X) + h\nu \rightarrow CH_2OH^* \rightarrow CH_2O(X)+H$, CHOH(X) [cis/trans] +H

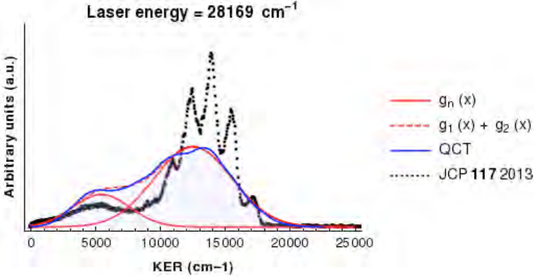
We have completed, and submitted for publication[2] an initial full 9 dimensional, 3 quasi diabatic state, representation of D_0 and D_1 the two lowest coupled adiabatic PESs that describe photodissociation CH_2OH through the D_1 state and have used those results to analyze photodissociation studied in the group of Reisler (USC)[3]. We are currently finishing a more complete/accurate representation of three states D_0, D_1 and D_2 for CH_2OH using a more elaborate functional form. The description is based on an MRCISD expansion of ~67 million configuration state functions (CSFs) which is capable of describing all channels in the above captioned reaction.

When representing nonadiabatic processes it is important to get an accurate representation of the seam of conical intersections and its local topography. The figure below addresses this issue



reporting four points on the 1^2A- 2^2A seam of conical intersection in the CH_2O-H dissociation channel. For each point R(O-H) is fixed at the indicated value and the remainder of the internal coorindates optimized to minimize the crossing energy. The optimization is performed separately for the *ab initio* and $\mathbf{H}^d$ representations. *None* of these *ab initio* points were included in the data used to build $\mathbf{H}^d$. Only the minimum energy crossing (at R(O-H) ~ 2.6 a_0) was so included in this region The agreement between the $\mathbf{H}^d$ and *ab initio* determined energies is seen to be excellent. Similarly good agreement is found for the **g** and **h** vectors. These results strongly support the ability of our representation to accurately describe the vicinity and locus of a conical intersection seam.

In the figure below classical trajectory surface hopping techniques based on $\mathbf{H}^d$ were used to simulate kinetic energy release (KER) spectra reported by Reisler,[3] .



in which CH_2O + H is produced. Note that this figure is based on 10 thousand trajectories which would not be possible using direct dynamics. The issue here is the origin of bimodal character clearly evident in the experimental spectrum (dashed black line). The simulated spectrum, solid blue line, is bimodal, being well described as the sum (dashed red line) of two gaussians g_1 and g_2, the solid red lines. An analysis of the trajectories shows that the slow hydrogens are produced in an indirect or quasi-statistical manner, with a hop to D_0 preceding a significant residence on D_0 prior to H dissociation. On the other hand, the fast hydrogens are produced by trajectories that, while they may oscillate on D_1 prior to a surface hop, following transfer to D_0 the H dissociates directly.

Work in Progress/Future Work

We are continuing our work on the multichannel, multistate photodissociation of hydroxymethyl. It is known from experiments and confirmed by our simulations that even at energies well above the threshold for producing HCOH[*cis, trans*] when only D_1 is excited essentially no HCOH is produced. The situation changes dramatically when D_2 is excited, with significant amounts of hydroxymethylene produced. In this case both $D_2 - D_1$ and $D_1 - D_0$ seams of conical intersctions are expected to accessed. The completion of the enhanced three state global quasi diabatic representation of the $1,2,3^2A$ states of hydroxymethyl noted above will enable both KER simulations and mechanistic inferences. In particular the determination of contributions of the energetically accessible conical intersection seams will provide valuable sights into the mechanisms of nonadiabatic processes.

A. Representing PESs coupled by conical intersections for significantly larger molecules: $C_6H_5OH(\tilde{X})$ + hv → $C_6H_5OH(\tilde{A})$ → $C_6H_5O(\tilde{X}, \tilde{A})$+ H

The photodissociation of phenol, $C_6H_5OH(\tilde{X}^1A')$+hv → $C_6H_5OH^*$ → $C_6H_5O(\tilde{X}^2B_1,\tilde{A}^2B_2)$ + H is a problem of considerable current interest. At the time of preparing this report a four coupled diabatic state representation of the S_0, S_1, S_2, states of phenol capable of describing the above noted photodissociation processes is (almost) complete! A*b initio* electronic structure data for the 1,2,3,4^{1}A states was obtained exclusively from an MRCISD expansion comprised of over 100 million CSFs! Electronic structure data at ~4700 nuclear configurations was required to construct the $\mathbf{H}^d$.

This representation of a three electronic state photodissocation process in a molecule with 33 degrees of freedom based on accurate MRCISD wave functions is unique and will provide unprecedented opportunities for studying nonadiabatic photodissociation.

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