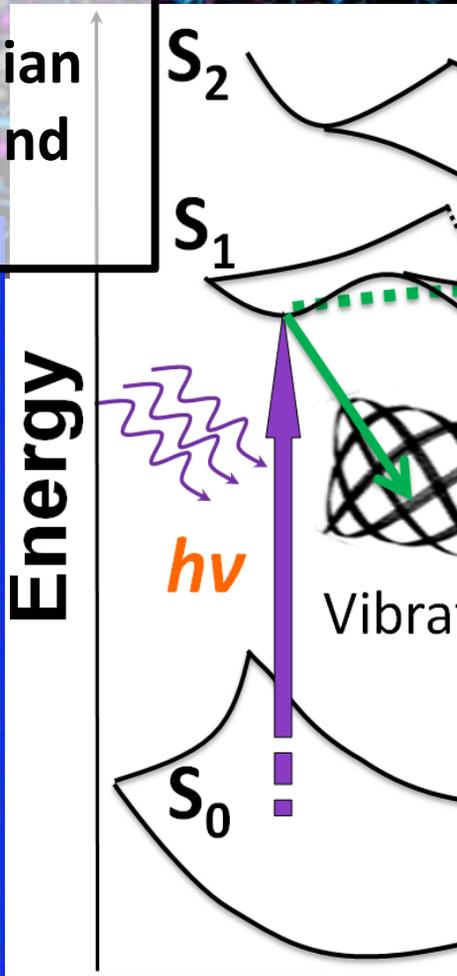
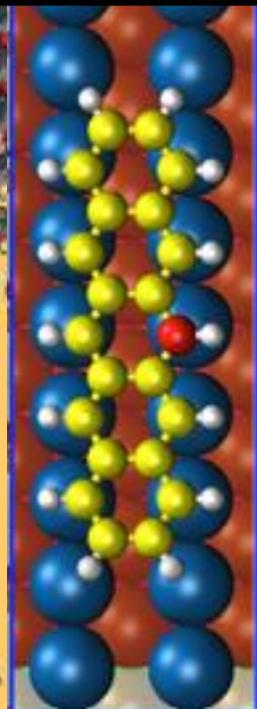
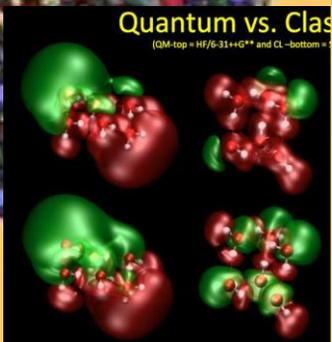
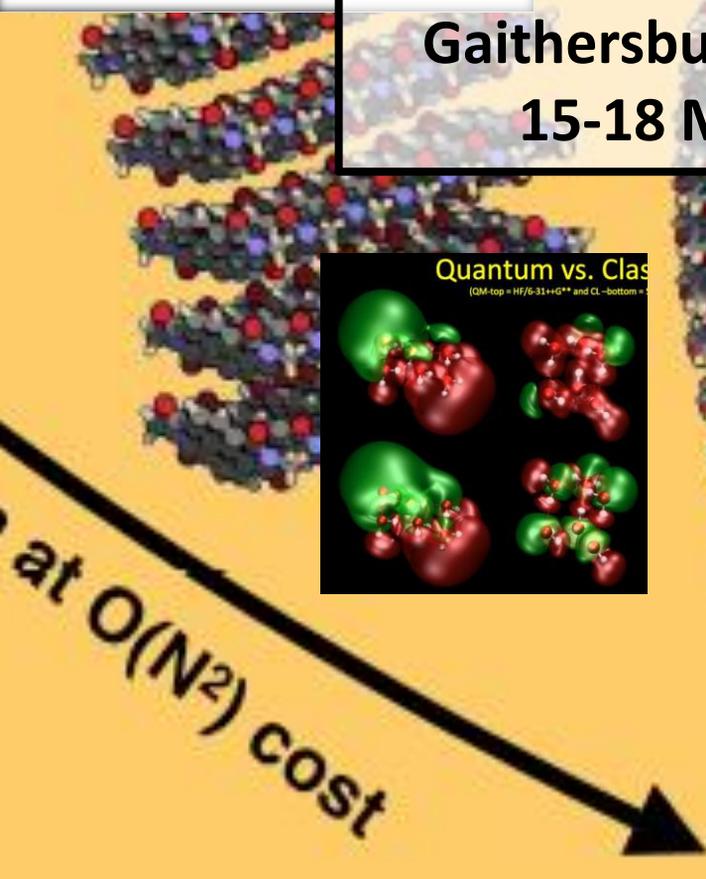
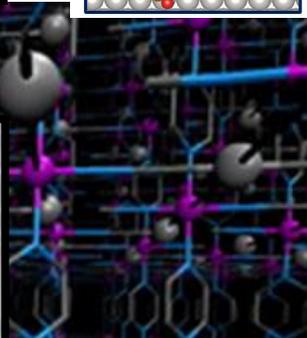


**Computational and
Theoretical Chemistry PI
Meeting**
**Marriott Washingtonian
Gaithersburg Maryland**
15-18 May 2016



FORWARD

This abstract booklet provides a record of the U.S. Department of Energy second 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, and SciDAC efforts.

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.

In recognition of the 30th anniversary of the Car-Parrinello method, the agenda starts with an invited talk by Professor Roberto Car who will describe SciDAC-supported successes associated with *ab initio* molecular dynamical simulations for applications to water.

Also featured is a briefing by Professor Theresa Windus on a recent community-generated report on challenges associated with transitioning to the exa-scale computing era. In addition to many talks, there will be a poster session on Monday evening. 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 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 from the Fundamental Interactions Team!

Mark Pederson, Gregory Fiechtner, Wade Sisk, and Jeff Krause

15-May 2016

SHORT AGENDA 2016 CTC PI Meeting

For more information and registration: <http://www.orau.gov/ctc2016/>

Abstract Booklet available at:

<http://science.energy.gov/bes/csgb/principal-investigators-meetings/>

15 May 3:00-6:00 PM	Registration	
15 May 7:30PM	Dinners at nearby restaurants	
16 May 7:00	Breakfast	
16 May 8:00	Welcome	Mark Pederson
	CHAIR: Thanos Panagiotopoulos	
16 May 8:15	Water: A case study in Ab Initio Simulations	Roberto Car
16 May 9:00	Liquids, Electrolytes and Polarization	Shawn Kathmann, Christine Isborn, Margaret Cheung
16 May 10:00	Coffee	
	CHAIR: So Hirata	
16 May 10:30	New Techniques in Electronic Structure	Dominika Zgid, Francesco Evangelista, Filipp Furche
16 May 12:00	Working Lunch	
	CHAIR: Jianwei Sun	
16 May 13:30	Beyond Density Functional Theory	Adrienn Ruzsinszky, Neepa Maitra, Lin Lin
16 May 15:00	Coffee	
	CHAIR: Chris Cramer	
16 May 15:30	Challenges for the Exascale Era	Theresa Windus
	CHAIR: Eric Neuscamman	
16 May 16:15	QMC	Richard Dawes, Shiwei Zhang
16 May 17:15	CHAIR: Sapna Sarupria and John Pask	90 second poster introductions
16 May 18:10	DINNER AT MEETING HOTEL	
16 May 20:00-22:00	<p style="text-align: center;">POSTER SESSION Chaired by Sapna Sarupria and John Pask</p> <p style="text-align: center;">Your poster may be 4ft wide [horizontal] by 4ft tall [vertical]. Push pins will be available. You may ship your poster may be sent directly to:</p> <p style="text-align: center;">CTC PI MEETING Gaithersburg Marriott Washingtonian Center 9751 Washingtonian Boulevard Gaithersburg, MD 20878-5359</p>	Margaret Cheung [12], Barry Dunietz[15], Chris Cramer[3], Marivi Fernandez-Serra[8], Laura Gagliardi[17], Koblar Jackson[13], Tom Henderson[9], Anna Krylov[7], Tom Miller[6], Eric Neuscamman[18], Anders Niklasson[10], John Pask[16], Sapna Sarupria[4], Greg Schenter[5], Kevin Shuford[1], Ilja Siepmann[2], Sotiris Xantheas[20], David Yarkony[11], Kuang Yu [19], Rajendra Zope[14]
17 May 7:00	Breakfast	

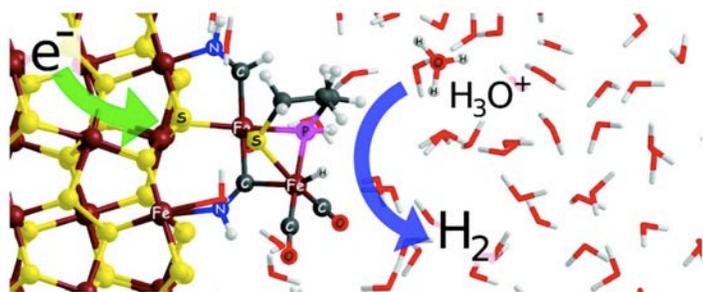
CHAIR: James Evans		
17 May 8:30	Reactions on Surfaces	Jeff Greeley, Abdelkader Kara, Christine Aikens
10AM	Coffee	
CHAIR: Ilja Siepmann		
17 May 10:30	Field Driven Interactions with Matter	Serdar Ogut, James Lewis
17 May Noon	Lunch	
CHAIR: Henry Schaefer		
17 May 1:30	Computational Chemistry	Steven Klippenstein, Piotr Piecuch, Toru Shiozaki
17 May 3:00	Coffee	
CHAIR: Laura Gagliardi		
17 May 3:30	Porous Frameworks	Jordan Schmidt, Karl Johnson, Francesco Paesani
17 May Evening	DINNER OUT ON YOUR OWN	
CHAIR: Anna Krylov		
18 May 7:00	Continental Breakfast	
18 May 8:30	Spin, Spin-Orbit, and Magnetism in Molecular Systems	Xiaosong Li, Juan Peralta, Shiv Khanna
18 May 10:00	Coffee	
CHAIR: George Schatz		
18 May 10:30	Excitonics and Charge Transfer	Michael Galperin, John Herbert, Alan Aspuru-Guzik
18 May noon	Closing Remarks	Mark Pederson

Water: a case study in ab-initio simulations

Roberto Car,

Princeton University, Princeton, New Jersey 08544, USA

The unusual properties of water, including the thermodynamic anomalies of the liquid, the existence of distinct amorphous ice forms, and the abnormal mobilities of the water ions, derive from the tetrahedral network of hydrogen bonds that hold the molecules together in condensed phase. This network of bonds facilitates chemical reactions in solution as exemplified in the graphics below illustrating the special role that water plays in chemistry.



Water mediated proton transfer plays a key role in the formation of molecular hydrogen resulting from the recombination of electrons from the catalyst and protons dissolved in water. (F. Zipoli et al. *J. Am. Chem. Soc.* **132**, 8593 (2010))

Ab-initio molecular dynamics simulations highlight the interplay of molecular dynamics and electronic structure and can provide, in principle, a unified picture of all these phenomena. However, severe difficulties have challenged the achievement of this goal and the predictive power of the approach when applied to water. These difficulties include limitations of density functional theory approximations, importance of quantum effects in the nuclear dynamics, as well as sampling limitations and computational cost. In this talk I will review recent progress to overcome these limitations and discuss future directions in this research. Connections of theory, simulation, and experiment will be stressed.

Grant No. DE-SC0008626 "Advanced modeling of ions in solutions, on surfaces, and in biological environments"

Publications acknowledging this grant in the last 4 years:

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2. W. Hu, L. Lin, C. Yang, J. Dai, J. Yang: Edge-modified phosphorene nanoflake heterojunctions as highly efficient solar cells, *Nano Lett.* **16**, 1675 (2016)
3. J. Sun, B.K. Clark, S. Torquato, R. Car: The phase diagram of high-pressure superionic ice, *Nature Comm.* **6**, 8156 (2015)
4. B. Santra, R. A. DiStasio, F. Martelli, and R. Car: Local structure analysis in ab-initio liquid water, *Mol. Phys.* **113**, 2829 (2015)

5. N. Ferri, R. A. DiStasio Jr., A. Ambrosetti, R. Car, and A. Tkatchenko: Electronic properties of molecules and surfaces with a self-consistent interatomic van der Waals density functional, *Phys. Rev. Lett.* **114**, 176802 (2015)
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8. R. A. DiStasio, Jr., B. Santra, Z. Li, X. Wu, and R. Car: The individual and collective effects of exact exchange and dispersion interactions on the ab-initio structure of liquid water, *J. Chem. Phys.* **141**, 084502 (2014)
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12. J. C. Palmer, R. Car, P. G. Debenedetti: The liquid-liquid transition in supercooled ST2 water: a comparison between umbrella sampling and well-tempered metadynamics, *Faraday Discuss.* **167**, 77 (2013)
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14. B. Santra, J. Klimes, A. Tkatchenko, D. Alfe, B. Slater, A. Michaelides, R. Car, M. Scheffler: On the accuracy of van der Waals inclusive density-functional theory exchange-correlation functionals for ice at ambient and high pressure, *J. Chem. Phys.* **139**, 154702 (2013)
15. C. Swartz and X. Wu: Ab initio studies of ionization potentials of hydrated hydroxide and hydronium, *Phys. Rev. Lett.* **111**, 087801 (2013)
16. A. Bankura, V. Carnevale, M. L. Klein: Hydration structure of salt solutions from ab-initio molecular dynamics, *J. Chem. Phys.* **138**, 014501 (2013)
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Nucleation Chemical Physics

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Program Scope

The objective of this work is to develop an understanding of the chemical physics governing nucleation. The thermodynamics and kinetics of the embryos of the nucleating phase are important because they have a strong dependence on size, shape and composition and differ significantly from bulk or isolated molecules. The technological need in these areas is to control chemical transformations to produce specific atomic or molecular products without generating undesired byproducts, or nanoparticles with specific properties. Computing reaction barriers and understanding condensed phase mechanisms is much more complicated than those in the gas phase because the reactants are surrounded by solvent molecules and the configurations, energy flow, quantum and classical responses to internal and external electric fields and voltages, and ground and excited state electronic structure of the entire statistical assembly must be considered.

Recent Progress and Future Directions

Charge and Field Fluctuations in Aqueous NaCl

The observations of luminescence during crystallization as well as electric field induced crystallization suggest that the process of crystallization may not be purely classical but also involves an essential electronic structure component. Strong electric field fluctuations may play an important role in this process by providing the necessary driving force for the observed electronic structure changes.

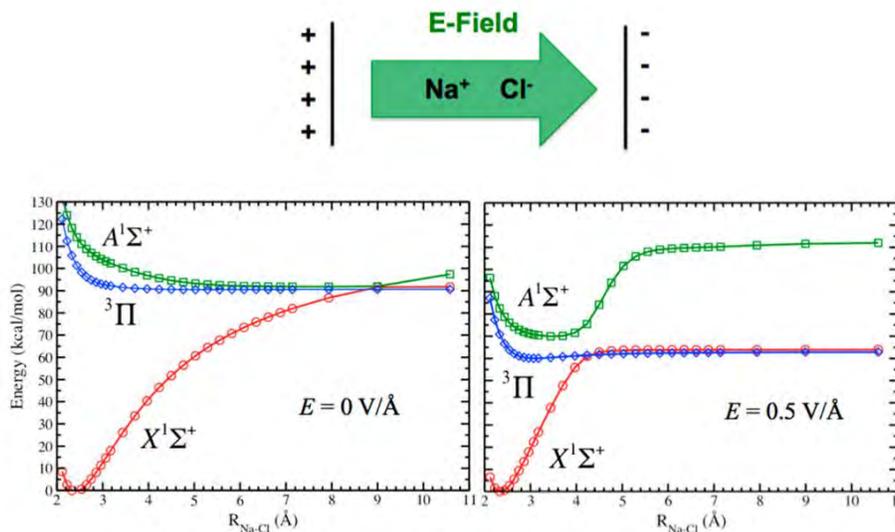


Figure 1. Potential energy curves for the NaCl dimer in vacuum without (left-diabats) and with (right-adiabats) an external electric field of 0.5 V/Å pointing from Na⁺ toward Cl⁻ (top). The influence of the electric field moves the zero field avoided crossing from 9 to 4 Å, and the first excited singlet and triplet states become stabilized by about 30 kcal/mol relative to the ground singlet state minimum.

Here we provide an initial benchmark analysis to understand the influence of electric fields on ground and excited electronic states of the NaCl dimer (see Figure 1). Our high-level electronic structure calculations using MOLPRO (MRCI/aug-cc-pvtz) on the NaCl dimer show that an electric field of 0.5 V/\AA can dramatically alter the electronic states available to the system. As a consistency check we computed the ensemble averaged classical electric field distributions inside aqueous electrolytes and discovered that the fields on the Na^+ and Cl^- ions are extremely large ($\sim 1 \text{ V/\AA}$) and thus may alter the ground and excited electronic states in the condensed phase. The importance of electric field fluctuations driving electron transfer has been a topic of intense research since the seminal work of Marcus. The main objective of this work is to provide basic understanding of the fluctuations in charge, electric potentials, and electric fields, both classically and quantum mechanically, for concentrated aqueous NaCl electrolytes. For example, using various isomers of $(\text{H}_2\text{O})_6$ as a prototypical system, one can readily see the differences between quantum and classical voltage distributions shown in Figure 2. Our published calculations and analyses provide the first steps toward understanding the magnitude and fluctuations of charge, classical point charge sources of electric potentials and fields in aqueous electrolytes and what role these fields may play in driving charge redistribution/transfer during crystallization as well as inducing crystal formation itself.

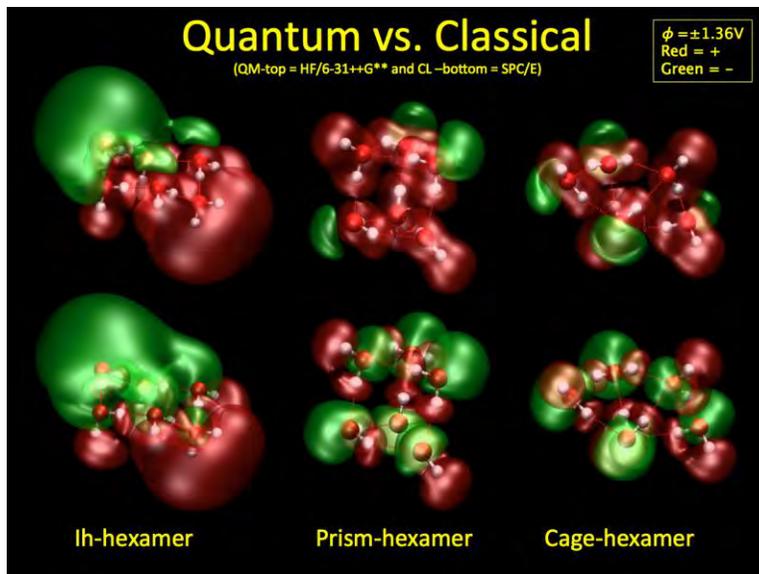


Figure 2. Quantum (top) versus classical (bottom) voltage isosurfaces (ϕ) for the Ih, prism, and cage isomers of the water hexamer, where the red and green isosurfaces are at $+1.36\text{V}$ and -1.36V , respectively. The nuclear configurations are exactly the same for consistency. The quantum voltages are from HF/6-31++G** level of theory and basis set and the classical voltages are due to the SPC/E point charges.

Quantum Voltages and Valence Electrons

Voltages and fields inside matter are relevant to crystallization, materials science, biology, catalysis, and aqueous chemistry. The variation of voltages in matter can be measured by electron holography. Complimentary, using modern supercomputers and a sufficiently accurate level of theory allow the prediction of quantum voltages with spatial resolutions of bulk systems well beyond what can be currently measured. Of particular interest is Bethe's Mean Inner Potential (V_0) – the spatial average of these quantum voltages referenced to the vacuum. We have established a protocol to reliably evaluate V_0 from quantum calculations. Voltages are very sensitive to the distribution of electrons and provide metrics to understand interactions in condensed phases (see Fig. 3). We find excellent agreement with measurements of V_0 for vitrified water (expt = $+3.5 \pm 1.2\text{V}$, theory = $+3.8 \pm 0.2\text{V}$) and salt crystals (expt = $+8.3 \pm 1.3\text{V}$, theory = $+7.9 \pm 0.2\text{V}$). The changes in V_0 upon bond formation in a H_2O molecule reveal a far-field picture where an increase in electron density results in a decrease in voltage due to better screening of the

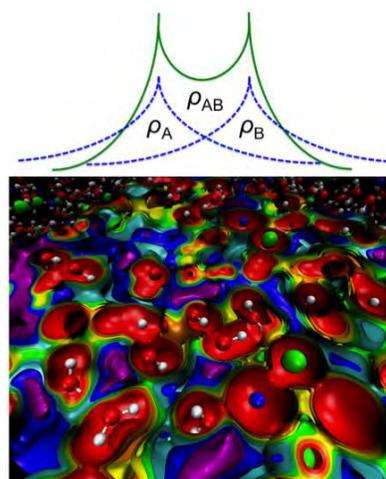


Figure 3. As atoms and molecules come together to form liquids and solids their electrons redistribute and this is reflected in the voltage distributions.

nuclear cores. We found that, in contrast to the positive definite voltages of isolated atoms, once the electrons are allowed to transfer and redistribute to form bonds, lone pairs of electrons, and ions such that about 40% of the total volume of the bulk electrolyte contains negative voltages.

Vibrational Spectroscopy and Electric Fields

Molecular vibrational modes are an effective measure of electric fields and the fluctuations of the surrounding structure. The influence of electric fields on the vibrational response of molecules has a long history and is relevant to many chemical processes in condensed phases and their interfaces. The central concept is the use of a particular vibrational mode as a kind of antenna or probe capable of sensing the *effective* electric field fluctuations due to its surrounding environment. Early work in this area employed continuum descriptions of electrostatics while more recent work utilized electric fields arising from classical point charges. Here we report on recent work where we collaborated in a joint experimental-theoretical study to understand the influence of electric fields on the vibrational response of molecules in the $\text{Cs}^+(\text{H}_2\text{O})_6 = \text{CsW6}$ cluster. This work stands as distinct from previous studies in that we are approaching the electric field coupling to vibrational shifts from an *ab initio* perspective yielding more “exact” electric field strengths in the absolute sense as there is much uncertainty in these fields from continuum, point charges, or polarizable sources. Specifically, the electric fields on the Hydrogen atom sites are calculated as those arising from the quantum mechanical charge densities of all the other atoms in the system excluding only those atoms with the water molecule for which the field is being evaluated. These electric fields are then projected onto the OH bond vectors corresponding to each vibrational antenna. It is in this sense that these fields must be considered as *effective* electric fields arising from the surrounding atoms as this construction formally neglects the electric fields arising from the atoms within the molecule for which the field is being probed as well as the response of the surrounding environment to this probe’s charge distribution.

Using this approach we are able to make spectral assignments as presented in Figure 2, noting that the electric field-to-frequency mapping spectrum (blue curve), using a frequency map that is quadratic in the projected field strength, provides a description of the experimental vibrational spectra (red curve). It is important to note that the electric fields are very sensitive to the bonding structural patterns and hence provide good order parameters for specific cluster configurations. Our projected electric field analysis recovers the anharmonic vibrational shifts in excellent agreement with experiment and provides compelling evidence of the utility of *ab initio* field vibrational and structural order parameters.

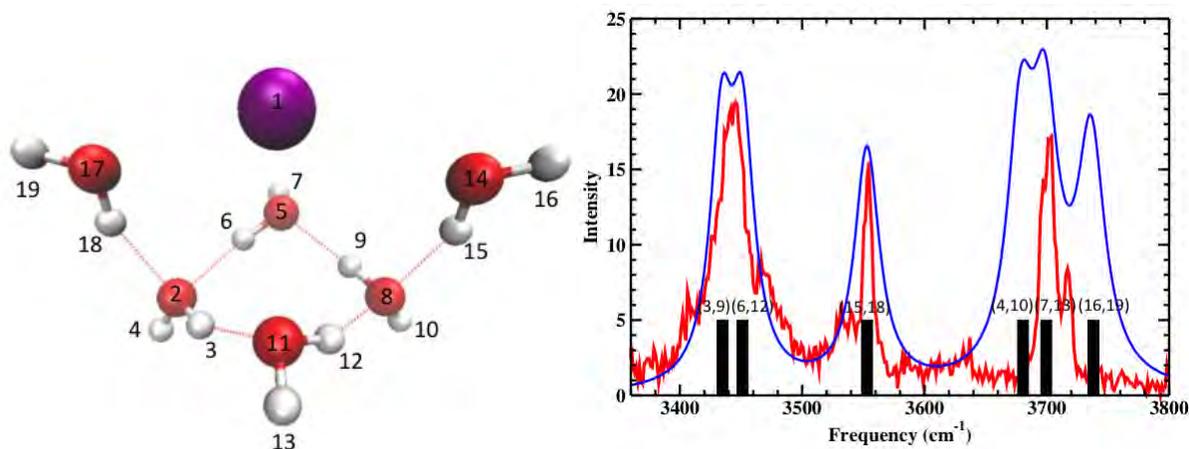


Figure 4. (Left) Structure of CsW6. (Right) Experimental IR spectra (red) and the quadratic field-to-frequency mapping (blue) for the CsW6 cluster. The black sticks denote the 6 doublet electric fields corresponding to the Hydrogen atom indices shown on the left.

Direct PNNL collaborators on this project include M. Valiev, G.K. Schenter, C.J. Mundy, X. Wang, J.

Fulton, L. Dang, and M. Baer and Postdoctoral Fellow Bernhard Sellner. Outside collaborations with the University College London include Stephen Cox and Angelos Michaelides on heterogeneous ice nucleation (Chemistry), Jake Stinson and Ian Ford on sulfuric acid-water nucleation as well as Mark Johnson at Yale on connections between electric fields and vibrational spectroscopy have been mutually beneficial.

Acknowledgement: This research was performed in part using the DOE NERSC facility. Battelle operates PNNL for DOE.

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- Communication** – H. Wen, G.L. Hou, S.M. Kathmann, M. Valiev, and X.B. Wang, “Solute anisotropy effects in hydrated anion and neutral clusters”, *Journal of Chemical Physics*, **138**, 031101 (2013).
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DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION

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The development of next generation energy conversion and catalytic systems requires a fundamental understanding of the interplay between photo-excitation and the resulting proton and electron transfer processes that occur in solution. To address these challenges requires accurate and efficient methods to compute ground and excited states, as well as the ability to treat the dynamics of electrons, protons, and electronic energy transfer in the presence of solvent fluctuations occurring over a range of time-scales. This work will develop accurate and efficient theoretical models for solution phase reactions. These developments will be used to create a highly scalable computational approach that allows for the accurate computation of electronic ground and excited states, and treats the dynamics of electrons and protons in the presence of solvent. These techniques will provide an improved understanding of photo-initiated excitations, electron transfer, and proton coupled electron transfer processes, and will also elucidate the key role that hydrogen bonding plays in tuning the energetics, selectivity, and rate of electron, proton, and energy transfer in solution.

In the past half year while funded by this grant, our team has made progress in understanding errors in modeling charge transfer via electron dynamics,¹ applying our newly introduced generalized quantum master equation approach to charge transfer in atomistic systems,² speeding up ab initio molecular dynamics with nuclear quantum effects (NQE) via ring polymer contraction,³ determining an accurate density functional theory method for ionization in solution,⁴ and developing network theory for creating a general approach for understanding the structural and dynamic properties of liquids and solutions.⁵ These advances in modeling and understanding solution phase reactivity can be broadly divided into three areas that we address in more detail below: electronic structure, dynamics, and analysis.

We investigated the effects of system size on the accuracy of density-functional ionization potentials and found that as the system size increases, delocalization error due to lack of exact exchange introduces a systematic underestimation of the ionization potential (IP). The problem with the electron density and the resulting underestimation of the IP is clearly seen when considering a series of isolated molecules (Figure 1). We find that including explicit solvent in the calculation can exacerbate the size-dependent delocalization error by extending the size of the quantum mechanical region. Difference densities show that instead of the electron being removed from a single solute molecule, DFT with local exchange (BLYP) removes some electron density from many molecules; using exact nonlocal exchange (M06-HF) fixes the error. The amount of exact exchange needed to make the computed IP size intensive agrees with optimally tuning long-range corrected hybrid functionals. However, this is not the case when using a polarizable continuum model, which tends to over-polarize the electron density, and also leads to a very small optimal tuning value.

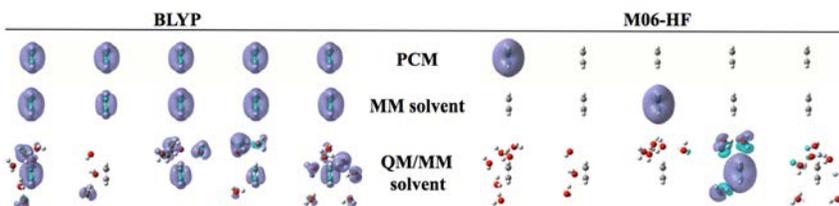


Figure 1. The BLYP and M06-HF density differences for the neutral and cation systems of five identical ethene molecules separated by 10 Å. Density differences are shown for three solvent environments: a polarizable continuum model (PCM), all molecular mechanical (MM) point charge solvent, and a combination of quantum mechanical (QM) and MM solvent molecules, with the twenty-five solvent molecules closest to a solute being treated as QM and the remaining sphere of waters treated as MM.

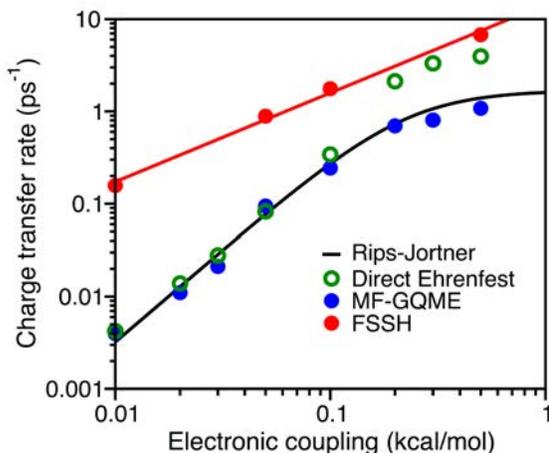


Figure 2. Charge transfer rate as a function of electronic coupling for electron transfer in atomistic solvent (water) shows the accuracy of our MF-GQME approach compared to fewest switches surface hopping. Rips-Jortner theory can be considered as the exact result in these regimes.

environments. This improvement in accuracy is accompanied by computational speed-ups of up to 3 orders of magnitude over a direct application of Ehrenfest theory in regimes of low electronic coupling (nonadiabatic regimes). In addition, we have also shown how our ring polymer contraction (RPC) approach can be extended to ab initio molecular dynamics simulations (AI-RPC). AI-RPC converges imaginary time path integral simulations, which exactly include NQEs of the static equilibrium properties on the nuclei and provide the basis for the CMD and RPMD approximations to quantum dynamics, at a cost over 35 lower than was previously possible. Indeed, including NQEs using this approach adds negligible computational cost over treating the nuclei classically. This acceleration allows us to perform ab initio path integral simulations for 100's of picoseconds which can be analyzed using network theory.

Initial intermolecular network theory analysis has focused upon quantifying the differences in structural organization and dynamics for liquid water using ab initio classical, ab initio RPMD, empirical potential classical trajectories, and empirical potential RPMD trajectories. As it pertains to proton transfer and proton coupled electron transfer, we are particularly interested short timescale dynamics, including changes in the observed librational motion (Type A in Figure 3), versus rotational motion, which can be classified into two major classes based upon the extent of rotation and the relative energies of the hydrogen bond immediately preceding bond breakage.

As a natural extension of this work, we are using excited state electronic structure (TDDFT), classical and quantum dynamics, and network analysis to better understand the role of quantum nuclei in excited state absorption processes. For neutral and charged molecules in aqueous solution, we are performing both classical and RP dynamics in which the nuclei are treated quantum mechanically. Using snapshots from both sets of dynamics, we are comparing the resulting TDDFT absorption spectra and analyzing how the sampled configurations differ for the classical and quantum ensembles, leading to differences in spectral width and shape.

Our research team has also made progress in treating the dynamics of electrons and nuclei. We are currently working to understand the limits of the adiabatic approximation of time-dependent density functional theory (TDDFT) in treating charge transfer. We have also recently demonstrated that our MF-GQME approach, which combines semiclassical theory with quantum master equations to yield an approach that is much more efficient than using either approach alone, is able to accurately obtain electron transfer rates for a wide range of electronic couplings in atomistic environments (see Figure 2). This work shows that the benefits of combining semiclassical and quantum master equation theory holds beyond linear system-bath coupling and harmonic

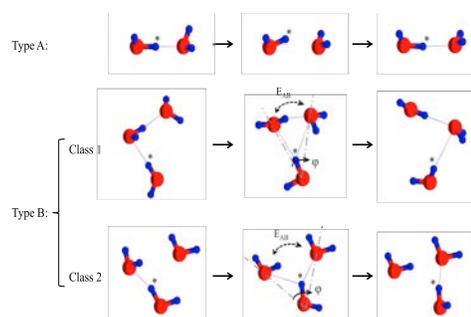


Figure 3. Illustration of the three major classes of motion of interest to the short time dynamics of proton transfer and proton coupled electron transfer.

Award No. DE-SC0014437: **DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION**

Postdocs Funded: Makenzie R. Provorse (University of California Merced), Lance Edens (Washington State University), Aaron Kelly (Stanford University: September-November), Ondrej Marsalek (Stanford University: November-current)

DOE Sponsored Research Publications:

- (1) Provorse, M. R.; Isborn, C. M. Electron Dynamics with Real-Time Time-Dependent Density Functional Theory. *Int. J. Quantum Chem.* **2016**, n/a – n/a.
- (2) Pfalzgraff, W. C.; Kelly, A.; Markland, T. E. Nonadiabatic Dynamics in Atomistic Environments: Harnessing Quantum-Classical Theory with Generalized Quantum Master Equations. *J. Phys. Chem. Lett.* **2015**, *6* (23), 4743–4748.
- (3) Marsalek, O.; Markland, T. E. Ab Initio Molecular Dynamics with Nuclear Quantum Effects at Classical Cost: Ring Polymer Contraction for Density Functional Theory. *J. Chem. Phys.* **2016**, *144* (5).
- (4) Sosa Vazquez, X. A.; Isborn, C. M. Size-Dependent Error of the Density Functional Theory Ionization Potential in Vacuum and Solution. *J. Chem. Phys.* **2015**, *143* (24).
- (5) Clark, A. E. Chapter Six - Intermolecular Network Theory: A General Approach for Understanding the Structural and Dynamic Properties of Liquids and Solutions. In *Annual Reports in Computational Chemistry*; Chemistry, D. A. D. B. T.-A. R. in C., Ed.; Elsevier, 2015; Vol. Volume 11, pp 313–359.

Molecular Dynamics Simulation on a Light-Harvesting Molecular Triad in Explicit Tetrahydrofuran Solvent Using Polarizable Force Fields

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Abstract

A light harvesting molecular triad is a synthetic molecule with covalent bonding between pyrrole-fullerene (C_{60}), diaryl-porphyrin (P), and carotenoid polyene (C) components. It is a donor-acceptor supramolecule that absorbs incident light in the visible region[1]. Charge separation upon electron excitation generates a giant dipole moment of ~ 150 Debye with a lifetime of ~ 300 ns[2]. However, its malleable conformation in solution prohibits its use for real-world applications. *The long-term goal of our research is to understand the relation between the distribution of the conformations of molecular triad that depends on solvent and its overall efficiency in charge transfer.*

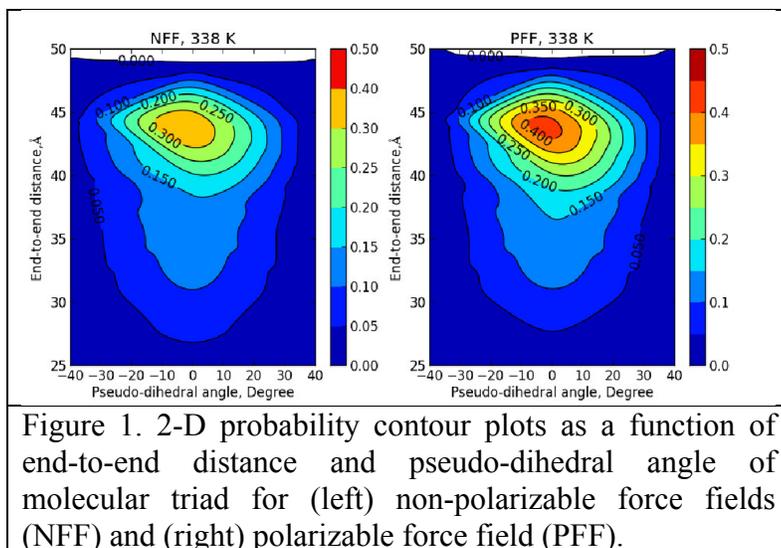


Figure 1. 2-D probability contour plots as a function of end-to-end distance and pseudo-dihedral angle of molecular triad for (left) non-polarizable force fields (NFF) and (right) polarizable force field (PFF).

Our group employed molecular dynamics simulations with non-polarizable force fields showed the structural stability of the triad for the ground and excited states [3-5]. Although the simulations with non-polarizable force fields describe the thermodynamics and structural properties of the triad well, they lack the effect of induced polarization that is critical to the charge transfer properties of organic photovoltaic (OPV) materials. This past year, we parameterized the polarizable force fields[6] for the individual component of the molecular triad as well as the THF solvent by matching their ensemble properties from simulations against the experimental measurements. We employed the Replica Exchange Molecular Dynamics simulations (REMD) to enhance the sampling of this very large system. We plotted the 2-D distribution plot with the end-to-end distance and the pseudo-dihedral angle of a molecular triad in Fig 1. The distribution of the triad from the simulations using the polarizable force fields is noticeably sharper than the non-polarizable ones. After the structural analysis, we found that the induced polarization stabilizes the rotational isomerization of the polyene chain that gives a sharp peak in Fig1.

Our next step is to develop the polarizable models for the excited states that dictate the efficiency or pathways of charge transfer in collaboration with Profs Barry Dunietz and Eitan Geva. The effect of the induced polarization and solvent chemical structure on the triad conformational landscape will be studied in details. The size of our simulations is exceptionally large that takes extraordinarily long time to converge. In order to expedite the simulation, we plan to compile the AMBER12 program with OpenACC to tap into the newly installed accelerators on the high performing computers from NERSC.

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Grant Numbers and Grant Titles

DE-SC0004832 Multiscale Investigation of Thermal Fluctuations on Artificial Photosynthetic

Postdoc: Oleg Starovoytov

1. G. Su, A. Czader, D. Homouz, G. Bernardes, S. Mateen, M.S.Cheung, "Multiscale simulation on a light-harvesting molecular triad", *J. Phys. Chem. B*. **116**, 8460-8473 (2012).
2. D. Balamurugan, A. J. A. Aquino, F. De Dios, L. Flores Jr., H. Lischka, M. S. Cheung, "Multiscale simulation of the ground and photo-induced charge-separated states of molecular triad in polar organic solvent: exploring the conformations, fluctuations and the free energy landscapes", *Journal of Physical Chemistry, B*, **117**, 12065-12075 (2013).
3. A. K. Manna, D. Balamurugan, M. S. Cheung, B. D. Dunietz, "Unraveling the mechanism of photo-induced charge-transfer in carotenoid-porphyrin-C60 molecular triad", *Journal of Physical Chemistry Letters*, **6**, 1231-1237 (2015).
4. O. Starovoytov, M.S. Cheung, "Simulations of molecular triad with polarizable force fields" to be submitted soon.

Systematically improvable methods for correlated electron systems

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The main research goal of my group is the design of ab-initio computational methods able to tackle difficult strongly correlated systems in which the motion of a single electron depends crucially on the motion of all the other electrons. Battery materials, oxide perovskites containing d-electrons, catalysis on metal oxide surfaces, and molecular magnets are examples of strongly correlated compounds that are important for the DOE mission. Most ab-initio quantum chemistry methods are too expensive for these materials, while most common materials science methods are not yet able to achieve truly predictive accuracy. Methods used in condensed matter physics are able to describe model systems but do not yield the high enough accuracy necessary to describe the intricate nature of electronic correlations in realistic systems.

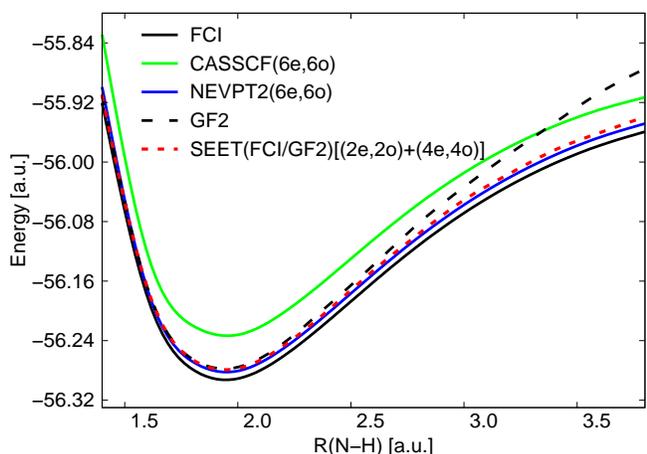


Fig. 1. Potential energy curve of NH_3 with 6-31G basis.

chemistry methods but did not require large memory storage and was avoiding divergencies typically present in CASPT2 and NEVPT2.

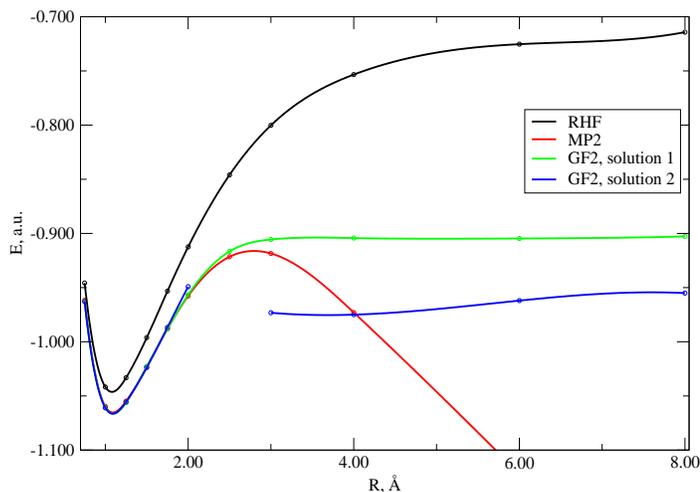


Fig. 2. 1D hydrogen crystal: electronic energies per unit cell for Hartree-Fock (RHF), 2nd-order Moller-Plesset perturbation theory (MP2), and two GF2 solutions.

My group has proposed a self-energy embedding theory (SEET) that can be understood as an embedding framework in which strongly correlated electrons are “immersed” into a correlated field coming from all other electrons present in the system. We calibrated SEET on model systems against CT-QMC, one of the most accurate methods in condensed matter physics, and obtained very accurate results confirming that SEET can describe well both strongly and weakly correlated regimes¹. Subsequently, we have calibrated SEET on a series of small molecular systems², see Fig. 1, showing that our method was able to work as well as the best quantum

The other main direction, we pursue in my group, aims to create black-box post DFT methods that describe all electrons on equal footing and are suitable for describing semiconductors. While semiconductors can currently be well described at the DFT level, this description is usually not sufficient once layered or doped systems are considered. To tackle this area, we have introduced a self-consistent second order Green’s function theory (GF2). Initially, to provide a series of benchmarks validating GF2, we applied it to molecular systems, showing that in the limit of a vanishing band gap this method avoids divergencies³⁻⁶. This was an unexpected result, defying a common belief that such divergencies ought to happen in a simple perturbation theory.

In 2015, we generalized GF2 to solids⁷, see Fig. 2, resulting in the first application of fully self-consistent Green's function method to an extended system with a full quantum chemistry Hamiltonian. The only other extended system that was studied by a fully self-consistent Green's function method was a model system, the electron gas. In this work, we were able to show that GF2, due to its self-consistent formulation, can describe metallic, insulating, and Mott phases, see Fig. 3. Perturbative Green's function approaches such as GF2 are interesting for two reasons. Firstly, few of them were investigated before and the best choice of correlated equations that balance the computational cost and accuracy for realistic solids still remains relatively unknown. Secondly, these approaches such as random phase approximation (RPA) are one of the higher rungs in the ladder of DFT functionals and are of interest to the DFT community.

The Green's function language is very suitable for obtaining experimentally relevant observables such as the

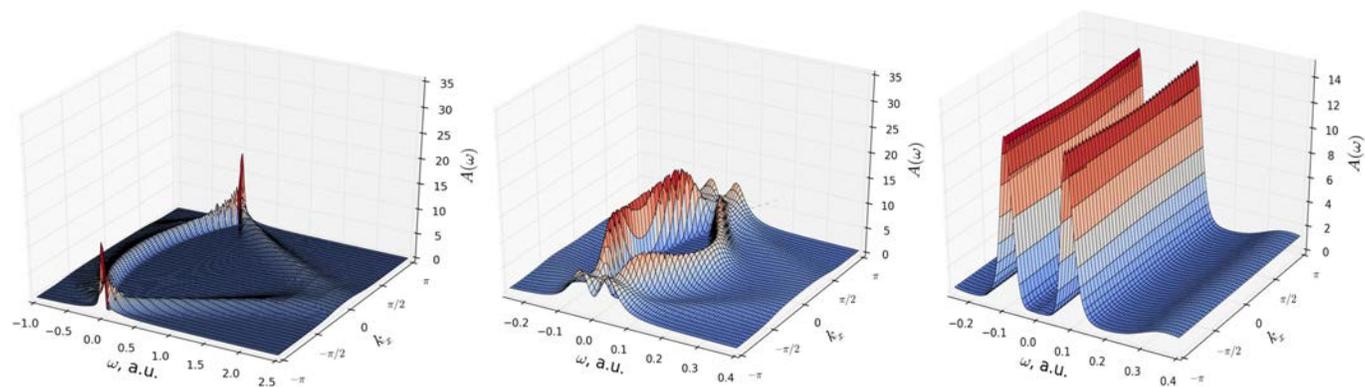


Fig. 3. 1D hydrogen crystal: Spectral functions for GF2 solutions 2 for two kinds of metallic phases $R=0.75$ and 1.75 A and a Mott solution for $R=4.0$ A interatomic separation.

density of states in solid state experiments. Currently, we are working on a new direction to use Green's functions in order to obtain thermodynamic quantities such as the electronic Gibbs energies and entropies critical for accessing the phase stability in solids. Moreover, we are implementing a code that evaluates partition function and temperature dependent susceptibility at the ab-initio GF2 and SEET level. We are planning to use these developments to investigate molecular systems undergoing a spin-crossover.

In my group, we recognize that, at present, Green's function methods when implemented deterministically, are too expensive to describe complicated solids, despite many conceptual advances introduced by us. This is why we worked on representing Green's functions for realistic systems in a compact manner⁵⁻⁶ making such approaches suitable to be used with large orbital spaces. Moreover, we recognize that due to the changing computational paradigm and availability of thousands processors with little memory, it is advantageous to use stochastic methods to express Green's functions. Currently, we are collaborating with Daniel Neuhauser from UCLA on a stochastic GF2 approach. Using these stochastic Green's function methods several thousands of orbitals can be treated when using parallel computers.

This year, we also plan to use SEET for a simple solid, first described in a deterministic manner, to deliver a series of correlated benchmarks for such a system. Here, a series of local correlation approaches will need to be investigated to localize orbitals near the gap that govern the chemistry of solids. To further pursue the work on the stochastic front, my group will work on attaching the stochastic GF2 to the SEET framework. These developments, when successful, have the potential of resulting in two methods: SEET and the stochastic GF2. They are systematically improvable, predictive, massively parallel and yielding the much sought after quantitative accuracy for strongly correlated molecules and solids.

Grant Numbers and Grant Titles

DE-SC0010381 Accurate Ab-initio Methods for Correlated Surface Problems

Postdocs: Jordan J. Phillips, Alexander A. Rusakov, Tran Nguyen Lan

Students: Alexei A. Kananenka, Alicia R. Welden, Blair A. Winograd

Publications

- [1] A. A. Kananenka, E. Gull, and **D. Zgid**, “[Systematically improvable multi-scale solver for correlated electron systems](#)”, Phys. Rev. B, 91, 121111(R) (2015), [arXiv:1410.5118](#)
- [2] Tran Nguyen Lan, Alexei A. Kananenka, and **D. Zgid**, “[Towards ab initio self-energy embedding theory in quantum chemistry](#)”, J. Chem. Phys. 143, 241102 (2015), [arXiv:1511.00986](#)
- [3] J. J. Phillips and D. Zgid, “[Communication: The description of strong correlation within self-consistent Green's function second-order perturbation theory](#)”, J. Chem. Phys. 140, 241101 (2014), [arXiv:1405.3273v1](#)
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Renormalization Group Approaches to Strongly Correlated Electrons

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Abstract

In this talk I will describe our efforts to develop numerically robust and systematically improvable electronic structure theories for strongly correlated electrons. Our focus is on novel many-body theories inspired by flow renormalization group methods. I will introduce the driven similarity renormalization group (DSRG), and discuss a multireference generalization of this method applicable to strongly correlated electrons. Within this context, I will consider the structure of a perturbative approximation of the DSRG equations and its generalization to non-perturbative (that is, coupled cluster-like) truncation schemes. In the last part of this talk, I will present preliminary applications of the multireference DSRG to study ground state potential energy surfaces and electronic excited states.

Recent progress

We have recently examined the similarity renormalization group (SRG) of Głazek and Wilson¹ and Wegner² in the context of quantum chemistry. In essence, the SRG is an approach to diagonalized operators using a series of infinitesimal transformations. Recently, the PI has reformulated the SRG into a practical quantum chemistry approach, the *driven* SRG (DSRG).³ As illustrated in Fig. 1, in the DSRG approach the Hamiltonian is diagonalized by a *continuous* unitary

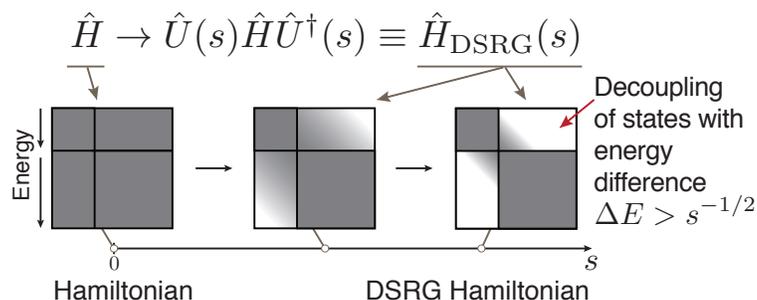


Fig. 1. Transformation of the Hamiltonian in the DSRG as a function of the flow parameter s .

operator which is a function of a flow parameter (s). As s goes from 0 to ∞ , the DSRG transformation produces a controlled downfolding of many-body interactions by decoupling high-energy processes from low-energy ones. This feature allows the reduction of a full many-body Hamiltonian with strongly and weakly interacting electrons to a compact effective Hamiltonian that describes a set of strongly interacting electrons with modified many-body interactions. The DSRG transformation is also a *renormalization* of the Hamiltonian, that is, as the flow parameter s goes from zero to infinity, the off-diagonal elements of the Hamiltonian are progressively zeroed, with a rate that depends on the corresponding energy denominators. This unique feature makes the DSRG robust against numerical instabilities that afflict perturbative and nonperturbative multireference approaches.

Our initial work on the DSRG led to the implementation of a single-reference version of the DSRG truncated to one- and two-body operators [SR-DSRG(2)].³ More recently, we showed how to generalize the DSRG to the case of a complete active space reference wave function.⁴ We reported the

implementation of a second-order perturbative approximation to the multireference DSRG (DSRG-MRPT2) and applied it successfully to a series of benchmarks systems (HF, N₂, and *para*-benzyne).

Future plans

- Derive and implement a nonperturbative version of the multireference DSRG that aims at achieving the accuracy of the CCSD(T) method, the “gold standard” of single-reference quantum chemistry.
- Implement multistate and equation-of-motion MR-DSRG excited state methods for near-degenerate ground and electronic excited states.
- Treat large active spaces via a combination of the MR-DSRG with the Density Matrix Renormalization Group (DMRG).
- Create a low-scaling Laplace-transformed atomic orbital-based implementation of the DSRG-MRPT2 for systems with hundreds of atoms.

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Does Response Theory Work for Non-Adiabatic Molecular Dynamics?

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Abstract

Non-adiabatic processes are critical for the lifetime and fate of electronically excited states in molecules, materials, and light-emitting devices. Non-adiabatic transitions between Born-Oppenheimer potential energy surfaces underly exciton annihilation, blinking, luminescence quenching, and other decay processes turning radiative energy into heat.

In the past 3.5 years, we established hybrid time-dependent density functional theory (TDDFT) in combination with Tully's fewest switching surface hopping algorithm as a workhorse for non-adiabatic molecular dynamics (NAMD) simulations of light-driven processes [1]. We extended SH-TDDFT to tackle homolytic bond breaking, developed non-orthonormal Krylov space methods to speed up hybrid TDDFT (currently under review), made our methods available in Turbomole [2], and applied them to photoinduced cycloreversion [1], transition metal dyes [3], and photoreactive rare-earth complexes [4, 5].

Derivative couplings between excited Born-Oppenheimer states are a key ingredient for NAMD simulations. We used cubic response theory from the ground state to derive analytical expressions for these couplings [6]. However, these couplings exhibit unphysical divergences whenever the energy difference between the two states, Ω_{mn} , matches *any other* excitation energy from the ground state. We have recently observed that these divergences are not limited to TDDFT, but also appear in correlated wavefunction

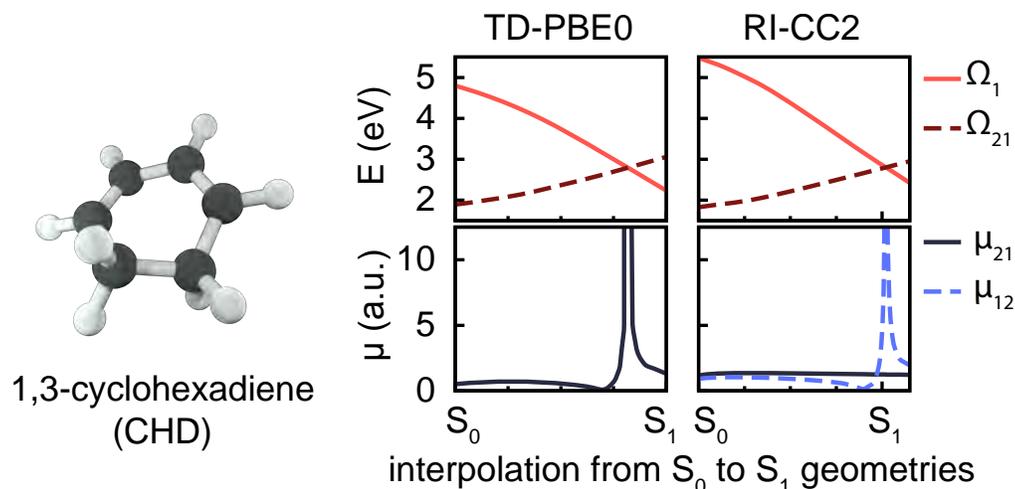


Figure 1: The transition dipole moment between the first two excited states, μ_{12} , of CHD diverges when the energy difference $\Omega_{21} = \Omega_2 - \Omega_1$ matches the excitation energy Ω_1 . RI-CC2 stands for approximate coupled cluster singles doubles response theory (CC2) using resolution-of-the-identity (RI).

methods such as coupled cluster or multi-configurational self-consistent field response theory, and also affect other properties such as transition dipole moments, see Fig. 1. The divergences lead to unphysically strong coupling between states for certain molecular structures and thus incorrect NAMD.

While these divergences can be empirically corrected, they raise fundamental questions about the validity of higher-order response theory for an approximate ground state. We are currently investigating several strategies to formulate reliable state-to-state properties either through improving or obviating the quadratic response function. We are also studying the effect of this incorrect pole structure on other non-linear response properties such as hyperpolarizabilities and two-photon absorption.

Our progress in method development has recently enabled us to apply SH-TDDFT to photocatalytic water splitting of water by TiO_2 nanoclusters. Non-adiabatic processes in TiO_2 based photocatalysts lead to exciton annihilation and electronically excited trap-states which inhibit the reactivity. While these processes have been studied spectroscopically, a mechanism of the non-radiative decay and the nature of the localized trap states are poorly understood. We are currently investigating how particle size and shape affects the non-adiabatic dynamics of photoexcited TiO_2 clusters. Photoinduced heterolytic water splitting is observed in a 36-atom model cluster, see Fig. 2, but the quantum yield is relatively low. In the remaining time of the project, we plan to include solvation effects and validate our models by comparison to experimental results.

Grant Numbers and Grant Titles

DE-SC0008694 Non-Adiabatic Molecular Dynamics Methods for Materials Discovery

Postdocs: Mikko Muuronen, Shane M. Parker

Students: Saswata Roy, Jordan C. Vincent

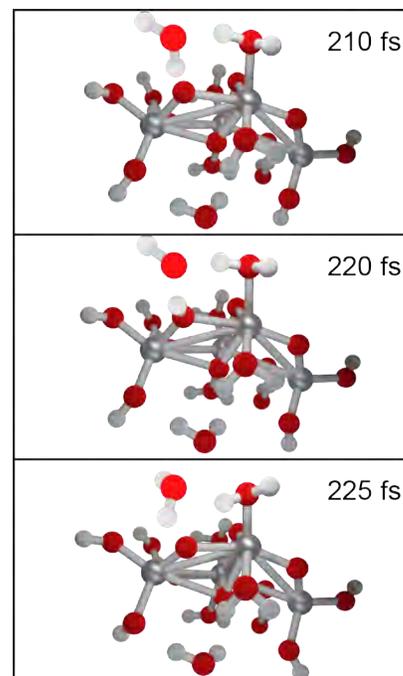


Figure 2: Snapshots showing heterolytic water splitting in a SH-NAMD PBE0-D3/SV(P) trajectory of $(\text{TiO}_2)_4 \cdot 8 \text{H}_2\text{O}$. The simulations were started in the S_1 state.

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Department of Energy under Grant No. DE- SC0010499

Project title: Exploring the Random Phase Approximation for Materials and Chemical Physics

The Renormalized Random Phase Approximation with Kernel Correction for Materials Science

Scope of the work

In this work we test the performance of the fully nonlocal random phase approximation (RPA) for challenging problems in materials chemistry and physics. Direct RPA includes the full exact exchange energy and a nonlocal correlation energy with an approximate but universal description of long-range van der Waals attraction. RPA still cannot be a benchmark electronic structure method without a correction for its short-range correlation energy which is too deep. The short-range error of RPA can be corrected by a spatially nonlocal, exchange-only kernel. Such kernels could be a more reliable and “intrinsic” approximation to capture accurate ground-state energy differences than the expensive SOSEX and other beyond-RPA corrections.

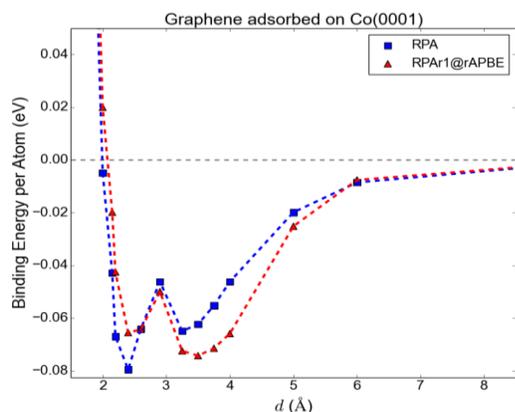
Recent progress:

Transition Pressures from RPA and kernel-corrected RPA:

(a) R. G. Hennig *et al. Phys. Rev. B*, **82**, 014101 (2010)

Phase transition pressures of materials can be difficult to describe with semi-local DFT. Previous works have shown that the RPA is more accurate than most semilocal approximations for the insulator-metal transition of Silicon diamond to beta-tin. RPA's accuracy is difficult to benchmark, however, as reported DMC results predict a slightly larger transition pressure and energy difference between phases. We find that addition of a kernel correction to RPA reduces the energy difference between phases as well as the transition pressure. Within this project we tested the renormalized PBE kernel (rAPBE) as a correction to RPA to various semiconducting/metallic systems. In order to reduce the computational cost of the kernel correction we tested first order RPA renormalization (RPA_{r1}) and find that RPA_{r1} reproduces the energy difference of the traditional ACFD approach by about 20 meV for the rAPBE kernel. The GPAW code was used to compute the RPA and rAPBE results.

Graphene adsorption on the Co(0001) surface:



Adsorption of graphene on metal surfaces requires an accurate description of dispersion interactions. This is especially true for graphene on Ni(111) and Co(0001) where both a chemi- and physisorption minimum occur. Neither semi-local functionals nor van der Waals density functionals are able to capture the double minimum due to the competition of both dispersion and short-ranged interactions. We are considering the renormalized RPA ((RPAr1) with rAPBE kernel for this problem. GPAW was used to perform these calculations.

(a) T. Olsen and K. S. Thygesen, Phys. Rev. Lett., 112, 203001 (2014)

(b) T. Olsen and K. S. Thygesen, Phys. Rev. B, 87, 075111 (2013)

RPA applied to transition metal chemistry:

RPA has proven to be very accurate for main group thermochemistry, yielding superior results in comparison to other semi-local and even hybrid functionals. Transition metal chemistry can be challenging for semi-local DFT due to the delicate interactions between electrons in the nd -shell and the need to describe both static and dynamic correlation through a wide range of bond lengths and strengths. We applied RPA to three literature test sets that survey a variety of transition metal bonding types in order to assess their performance. We also include results for the SCAN meta-GGA, to compare the RPA results. SCAN improves the GGA description for 2 out of 3 tests, but only improves over TPSS for the FP06 set. Self-interaction errors are still problematic, and a global hybrid is expected to improve SCAN's performance. Evaluating RPA on top of SCAN orbitals results in an improvement for all three sets due to the self-interaction freedom of RPA and its ability to capture static and dynamic correlation. We are in the process of evaluating the impact of mixing exact exchange in the reference determinant and energy since we recently showed a dual-hybrid of RPA could lead to even further improvements for energy differences. We are also exploring the basis set dependence of RPA for these reaction energies since we encountered some difficulties extrapolating to the infinite basis set limit for some systems. Turbomole was used to perform these calculations, employing basis sets of quadruple-zeta quality.

(a) P.D. Mezei, A. Ruzsinszky, and G.I. Csonka, J. Chem. Theory Comput., **2015**, 11,4615

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MAD (kcal/mol)	Description	PBE	TPSS	SCAN	RPA
FP06 ^(b)	18 bond and reaction energies of	10.8 ^(b)	10.2 ^(b)	8.8	7.4

	3d complexes				
JB09^(c)	32 average ligand dissociation energies of 3d complexes	10.4 ^(c)	8.6 ^(c)	9.5	5.1
SG13^(d)	82 energy barriers with Ni or Pd model catalysts	3.9 ^(d)	3.8 ^(d)	5.1	1.6

Publications acknowledging this Grant in 2013-2015

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Future plans

1. GW Band Gaps:

Our research group has started applying the SCAN meta-GGA as a reference to perturbative GW band gap calculations. Given SCAN's improvement of total energies and energy differences for solids and molecules in comparison to previous non-empirical functionals, SCAN may also improve the description of the band structure. Quasiparticle effects are still necessary for difficult systems such as transition metal oxides, but SCAN could provide for an efficient starting point for high throughput calculations if G0W0 corrections on top of SCAN are relatively accurate. For CoO, MnO, and ZnO, we find that SCAN does improve the GGA description, and the first GW iteration further increases the gap, but self-consistency still plays an important role. Further work is needed to understand the broader performance for other magnetic and complex oxides. VASP was used to perform these calculations; we included local field (LF) effects in W through the ALDA approximation.

2. CO/CO₂ adsorption on metal surfaces:

CO and CO₂ adsorption calculations on the metal surfaces have proven computationally demanding within the infinite-order RPA approximation. Our work with renormalized RPA on graphene adsorption on metal surfaces has opened an effective way to apply RPA to other adsorption problems. We will be considering the renormalized RPA ((RPA_r1) with rAPBE kernel to the CO/CO₂ adsorption problem.

Electron-Ion Dynamics with Time-Dependent Density Functional Theory

Neepta T. Maitra

Hunter College and the Graduate Center of the City University of New York

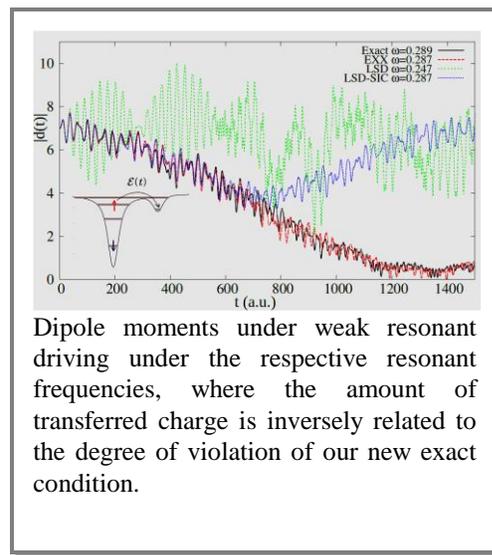
Abstract

To improve the reliability of time-dependent density functional theory (TDDFT) simulations of electron-ion dynamics, I have been exploring features of the exact exchange-correlation functionals in non-perturbative dynamics, as well as the features of the exact potentials arising from electron-ion coupling. The goal is to eventually derive more accurate functionals and methods based on these investigations that predict materials properties and light-matter interactions better.

One of our main results has involved the discovery and analysis of new step features in the exact exchange-correlation potential that are typically present in non-perturbative dynamics and that are completely lacking in approximations used today. They are responsible for the observed failure of approximate functionals to capture charge-transfer when beginning in a ground-state. Full charge-transfer *dynamics* is harder for functionals than calculating charge-transfer energies.

Another main result is that we uncovered a new exact condition on the functional with general implications for time-resolved spectroscopy. When a field driving a system 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, typically violated by approximations.

Earlier work with collaborators from MPI-Halle derived a new formalism for coupled electron-ion dynamics where the exact molecular wavefunction can be factored into nuclear and electronic wavefunctions. The nuclear wavefunction satisfies a Schrodinger equation with a scalar potential, called the time-dependent potential energy surface (TD PES) 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 TD PES, we found that quasiclassical propagation of an ensemble of nuclear trajectories on the exact TD PES 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. We 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, and charge-resonance enhanced ionization. Errors in the localization asymmetries and ionization rates predicted by the traditional potentials can be explained by features in our exact potential.



Grant Numbers and Grant Titles

DE-SC0008623 and DESC0015344 , Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

Postdoc(s): Johanna I. Fuks

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

1. J. I. Fuks, S. E. B. Nielson, M. Ruggenthaler, and N. T. Maitra, *Time-Dependent Density Functional Theory Beyond Slater Determinants*, Physical Chemistry Chemical Physics, to appear (2016); **DOI:** 10.1039/C6CP00722H
2. E. Khosravi, A. Abedi, and N. T. Maitra, *The exact potential driving the electron dynamics in enhanced ionization*, Physical Review Letters **115** 263002 (2015).
3. Y. Suzuki, A. Abedi, N. T. Maitra, and E.K.U. Gross, *Laser-induced electron localization in H₂⁺: Mixed quantum-classical dynamics based on the exact time-dependent potential energy surface*, Physical Chemistry Chemical Physics **17**, 29271 (2015).
4. J. I. Fuks, K. Luo, E. D. Sandoval, and N. T. Maitra, *Time-Resolved Spectroscopy in Time-Dependent Density Functional Theory: An Exact Condition*”, Physical Review Letters **114**, 183002 (2015).
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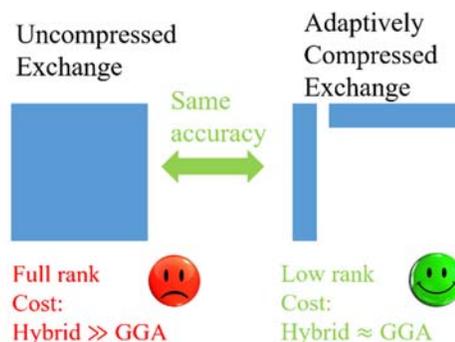
Efficient Compression of the Fock Exchange Operator

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Abstract

The Fock exchange operator plays a central role in modern quantum chemistry and materials science, in the context of both Hartree-Fock calculations, and Kohn-Sham density functional theory (KSDFT) calculations with hybrid exchange-correlation functionals. If the exchange operator is constructed explicitly, the computational cost scales as $O(N_e^4)$ where N_e is the number of electrons of the system. The cost can be reduced to $O(N_e^3)$ by iterative algorithms especially for large basis sets such as planewaves. Iterative algorithms avoid the explicit construction of the exchange operator, but the preconstant is still very large compared to that in KSDFT calculations with LDA/GGA functionals. Hence hybrid functional calculations for systems with hundreds of atoms or even less can be challenging computational tasks.



We have been exploring two new directions for compressing the Fock exchange operator to reduce the computational cost.

1. The Fock exchange operator is defined using the entire density matrix rather than the electron density, and the exchange operator is close to be a full rank operator. We develop the adaptively compressed exchange operator (ACE) formulation [1], which can greatly reduce the computational cost associated with the Fock exchange operator without loss of accuracy. The ACE formulation does not depend on the size of the band gap, and thus can be applied to insulating, semiconducting as well as metallic systems. In an iterative framework for solving Hartree-Fock-like systems such as in planewave based methods, the ACE formulation only requires moderate modification of the code. The ACE formulation can also be advantageous for other types of basis sets, especially when the storage cost of the exchange operator is expensive. Numerical results indicate that the ACE formulation can become advantageous even for small systems with tens of atoms. In particular, the cost of each self-consistent field iteration for the electron density in the ACE formulation is only marginally larger than that of the generalized gradient approximation (GGA) calculation, and thus offers orders of magnitude speedup for Hartree-Fock-like calculations.
2. For systems with finite HOMO-LUMO gaps, the Fock exchange operator can further be compressed with localization techniques. Given a set of Kohn-Sham orbitals from an insulating system, we develop a simple, robust, efficient and highly parallelizable method to construct a set of, optionally orthogonal, localized basis functions for the associated subspace. Our method explicitly uses the fact that density matrices associated with insulating systems decay exponentially along the off-diagonal direction in the real space representation. Our method avoids

the usage of an optimization procedure, and the localized basis functions are constructed directly from a set of selected columns of the density matrix (SCDM) [2]. Consequently, the only adjustable parameter in our method is the truncation threshold of the localized basis functions. We demonstrate the numerical accuracy and parallel scalability of the SCDM procedure using orbitals generated by the Quantum ESPRESSO software package. We also demonstrate a procedure for combining SCDM with Hockney's algorithm to efficiently perform Hartree-Fock exchange energy calculations with near linear scaling. We recently extend the SCDM algorithm to the case of k-point sampling, with computational complexity that is $O(N_k \log N_k)$ where N_k is the number of k points. We also interfaced SCDM with the Wannier90 package to provide a robust and parameter-free initial guess for computing maximally localized Wannier functions. Initial results indicate that the spread of the SCDM initial guess is already very close to the spread of the optimized Wannier functions even for complex metal oxides such as Cr_2O_3 .

Grant Numbers and Grant Titles

DOE SciDAC-3, "Discontinuous methods for accurate, massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles."

DOE SciDAC-3, "Advanced Modeling of Ions in Solutions, on Surfaces, and in Biological Environments."

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

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5. A. Damle, **L. Lin** and L. Ying, Compressed representation of Kohn-Sham orbitals via selected columns of the density matrix, J. Chem. Theory Comput. 11, 1463, 2015
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Multiple Coupled Potential Energy Surfaces with Application to Combustion

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Program Scope: Hydrocarbon combustion involves the dynamics of numerous small radicals such as HO₂, HCO, and HOCO. HOCO is an intermediate in the HO + CO → H + CO₂ reaction which is the last and heat releasing step in hydrocarbon combustion and the subject of many ongoing studies. Accurate calculations of their potential energy surfaces (PESs) are possible using traditional quantum chemistry methods such as MRCI. However, multistate and non-adiabatic processes can be important, and tunneling effects may supersede the more common kinetic or thermodynamic control of rates and branching ratios. Significant fractions of molecular products can also result from radicals roaming far from conventional minimum energy paths and tight transition states. Dynamical calculations for these relatively simple systems are very sensitive to the detailed topography of their global potential energy surfaces (PESs).

This project combines developments in the areas of PES fitting and multistate multireference quantum chemistry to allow spectroscopically and dynamically/kinetically accurate investigations of key molecular systems (such as those mentioned above), many of which are radicals with strong multireference character and have the possibility of multiple electronic states contributing to the observed dynamics. A main goal is to develop general strategies for robustly convergent electronic structure theory for global multichannel reactive surfaces. Combining advances in *ab initio* methods with automated interpolative PES fitting allows the construction of high-quality PESs incorporating thousands of high level data to be done rapidly through parallel processing on high-performance computing (HPC) clusters. New methods and approaches to electronic structure theory will be developed and tested through applications. Some effort will be applied to the development of Quantum Monte Carlo (QMC) and working to apply these methods in the context of global PESs. The feasibility of capturing a larger fraction of the correlation energy than is possible with traditional electronic structure approaches will be tested on suitable combustion related systems. Strategies will be developed to generate QMC data in the context of a *distributed high-throughput computing* model in which 10s or even 100s of thousands of processors are used.

Recent Progress: This section describes recent progress achieved along various directions of the project occurring over the past 12 months since the last report from April 2015. The initial start date of this project was 07-15-2013.

Progress with dynamics, PES fitting methods and the underlying electronic structure methods has culminated in three review articles. The first (already available) is a *Molecular Physics* review of methods for *Automated Construction of Potential Energy Surfaces* and includes an author profile.¹ The second (appearing later this year), for *International Reviews of Physical Chemistry*, describes *Electronic Structure Considerations for ab initio based Potential Energy Surfaces*.² The third (available) involved participation in a project spearheaded by Hua Guo, a JPC A review on fitted PESs and the quantum dynamics of X + H₂O (X = F, Cl and O) reactions.³

Experimental and theoretical studies of the electronic transitions of MgC.⁴ In the 2014 report a previous study of BeC⁵ was described in which vibronic calculations were able to help assign and interpret electronic spectra of that system recorded by the group of Michael C. Heaven (Emory). Heaven's efforts to observe similar transitions in MgC have so far been unsuccessful. New vibronic calculations were performed for the MgC system using the dynamically weighted multistate scheme to produce MRCI/CBS quality potential curves. A diabaticization procedure was used along with a DVR method including a complex absorbing potential (CAP) to solve for the vibronic levels and their lifetimes/widths.

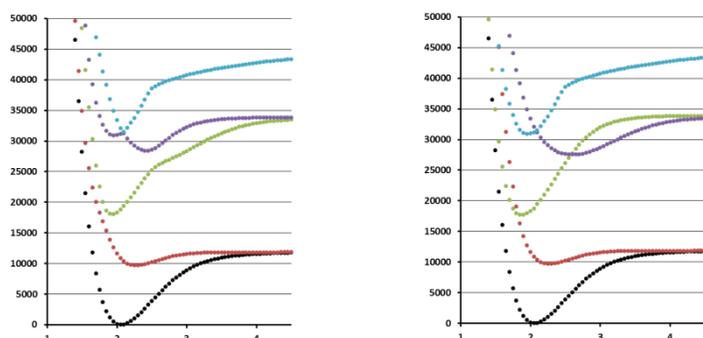


Figure 1. Electronic states of MgC plotted in adiabatic (left) and diabatic representations (right). The zero of the energy is the minimum of the $X^3\Sigma^-$ electronic ground state (shown in black).

Despite difficulties with the experiments, our complete set of theoretical predictions for all bound vibrational and well as vibronic states and lifetimes has now been published in JCP.⁴ The first author of the paper was a graduate student supported by this project (Phalgun Lolur). Phalgun has since graduated with his PhD and gone on to a postdoc position with Bill Green at MIT, thus continuing to work on combustion and contribute to this program.

Non-Born-Oppenheimer molecular dynamics of the spin-forbidden reaction of $O(^3P) + CO(X^1\Sigma^+) \rightarrow CO_2(\tilde{X}^1\Sigma_g^+)$.

A successful collaboration with Ahren Jasper (Sandia) was reported previously describing high pressure studies of the kinetics of this spin-forbidden reaction.⁶ In 2014, new experimental data for this system was obtained by Kristie Boering (UC-Berkeley) and co-workers. Those molecular beam experiments produced data for the isotope exchange and electronic quenching processes that occur in the low-pressure limit (CO_2 products are not formed in the absence of stabilizing collisions). Simulating those experiments required extending both the coordinate and energy ranges of the PESs (so that product states could be precisely resolved). This was achieved using the same automated PES generation strategy (restarting the PESs with newly defined limits). Remarkably, robust convergence was obtained in the electronic structure calculations and estimated fitting errors of only a few wavenumbers were again obtained even with the extended ranges (the total energy range of the singlet PES now exceeds 300 kcal/mol). Trajectories calculations by Jasper are in good agreement with the experiments. A limited set of fully quantum calculations were performed by Hua Guo providing some additional insight (fully quantum reactive scattering calculations are challenging due to the deep well depth). The paper faced some delays due to coordinating with professor Boering and the other coauthors, but is now in preparation.

IMLS-PIP fitting. A large set of ~100,000 high-level multireference data were computed for methane.⁷ The IMLS interpolation approach was combined with permutation invariant

polynomials (PIP) to fit the 9D PES in a 25,000 cm^{-1} energy range to better than a wavenumber using about 200 local expansions. This was used as a benchmark to assess the accuracy of another fit to the same data set by H. Guo using the NN-PIP method. Guo's fit was found to be very accurate and quick to evaluate. 9D vibrational calculations by T. Carrington confirm that the data is of spectroscopic quality. The lowest levels are systematically 1-2 cm^{-1} higher than experiment. Having a fit with negligible fitting error permits direct assessment of ab initio methods as well as small corrections. Future plans include testing some small corrections such as relativistic and diagonal Born-Oppenheimer (DBOC). Since the data set is multireference it is also suitable for extension to permit dissociation to $\text{CH}_3 + \text{H}$ and $\text{CH}_2 + \text{H}_2$ and would be useful as a highly accurate PES for dynamics studies. The dissociation energy to $\text{CH}_3 + \text{H}$ was found to be within about 40 cm^{-1} of the best estimates by Ruscic.

The IMLS-PIP approach was applied to a 15D test set of A. F. Wagner and D. L. Thompson composed of ~400,000 data for **ethyl radical**. This system combines a more complex topography, higher dimensionality and additional permutation symmetry. An initial fit of the lower energy region (below 67 kcal/mol) was obtained with an RMS fitting error of 0.2 kcal/mol using a single PIP expansion. Al Wagner plans to use the PES in an ongoing trajectories study.

QMC. We have been developing scripts and testing methods to use multi-configurational trial wavefunctions in VMC/DMC calculations of PECs for small molecules using a code called CASINO. A tutorial is now available on our website, <http://web.mst.edu/~dawesr/educational.html>. We have managed to produce highly accurate PECs for CO and N_2 using QMC. The PECs compare well with the best ab initio references and experimental quantities (vibrational levels etc). However, the cost was found not to be competitive with standard electronic structure approaches for small systems. (The scaling with number of electrons is n^3 for QMC so it will certainly be more competitive for larger systems where the e.g. n^7 scaling of traditional methods becomes prohibitive).

We have also connected with Paul Kent (Oak Ridge) and begun testing his QMCPACK code which we find to be significantly faster for multiconfigurational applications and can handle open shell systems whereas CASINO cannot.

A paper describing this benchmark study is close to submission.

We have also connected with Ali Alavi and begun testing an entirely different QMC based electronic structure approach called FCIQMC in which Monte Carlo methods are used to explore the active and virtual spaces of a specific basis set and approximate the FCI limit. This approach preliminarily seems more cost effective and promising for the sorts of applications that are of interest to us.

MCTDH: Rotationally inelastic scattering. A time-dependent quantum dynamics method called MCTDH was applied to studying inelastic scattering at high collision energies where more typical time-independent calculations (Molscat) become prohibitively expensive. Using an IMLS-based PES for CO+CO constructed for a previous ro-vibrational spectroscopy study,⁸ time-independent Molscat calculations (for the low energy range) were combined with time-dependent MCTDH calculations to cover an extended energy range. Where the two approaches overlap, reasonable agreement was obtained between the two.

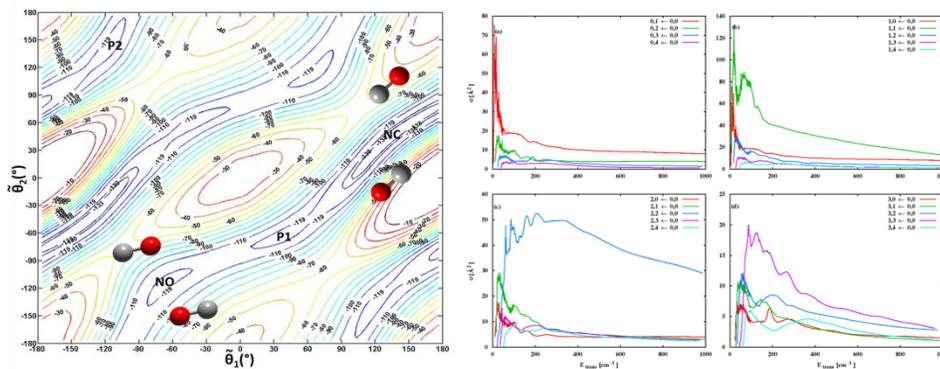


Figure 3. (at left) a plot of the PES for CO-dimer showing low-energy channels for geared motion. (at right) scattering cross-sections for rotational excitation showing increased propensities for equally excited products (possibly imparted by the features of the PES).

The paper describing this study appeared in the special JPC “100 years of combustion chemistry at Argonne” issue.⁹

The MCTDH method was extended to treat other scattering systems including CO₂:CO₂. A further application of MCTDH involved collaboration with Hua-Gen Yu and Hua Guo in which 9 dimensional vibrational states were obtained for the simplest Criegee intermediate, CH₂OO.¹⁰

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Quantum Monte Carlo calculations for chemical bonding and reactions

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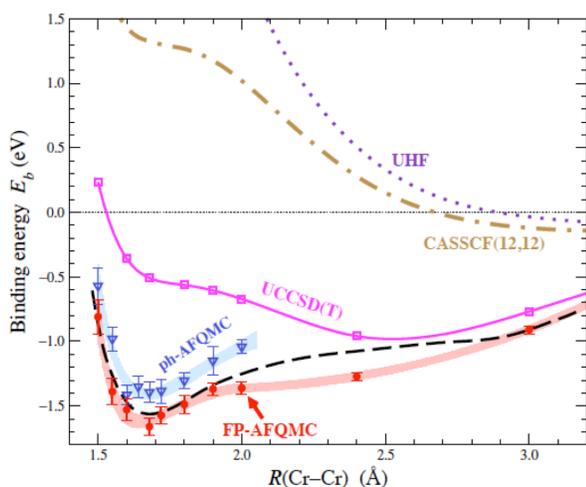
Abstract

This program focuses on the development and application of the auxiliary-field quantum Monte Carlo (AFQMC) method for chemical binding and reactions. The AFQMC approach was developed by the PIs and collaborators. It has shown promise to provide a highly accurate description of correlated electron systems, from molecules to solids. Unlike most other explicitly many-body wavefunction approaches, the AFQMC method scales as a low order polynomial of system size, similar to independent-electron methods such as in density functional theory (DFT). Since the AFQMC algorithm has the form of an entangled ensemble of mean-field calculations, it is significantly more computationally costly than traditional DFT calculations. A principal objective of this project is to develop new computational strategies to achieve improved speed and even better scaling with system size.

Applications of the present program have mostly been in problems relevant to hydrogen storage and transition metal systems, although the development of the theoretical and computational capability will have cross-cutting impacts beyond specific systems. The techniques and codes we are developing are general and applicable to other systems.

Recent progress includes:

- the development of a downfolding approach which allows realistic quantum-chemistry-like calculations in solids, including transition metal oxides
- embedding AFQMC in DFT to extend length scales and speed up many-body calculations, with which we were able to determine the stability and magnetic state of Co adsorption on graphene
- systematic improvement with constraint release in AFQMC, which enabled near-exact calculations in the chromium dimer in large basis sets (see figure)
- excited state method development and calculations of band gaps in solids
- the introduction of frozen-core with the framework of AFQMC which eliminated pseudopotential errors in quantum Monte Carlo



Bond breaking in Cr_2 . An accurate potential energy curve (PEC), with spectroscopic constants in good agreement with experiment, is obtained by AFQMC. The Cr_2 is a landmark challenge for strong electron correlations, with sextuple bond, weak binding, very short bondlength, and a “shoulder” structure in its PEC. AFQMC calculations used $cc\text{-}pwCVxZ\text{-}DK$ basis sets, with $x=2,3,4$ under the phaseless approximation, and $x=2,3$ for near-exact free-projection. Extrapolation to the complete basis set (CBS) limit was performed.

As an orbitally based wave function method, the AFQMC theoretical framework has close relations to many-body quantum chemistry methods. When expressed in a one-particle Gaussian type orbital (GTO) basis, both approaches use exactly the same Hamiltonian. Thus, many efficient techniques developed for correlated quantum chemistry methods can be directly imported. This was done, for example, using resolution of the identity techniques to remove a bottleneck in the handling of two-body interaction matrix elements for large basis sets. The current project has realized several others, and we will continue to integrate AFQMC into the toolkit for quantum chemistry.

In this talk, I will give a general overview of quantum Monte Carlo calculations in the context of quantum chemistry, and describe our recent progress with AFQMC. Connections with other, more "standard" quantum chemistry approaches will be discussed, and potential overlaps and cross-fertilization will be highlighted. The frozen-core approach mentioned above and the development in embedding AFQMC in DFT both illustrate such potential. Results on applications in molecular systems will be discussed. A number of collaborations with other quantum chemistry groups are on-going, and I will give a brief progress report on the results from these collaborations.

Grant Numbers and Grant Titles

DE-SC0001303 Quantum Monte Carlo calculations of chemical binding and reactions

[Also part of CMCSN team DE-FG02-11ER16257 “Quantum chemistry via walks in determinant space” with Cyrus Umrigar (PI, Cornell), Gustavo Scuseria (Rice), and Miguel Morales (LLNL), 2011-14]

PIs: Henry Krakauer (hxkrak@wm.edu); Shiwei Zhang (shiwei@wm.edu)

Postdoc(s): Fengjie Ma (partial); Wirawan Purwanto (partial)

Student(s): Yudistira Virgus

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

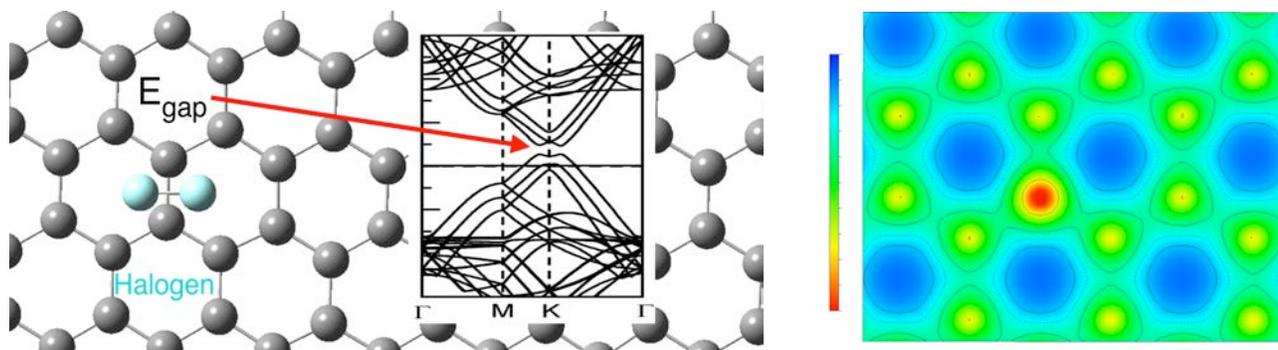
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Altering the Properties of Two-Dimensional Materials

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Presentation Abstract

The unique structure of two-dimensional materials generates novel optical, transport, and mechanical properties. Structural modifications to the repeating unit can yield unexpected results. Herein, using first principles calculations, we show how perturbing the interface substantially alters the electronic properties of the material. The systems examined include a doped graphene monolayer, halogen adsorbed surfaces, and strained TiS_2 . In each case, interactions at the interface produce material properties that deviate markedly from the pristine structure. This work demonstrates different routes to modulate the electronic properties of various two-dimensional materials. Understanding, and ultimately controlling, these effects is important for new applications in electronics and solar energy.



Grant Numbers and Grant Titles

DE-SC0010212 Plasmon Enhanced Photovoltaics: Modeling Energy and Charge Transfer in Solar Nanoassemblies

PI: Kevin L. Shuford

Postdoc(s): Alessia Polemi, Chengyong Xu, Olga Samoylova

Student(s): 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

We have begun studying the electronic, optical, and transport properties of titania and low dimensional nanomaterials such as graphene and early transition metal dichalcogenides. As described in the presentation abstract, we have recently completed studies on pnictogen-doped graphene, multilayer graphene interacting with halogens, and 1T-TiS₂ under strain. Plane wave DFT was used to compute equilibrium geometries and band structures. In each case, the electronic properties are altered via interactions at the interface. By controlling these perturbations, the properties of the material can be tuned with some degree of selectivity. These calculations are a necessary step toward 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 performing molecular quantum chemical calculations on common Ru dyes, porphyrins, and organic donor-acceptor molecules. Future work will examine these molecules interacting with plasmonic and semiconductor surfaces.

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J. Ilja Siepmann

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

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Abstract

The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including **metal-organic frameworks** (MOFs), **zeolites**, and **porous polymer networks** (PPNs). 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. Towards that end, the NMGC (i) develops state-of-the-art predictive theories (from high-level electronic structure methods to validated molecular mechanics force fields), predictive modeling tools, applets, databases, and web-based repositories, and (ii) employs them to increase the pace of materials discovery and to understand the fundamentals of interactions and mechanisms that govern performance of nanoporous materials. 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 Monte Carlo and molecular dynamics simulations, electronic structure calculations, scientific computation, and applied mathematics. The majority of the completed and on-going projects benefit from iterative feedback where computational modeling is instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis, characterization, and validation.

The NMGC research efforts have already led to more than 70 publications. In this presentation, we highlight the key achievements of selected application projects, a software tool, and a database/web tool that are central to the goals of the NMGC: (i) Discovery of MOFs for pre-combustion CO₂/H₂ separation using a genetic algorithm for efficiently identifying top-performing MOFs from a set of 50,000 hypothetical structures; the predictive modeling led to a target MOF in the optimal region for selectivity and working capacity that has been synthesized and good agreement with prediction is found (see **Fig. 1**); (ii) Discovery of zeolites for sweetening of highly sour natural gas using high-throughput simulations to probe the performance of 385 zeolites for binary H₂S/CH₄ and H₂S/C₂H₆ mixtures at multiple state points and of 16 high-performing zeolites for a quinary H₂S/CO₂/CH₄/C₂H₆/N₂ mixture (see **Fig. 2**); (iii) Discovery of the NU-1000 MOF for the selective hydrolysis of organophosphonate chemical warfare agents; NU-1000 yields faster hydrolysis than any other MOF to date and also selectively produces only the non-toxic product of VX hydrolysis; (iv) Discovery of a MOF that catalyzes the ethane-to-ethanol conversion via a high-spin Fe^{IV}-oxo intermediate via a multi-step modeling process involving the detection of MOFs with open Fe sites from the core MOF database, selection of unique MOFs with coordination environments that may stabilize a high-spin Fe^{IV}-oxo intermediate, determination of the ground spin state of seven promising candidates and computation of rate-determining transition state barrier; (v) a Python tool for the computation of mixture adsorption isotherms; and (vi) the Nanoporous Materials Explorer.

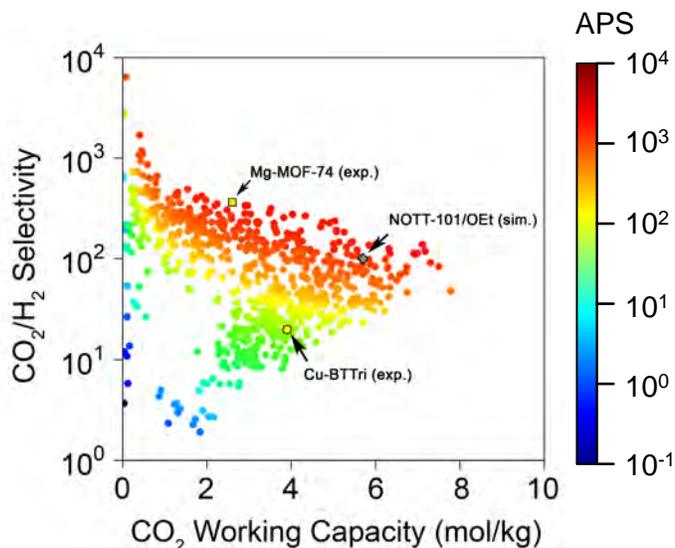


Fig. 1: Predictive modeling of MOFs for CO₂/H₂ separation. The coloring indicates the Adsorbent Performance Score (APS). Available experimental data points and a target MOF in the optimal region for selectivity and working capacity are labeled.

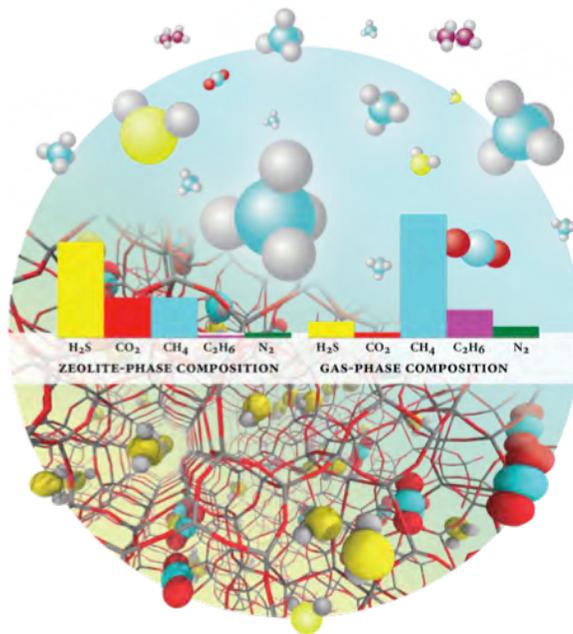


Fig. 2: Illustration of an adsorption-based process for the removal of H₂S and CO₂ from sour natural gas.

In collaboration with the Materials Project, the NMGC has developed the *Nanoporous Materials Explorer* [https://materialsproject.org/wiki/index.php/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. NMGC researchers have created a database of computation-ready experimental (CoRE) MOF structures [<http://gregchung.github.io/CoRE-MOFs/>] and developed a Python tool for the computation of mixture adsorption isotherms using data from unary isotherms and the ideal adsorbed solution theory [<https://github.com/CorySimon/pyIAST>]. The collaborative NMGC activities have also strengthened the training of a large number of postdoctoral associates and of graduate, undergraduate, and high school students.

Conventional approaches aimed at discovery and development of nanoporous materials for storage, separation, and catalysis applications are hampered by the large number of already synthesized zeolites and MOFs, the much larger number of hypothetical zeolite and MOF structures, and the large number of potential applications, i.e., it would be impossible to synthesize a significant fraction of these materials and to characterize their performance for a variety of applications. The MGI approach employed by the NMGC allows one to explore thousands of materials for a plethora of applications in a relatively short time frame. NMGC research has led to the discovery of zeolites for extraction of ethanol from aqueous solution (Patent Application PCT/US15/41566), for hydrocarbon dewaxing (Patent Application PCT/US15/41544), and for sweetening of highly sour natural gas mixtures (Provisional Patent Application 62235870), and of MOFs for Kr/Xe and CO₂/H₂ separation and for ethane-to-ethanol conversion.

Over the next two years, 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.

Grant Number and Grant Title

DE-FG02-12ER16362 Nanoporous Materials Genome: Methods and Software
to Optimize Gas Storage, Separation, and Catalysis

Postdoc(s): Peng Bai, Yongchul Chung, Bahman Elyassi, Laura Fernandez, Emmanuel Haldoupis, Mustafa Kucukkal, Rachel Klet, Samuel Keasler, Kyuho Lee, Wei-Guang Liu, Andreas Mavrantakis, Remi Maurice, Liang R. Niestemski, Abdullah Ozkanlar, Manuel Ortuno, Samuel Odoh, Nora Planas, Payal Parmar, Shuanglin Qu, Pere Miro, Dai Tang, Jeffrey Van Humbeck, Konstantinos Vogiatzis, Jian Wu, Xuefei Xu

Student(s): Joshua Borycz, Philip Bunting, Yi Bao, Zachary Brown, Nicholas Blando, Jeff Camp, Yuexing Cui, Allison Dzubak, Lucy Darago, Miguel Gonzalez, Huiliang Shi, Josh Howe, William Isley, Mi Young Jeon, Olga Karagiardi, Aaron League, Jason Lee, Marianne Lalonde, Michelle Liu, Shaohong Li, Sijie Luo, Xi Li, Greg Man, Narbe Mardirossian, Sara Marquez, Dalar Nazarian, Julia Oktawiec, Doug Reed, N. Dilip Rangnekar, Cory Simon, Jeffrey Sung, Mansi Shah, Meera H. Shete, Samuel Stoneburner, Pragma Verma, Bo Wang, Chun-Hung Wang, Jon Witte, Dianne Xiao, Hongda Zhang, Tiechen Zhou

Ten Publications Acknowledging this Grant (selected from 75 publications)

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Modeling Catalysis on Metal-Organic Framework Nodes

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Abstract

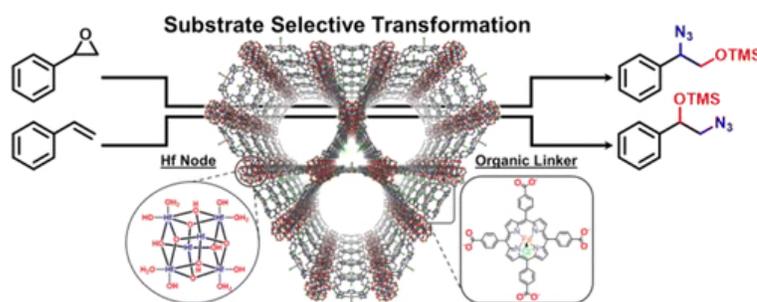
Metal-organic frameworks (MOFs) offer the potential to combine some of the best features of heterogeneous and homogeneous catalysts. In the former arena, they are robust crystalline solids whose nodes may be metal-oxide clusters directly analogous to the typical inert supports that are employed in heterogeneous reactor vessels; in the latter arena there is the potential to use the isolation of the individual nodes one from another to prevent agglomeration and sintering of deposited catalytic atoms or clusters so as to achieve precise control over catalytic functionality, as is typical in homogeneous catalysis.

Working with experimental partner groups who bring synthetic and characterization expertise to our collaboration, we, together with other theory groups at Minnesota, have undertaken the analysis of a number of reactions catalyzed by the deposition of active sites (sometimes by gas-phase atomic layer deposition (ALD)),

sometimes by solution processing) onto MOF nodes, seeking to assess molecular and electronic structures, as well as reaction energetics, at the atomic level of detail. Significant challenges are associated with modeling relevant size scales, as well as the complexities of the experimental deposition process and the potential heterogeneity that may be entailed under unfavorable circumstances.

Considering reactions of potential relevance to the liquefaction of shale-gas reactants (supported by the Inorganometallic Catalyst Design Center, an Energy Frontier Research Center), we have examined ALD processes not only to deposit reactive metals, but also other supporting layers to achieve core-shell-like supports. We have demonstrated hydrogenation of ethylene as well as its dimerization with deposited Ir atoms and Ni atoms. Insights into relevant species and reaction paths have been gained, although more is needed to fully characterize the range of potential reactive species.

Considering more complex reactions designed to exploit multiple catalyst sites for *different* reactions within a MOF (supported by the Nanoporous Materials Genome Center), we have explored tandem catalysis in the MOF Hf-PCN-222, which epoxidizes vinyl groups and nucleophilically opens the resulting epoxides with high degrees of stereoselection. Intriguing opportunities to inform future catalyst design arise when considering the varying levels of control associated with these different systems, and we continue to look for means to move theory into a more predictive mode in order to accelerate synthetic design.



Grant Numbers and Grant Titles

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Postdocs (*Cramer group only*): Andreas Mavrandonakis, Manuel Ortuño, Sonny Qiu, Samat Tussupbayev

Students (*Cramer group only*): Will Isley, Aaron League

Publications

Beyzavi, M. H.; Klet, R. C.; Tussupbayev, S.; Borycz, J.; Vermeulen, N. A.; Cramer, C. J.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. "A Hafnium-based Metal–Organic Framework as an Efficient and Multi-functional Catalyst for Facile CO₂ Fixation and Regioselective Epoxide Activations" *J. Am. Chem. Soc.* **2014**, *136*, 15861 (doi:10.1021/ja508626n)

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Sampling Rare Events In Aqueous Systems Using Molecular SimulationsRyan DeFever¹, Walter Hanger², Amy Apon³, Linh Ngo⁴, and Sapna Sarupria¹¹Chemical and Biomolecular Engineering²Electrical and Computer Engineering³School of Computing⁴Cyberinfrastructure Technology Integration

Clemson University, Clemson SC

Rare events correspond to events that occur with low frequency. These events usually have potentially widespread impact and are therefore, events of considerable interest. At the molecular level, important transitions such as self-assembly and phase transitions in aqueous systems are rare events – meaning that the waiting time involved to observe even a single event is larger than the typical timescales accessible to molecular simulations. This hinders the ability to calculate the kinetics of these transitions. In our proposed research we focus on developing novel methods and the software infrastructure that implements these methods effectively on high performance computing systems to enable the studies of rare events in molecular simulations. While we motivate our work through studies of heterogeneous ice nucleation, the methods and software infrastructure developed here is applicable to any system.

Proposed work: In our proposed research, we combine state-of-the-art tools in molecular simulations, BigData and multitasking handling systems, and visualization techniques to develop a robust infrastructure for performing rare event simulations. We specifically build on a method called forward flux sampling (FFS). We propose to develop a multidimensional FFS method (nDFFS) that will enable us to address the issue of finding appropriate order parameters for any given transition on-the-fly. This methodology has the potential of addressing the major knowledge gap – lack of an ability to find reaction coordinates on-the-fly – in simulations of rare events.

Previous Results: In our previous work, we have developed a software program called Scalable Forward Flux Sampling (ScaFFS) to perform large scale forward flux sampling (FFS) calculations efficiently and effectively in high performance computing (HPC) infrastructure. In FFS, transitions from state A to state B are sampled through several intermediate transitions by dividing the phase space between A and B into interfaces. Several simulations are initiated at a given interface and configurations from those which reach the next interface are harvested. Then several simulations are initiated from the harvested configurations at the “new” interface to obtain configurations for the next interface. This process is continued until the final state is reached. While the process is straightforward, the application of the method to realistic systems can result in large number of simulation jobs and huge amount of data. To handle these large jobs and amounts of data effectively, we have developed ScaFFS.

ScaFFS represents a collaboration of state-of-the-art techniques in molecular simulations with those from Big Data to enable rare event simulations at massive scales. ScaFFS is designed to be adaptive, data-intensive, high-performance, elastic, and resilient. ScaFFS uses Hadoop in a novel manner to handle the millions of simulations performed and files generated in FFS calculations. Through this approach we have been able to address all the challenges listed above. In addition, we do this in such a manner that the user only deals with the details of their FFS simulation. This is analogous to the MD software programs, where you only feed the details of the simulation system and parameters without worrying about how the parallelization would occur or what format the files can be written as. We use a similar approach here.

Advantages of ScaFFS (also summarized in Fig. 1):

- Able to decide interfaces on-the-fly based on user specified criteria.
- There is no need for modification to the source codes for simulation i.e. if MD is being performed then no source code modification of GROMACS/LAMMPS or any other software is required.
- The status of each job is tracked and if needed, failed jobs are automatically re-run.
- Each file is tracked and intermediate data is not stored. However, if needed, the user can specify to retrieve it.
- The jobs are distributed over the nodes efficiently.
- ScaFFS is capable of restarting the FFS simulation in case the calculations run over wall-time such that no data is lost.
- The biggest advantage from a user perspective is that the user needs to only modify one file that specifies all details about the FFS parameters and details of file storage etc.
- ScaFFS has been tested extensively in both the institutional shared HPC environment at Clemson University as well as the publicly available HPC resources at XSEDE.



Figure 1: User friendly features of ScaFFS

Specific goals of proposed research:

- Integration of nDFFS into ScaFFS: We will develop and integrate nDFFS method into ScaFFS thereby enabling us to run large scale simulations required to validate nDFFS on realistic systems.
- Validation of nDFFS method based on simulations of crystallization of Lennard Jones liquid: This system has been studied widely and the appropriate reaction coordinates for this transition have been determined based on other techniques.
- Heterogeneous ice nucleation: Specifically, we will study the nucleation of ice near silver iodide surfaces. This provides a “realistic” system for testing the nDFFS method. Finding the appropriate reaction coordinate will improve the efficiency of FFS significantly and will become an important aspect as the systems and processes get more complex.

The successful completion of our work will enable simulations to study the kinetics of complex processes -- an aspect that has greatly lagged behind so far. While our work is motivated by phase transitions and assembly processes in aqueous systems, rare events are relevant to a broad span of fields including telecommunications, finance, insurance, physics, chemistry, and biology. The techniques and software program developed here can easily be adapted to these systems. Therefore, our methodology and the simultaneous development of the software infrastructure to implement these methods will provide the broad scientific community with powerful tools to study previous inaccessible processes through molecular simulations.

Grant Number and Title:

DE-SC0015448 Sampling Rare Events In Aqueous Systems Using Molecular Simulations

Students: Ryan DeFever (PhD student)

Fluctuations and Phenomena

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Abstract

The objective of this project is to advance molecular simulation techniques to better understand fundamental properties and processes in complex environments, such as condensed phases and interfaces. We have focused on complexity associated with broken symmetries corresponding to vacuum/liquid, liquid/solid, and liquid/liquid interfaces or highly concentrated electrolytes. The characterization of these systems requires a description of molecular interaction that is more robust than what is required to describe bulk, homogeneous systems and requires understanding the balance between descriptions of molecular interaction and complexity. We will continue to develop a systematic connection between models of molecular interactions and collective behavior of molecular systems. This will lead to an improved knowledge of complex collective behavior on a macroscopic scale. The balance between representations of molecular interaction, statistical mechanical sampling techniques, efficiency and accuracy is required. Towards these ends, we have explored the influence of broken symmetry on equilibrium fluctuations.⁴ We explored how a simple hydrophobic hard sphere disrupts the hydrogen bonding structure and the resulting electric field and polarization density distributions. Future efforts will extend this work to dynamic response and perturbations that push the system beyond linear response. There is a dynamic consequence associated with the tuning of “frustrated charge models” to recover only equilibrium fluctuations.² Future work will focus on this by exploring the water exchange process about ions comparing the dependence on the descriptions of molecular interaction.^{1,2}

We will continue to develop a systematic connection between models of molecular interactions and collective behavior of molecular systems. This will lead to an improved knowledge of complex collective behavior on a macroscopic scale. The balance between representations of molecular interaction, statistical mechanical sampling techniques, efficiency and accuracy is required. Towards these ends, we have explored the influence of broken symmetry on equilibrium fluctuations.⁴ We explored how a simple hydrophobic hard sphere disrupts the hydrogen bonding structure and the resulting electric field and polarization density distributions. Future efforts will extend this work to dynamic response and perturbations that push the system beyond linear response. There is a dynamic consequence associated with the tuning of “frustrated charge models” to recover only equilibrium fluctuations.² Future work will focus on this by exploring the water exchange process about ions comparing the dependence on the descriptions of molecular interaction.^{1,2}

In our studies we search for the appropriate amount of explicit treatment of electronic structure that allows for efficient sampling of a statistical mechanical ensemble of a system of interest. We have established that a Density Functional Theory (DFT) description of molecular interaction provides a quantitative representation of the short-range interaction and structure when compared to Extended X-ray Absorption Fine Structure (EXAFS) measurements. To do this we continue to develop our MD-EXAFS approach.^{5,6,7} This approach has allowed us to characterize in detail the complex equilibrium associated with the dissociation of HCl in water,⁵ and gives us confidence that the short range molecular phenomena is effectively and accurately described by DFT electronic structure coupled to statistical mechanical sampling. Much of our future efforts will concentrate on characterizing fluctuations, taking advantage of effective potentials of mean force and linear response kernels from density, charge and

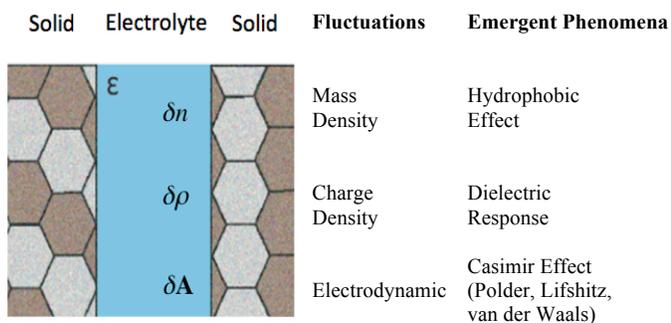


Figure 1. The connection between fluctuations and phenomena.

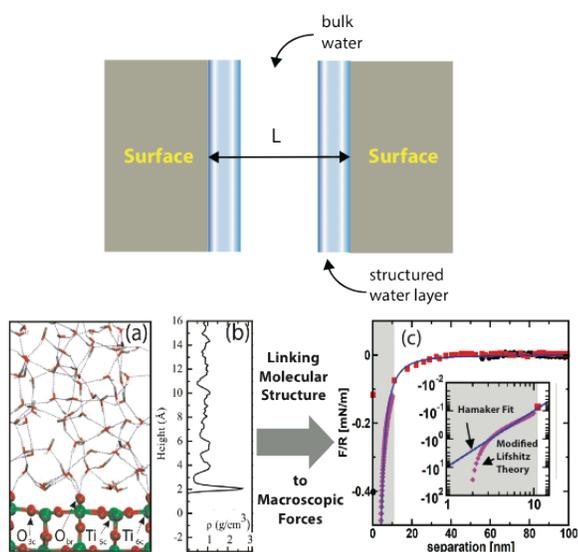


Figure 2. (top) Schematic of the structured water layer in the vicinity of two interfaces. (bottom) (a) Water on TiO₂ yielding a solvent response (b) that is incorporated into a modified Lifshitz theory for the forces between TiO₂. (c) Depicts how our modified Lifshitz theory (magenta), with no adjustable parameters, tracks the experimental Hamaker fit (blue) down to 4 nm.

electromagnetic fluctuations. [See Figure 1.]

To better understand collective many-body phenomena we are exploring the connection between: 1) the many-body decomposition of atom based potentials, 2) the partitioning of a system into an explicit sub-system and a bath and 3) transport and fluctuations of macroscopic mass, charge, and energy field densities, as well as electrostatic and electrodynamic fields. We expect that the relation between these frameworks will need to be better understood in order to impact understanding of more complex phenomena. We explored the consequences of solvent structure on the electrodynamic field fluctuations and consequently the Lifshitz force between the two solid surfaces.³ In this work we considered the water density responding to mica, TiO₂, and gold. In future efforts, we will close the connection between molecular and continuum descriptions of dispersion. [See Figure 2.]

Grant Numbers and Grant Titles: Molecular Theory and Modeling, PNNL, FWP # 16249

Postdoc(s): previous work: M. Baer (Pauling Post Doc), future work: T. Duignan and H. V. Annappureddy

Publications Acknowledging this Grant in the last 3-4 years:

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Accurate and systematically improvable density functional theory embedding for correlated wavefunctions

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Abstract:

The observation that many chemical processes are governed by changes within a localized subsystem has motivated the development of embedding strategies within the density functional theory (DFT) framework. In these approaches, an electronic structure calculation on a chemical system is partitioned into calculations on two subsystems: subsystem A, which is treated using an accurate wavefunction theory (WFT), and subsystem B, which is treated using the more computationally efficient DFT method. We describe a recently developed projection method that provides a straightforward, rigorous, and accurate approach to performing WFT-in-DFT embedding. We demonstrate that errors associated with WFT-in-DFT embedding can be systematically understood and controlled, and we demonstrate the new embedding approach for multi-reference calculations on conjugated systems and transition-metal complexes, including those related to hydrogen evolution catalysis and small-molecule activation.

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. In addition, we are applying the developed methodology to study excited-state processes relevant to photovoltaic applications.

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 the SciDac effort facilitate efficient implementations of the new theoretical approaches developed for multiple interacting states and strongly correlated systems.

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 2015-2016, the DOE support was acknowledged in nine papers.¹⁻⁹ One more paper is submitted for publication. Some of the recent results are highlighted below.

2.1 Dyson orbitals and absolute cross sections for photoionization

The calculation of absolute total cross-sections requires accurate wave functions of the photoelectron and of the initial and final states of the system. The essential information contained in the latter two can be condensed into a Dyson orbital:

$$\phi^d(1) = \sqrt{N} \int \Psi^I(1, 2, \dots, N) \Psi^F(2, \dots, N) d2 \dots dN \quad (1)$$

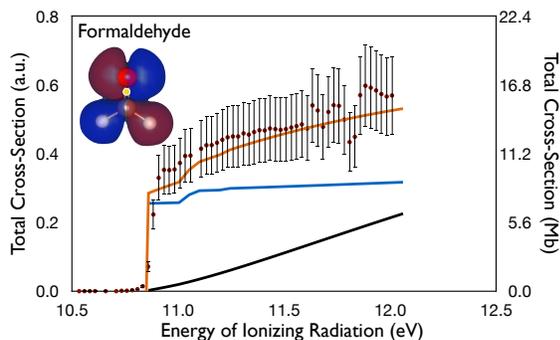


Figure 1: Absolute photoionization cross-section (in atomic units) for formaldehyde. Red dots show the experimental values. Blue and black lines correspond to the cross-sections computed using the Coulomb ($Z=1$) and plane ($Z=0$) waves, respectively. Orange line denotes cross-sections computed using the Coulomb wave with $Z=0.25$. Effective charge $Z < 1$ accounts for the non-point charge distribution in the polyatomic cation.

We employed correlated Dyson orbitals and tested approximate treatments of the photoelectron wave function, that is, plane and Coulomb waves, by comparing computed and experimental photoionization/photodetachment spectra.⁷ We found that in anions, a plane-wave treatment of the photoelectron provides a good description of photodetachment spectra. For photoionization of neutral atoms or molecules with one heavy atom, the photoelectron wave function must be treated as a Coulomb wave to account for the interaction of the photoelectron with the $Z=+1$ charge of the ionized core. For larger molecules, the best agreement with experiment is often achieved by using a Coulomb wave with a partial (effective) charge smaller than unity, as illustrated in Fig. 1. This likely derives from the fact that the effective charge at the centroid of the Dyson orbital, which serves as the origin of the spherical wave expansion, is smaller than the total charge of a polyatomic cation. The results suggest that accurate molecular photoionization cross-sections can be computed with a modified central potential model which accounts for the non-spherical charge distribution of the core by adjusting the charge in the center of the expansion. This simple approach is implemented in the *ezDyson* code, which is a free software available for download from the *iOpenShell* website; it provides a convenient tool for quick evaluations of the electronic cross-sections. Currently, we are developing a variational procedure for determining optimal Z from electronic structure calculations.

2.2 Methods for strongly correlated systems and applications to singlet fission

Singlet fission (SF), a process in which one singlet excited state is converted into two triplet states, and the reverse process, triplet-triplet annihilation (TTA), are of interest in the context of organic photovoltaic technology. From the electronic structure point of view, SF and TTA involve non-adiabatic transitions between regular excitonic states (delocalized states derived from the local S_1 states of the individual chromophores, with some admixture of charge resonance configurations) and multi-excitonic (ME) states. The latter can be described as singlet-coupled multiple local triplet states residing on the neighboring chromophores. Thus, these states feature tetraradicals character. Consequently, their description requires methods for strongly correlated systems. We have been successfully employing spin-flip methodology to tackle these states.

To derive insight from electronic structure calculations, one would like to be able to analyze the character of complicated multi-configurational wave functions in terms of local excitations, charge-resonance, and ME character. Such wave function analysis is also important for developing and validating model Hamiltonians (e.g., excitonic models). We have introduced a new method for quantifying the contributions of local excitation, charge resonance, and ME configurations in correlated wave functions of bi- and multi-chromophoric systems.^{3,4} The approach relies on

fragment-localized orbitals and employs spin correlators.^{3,4} The cumulant analysis can also be employed to analyze electronic structure of other strongly correlated systems, such as molecular magnets.

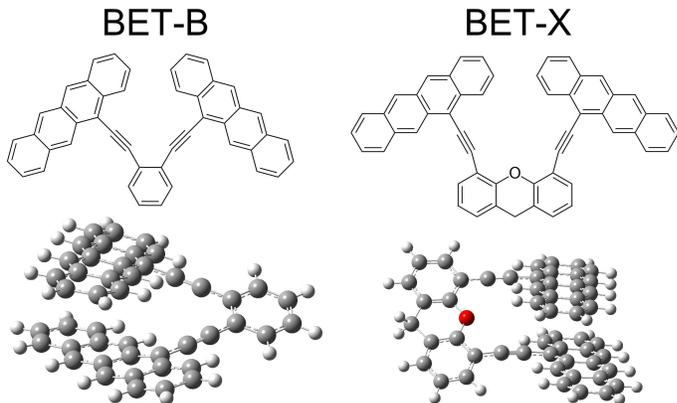


Figure 2: Covalently linked cofacial alkynyltetracene dimers from Ref. 8. The dimer on the left panel (BET-B) shows fast end efficient SF, whereas the structure on the right (BET-X) does not produce triplets. The calculations suggested excimer formation as a possible explanation for this behavior. The calculations of energies and couplings at excimer structures also provide an indirect support for Schmidt’s hypothesis, which attempts to reconcile the observed temperature-independent rate of the ME state formation in solid tetracene with endoergicity of the SF process.

Motivated by vigorous experimental efforts, we have investigated electronic structure factors in covalently linked tetracene dimers.^{8,9} Using covalent linkers, relative orientation of the individual chromophores can be controlled, maximizing the rates of SF. Structures with coplanar and staggered arrangements of tetracene moieties (see Fig. 2) have been found to exhibit rather different photochemical behavior.⁸ The electronic structure calculations and three-state kinetic model for SF rates provided explanations for experimentally observed low SF yields in coplanar dimers and efficient SF in staggered dimers.^{8,9} The calculations illuminated the role of the excimer formation in SF process. The structural relaxation in the S_1 state leads to the increased rate of the ME state formation, but impedes the second step, separation of the ME state into independent triplets. The slower second step reduces SF yield by allowing other processes, such as radiationless relaxation, to compete with triplet generation. The calculations of electronic couplings also suggested an increased rate of radiationless relaxation at the excimer geometries. Thus, the excimer serves as a trap of the ME state. We also investigated the effect of covalent linkers on the electronic factors and SF rates. We found that in all considered structures, the presence of the linker leads to larger couplings, however, the effect on the overall rate is less straightforward, since the linkers generally result in less favorable energetics. This complex behavior once again illustrates the importance of integrative approaches that evaluate the overall rate, rather than focusing on specific electronic factors such as energies or couplings.

2.3 Developing efficient tools for high-performance computing

We have extended our *libtensor* library to massively parallel platforms and to GPUs. *Libtensor* is an open-source general tensor library designed for high-performance implementations of many-body theories. The library features a convenient C++ API facilitating the implementation of complicated equations. The original version was multi-core parallel. We extended the library to distributed massively parallel architectures via the fusion with *CYCLOPS*. The code shows good scaling and enables large-scale coupled-cluster and equation-of-motion calculations. The paper presenting initial benchmarks has been submitted for publication.

We also developed a new hardware-agnostic contraction algorithm for handling contractions

of tensors of arbitrary symmetry and sparsity. The algorithm is implemented as a stand-alone open-source code *libxm* and is also integrated with *libtensor*, and with the *Q-Chem* quantum chemistry package. The new code enables canonical all-electron coupled-cluster and equation-of-motion coupled-cluster calculations with single and double substitutions with over 1,000 basis functions on a single quad-GPU machine. These results are being finalized for publication.

3 Current developments and future plans

In the near future, we plan to complete benchmarking of the new tensor contraction algorithm and publish the results. Our renewal proposal (2016-2019) included the following projects: (i) investigating spin-forbidden channels in combustion; (ii) implementing non-adiabatic couplings within EOM-CC; (iii) validating the theory for calculating ionization/detachment cross-sections; (iv) including contributions from resonance channels to cross-sections; (v) developing theory and computational tools for modeling XAS. Due to a significant budget cut, we anticipate that the progress will be slow. In the near future, we will primarily focus on topics (ii) and (iii).

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Development of new density functionals and new methods for analysis of convergence of ab initio molecular dynamics simulations.

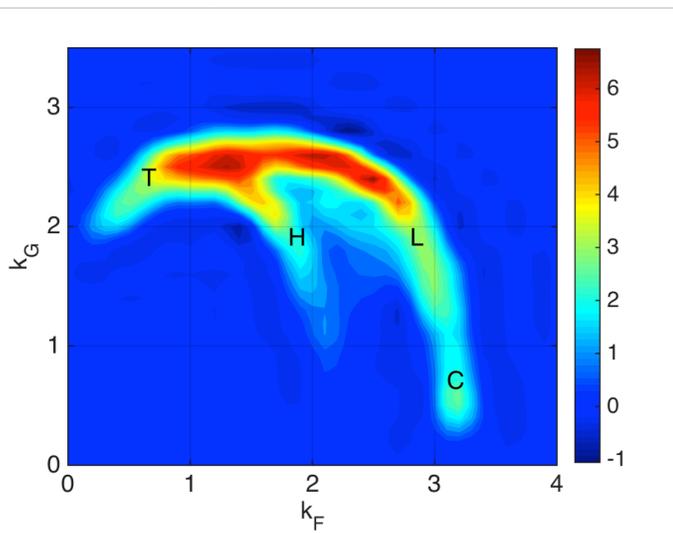
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Abstract

We describe a method, that we call data projection onto parameter space (DPPS), to optimize an energy functional of the electron density, so that it reproduces a dataset of experimental magnitudes. Our scheme, based on Bayes theorem, constrains the optimized functional not to depart unphysically from existing ab initio functionals. The resulting functional maximizes the probability of being the "correct" parametrization of a given functional form, in the sense of Bayes theory. The application of DPPS to water sheds new light on why density functional theory has performed rather poorly for liquid water, on what improvements are needed, and on the intrinsic limitations of the generalized gradient approximation to electron exchange and correlation. Finally, we present tests of our water-optimized functional, that we call vdW-DF-w, showing that it performs very well for a variety of condensed water systems.



Histogram of the electron density of the water molecule, in the equilibrium geometry, as a function of wavevectors $k_F = (3\pi^2\rho)^{1/3}$ and $k_G = |\nabla\rho|/\rho$. The labels C, H, L, and T indicate regions of parameter space dominated by the real-space regions of the oxygen core, hydrogen atoms, lone pairs, and electron tails, respectively. Atomic units are used.

In a second part, we present a method to evaluate the convergence of different parameters in ab initio molecular dynamics (AIMD). Monitoring convergence, as a function of basis set size and other precision parameters, is a necessary but costly process. It generally involves a new simulation for each parameter value, whose comparison is hindered by the statistical errors of each simulation. We describe an efficient method to monitor

convergence, using simple ideas from perturbation theory and thermodynamic integration. It involves comparing results with different parameters, for a moderate set of snapshots taken from a single simulation. We show how the convergence of many thermodynamic and structural properties can be accurately assessed as a function of typical precision parameters of AIMD simulations. While the changes of convergence tests are generally small, we show that our technique is useful to address even much larger changes, like those involved in comparing different electron density functionals.

Grant Numbers and Grant Titles

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Student(s): Michelle Fritz, Dan Elton, Adrian Soto-Cambres

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Local order of liquid water at metallic electrode surfaces Luana Pedroza, A. Poisier and M. V. Fernández-Serra, *J. Chem. Phys.* 142, 034706 (2015)

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Temperature and composition dependence of short-range order and entropy, and statistics of bond length: the semiconductor alloy $(\text{GaN})_{1-x}(\text{ZnO})_x$

Jian Liu, Luana S. Pedroza, Carissa Misch, Maria V. Fernández-Serra, Philip B. Allen, J. Phys. Cond. Matter, J. Phys.: Condens. Matter 26, 274204 (2014).

Symmetry Projected Coupled Cluster Theory

Gustavo E. Scuseria

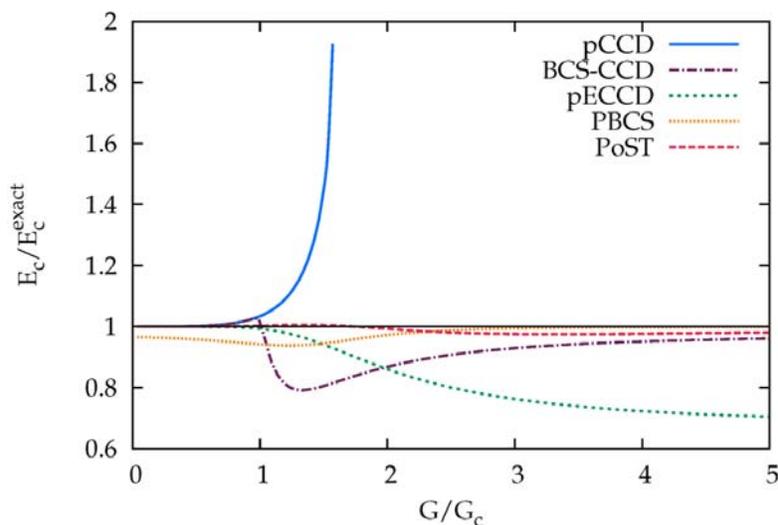
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Abstract

A precise accounting for electronic correlation effects is necessary for quantum mechanical calculations to reliably yield accurate results in molecular and solid-state systems. Correlation can be conceptually divided into weak correlations due to electrons avoiding one another because of the repulsive Coulombic interaction, and strong correlations which arise from quasi-degeneracies. Weak correlations can be handled by expansion about a mean-field reference state, while the hallmark of strong correlation is that the mean-field picture is qualitatively incorrect. Consequently, systems for which both kinds of correlation are important are exceptionally difficult to treat. Unfortunately, such problems are also ubiquitous.

In this proposal, we are exploring novel route toward combining techniques developed over the years to describe these two separate kinds of correlation into one powerful tool capable of treating all correlation effects on an equal footing. Strong correlations are taken into account by symmetry-projected mean-field methods, and the residual weak correlations are included using coupled cluster theory. We are implementing and testing the basic theory and plan to extend it to the calculations of properties, energy derivatives, and excited states. The combination of symmetry-projected mean-field techniques on the one hand and coupled cluster on the other will greatly extend the ability of quantum chemistry to accurately describe important physical and chemical processes, ranging from catalysis to superconductivity.

In this presentation I will discuss a novel theory based on a general polynomial ansatz of non-exponential type that is similar in spirit to single-reference coupled cluster doubles. It describes static and strong correlations quite accurately by incorporating symmetry projected collective states. The model, christened Polynomial Similarity Transformation (PoST), can be viewed as an interpolation between coupled cluster doubles (CCD) and symmetry projected Hartree-Fock-Bogoliubov. From the CCD perspective, the theory incorporates disconnected terms that model the effect of higher cluster operators. But fundamentally, the theory stands on its own as an effective two-body renormalization based on non-unitary similarity transformations. Mathematical details about the theory and our first results can be found in the preprint posted here: <http://arxiv.org/abs/1512.06111>



Grant Numbers and Grant Titles

DE-SC0001474 Computational and Theoretical Chemistry

Accurate Ground and Excited States via Symmetry Projection Combined with Coupled Cluster Theory

Postdoc(s): Thomas M. Henderson, Matthew R. Hermes

Ten Publications Acknowledging this Grant

1. Multi-reference symmetry-projected variational approaches for ground and excited states of the one-dimensional Hubbard model, R. R. Rodríguez-Guzmán, C. A. Jiménez-Hoyos, R. Schutski, and G. E. Scuseria, *Phys. Rev. B* **87**, 235129 (2013).
2. Entanglement and polyradical character of polycyclic aromatic hydrocarbons predicted by projected Hartree-Fock theory, P. Rivero, C. A. Jiménez-Hoyos and G. E. Scuseria, *J. Phys. Chem. B* **117**, 12750-12758 (2013).
3. Predicting singlet-triplet energy splittings with projected Hartree-Fock methods, P. Rivero, C. A. Jiménez-Hoyos, and G. E. Scuseria, *J. Phys. Chem. A* **117**, 8073-8080 (2013).
4. Multi-component symmetry-projected approach for molecular ground state correlations, C. A. Jiménez-Hoyos, R. Rodríguez-Guzmán, and G. E. Scuseria, *J. Chem. Phys.* **139**, 204102 (2013).
5. Excited electronic states from a variational approach based on symmetry-projected Hartree-Fock configurations, C. A. Jiménez-Hoyos, R. Rodríguez-Guzmán, and G. E. Scuseria, *J. Chem. Phys.* **139**, 224110 (2013).
6. Quasiparticle coupled cluster theory for pairing interactions, T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, *Phys. Rev. C* **89**, 054305 (2014).
7. Analytic energy gradient for the projected Hartree-Fock method, R. Schutski, C. A. Jiménez-Hoyos, and G. E. Scuseria, *J. Chem. Phys.* **140**, 204101 (2014).
8. Variational description of the ground state of the repulsive two-dimensional Hubbard model in terms of non-orthogonal symmetry-projected Slater determinants, R. R. Rodríguez-Guzmán, C. A. Jiménez-Hoyos, and G. E. Scuseria, *Phys. Rev. B* **90**, 195110 (2014).
9. Cluster-based mean-field and perturbative description of strongly correlated fermion systems: Application to the one- and two-dimensional Hubbard model, C. A. Jiménez-Hoyos and G. E. Scuseria, *Phys. Rev. B* **92**, 085101 (2015).
10. Polynomial Similarity Transformation Theory: A smooth interpolation between coupled cluster doubles and projected BCS applied to the reduced BCS Hamiltonian, M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, <http://arxiv.org/abs/1512.06111>

Next generation molecular dynamics using graph-based electronic structure theoryAnders M. N. Niklasson

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Abstract

Molecular dynamics simulations, where the forces are calculated on the fly from the electronic structure, are limited either to fairly small systems sizes or short simulation times. Recently we have found that graph theory provides a very efficient framework to calculate the electronic structure. The methodology combines a well-controlled (automatically tunable) numerical accuracy and a low computational cost with a natural low-communication parallelism, addressing some significant shortcomings of linear scaling electronic structure theory. Together with our development of a next generation quantum based molecular dynamics, which combines some of the most

powerful features of Car-Parrinello and regular Born-Oppenheimer molecular dynamics, the graph-based approach provides stable, highly accurate, and long-term energy conserving simulations within a highly scalable, low pre-factor linear scaling effort. Apart from quantum based molecular dynamics simulations, a number of applications can take direct advantage of our new formalism, including, for example, constrained and excited state molecular dynamics for charge transfer and photovoltaic systems as well as molecular dynamics driven sampling techniques. These developments are currently being pursued as well as some new opportunities that may enable a direct coupling of the evolution of the molecular trajectories to an on-the-fly spin dynamics.

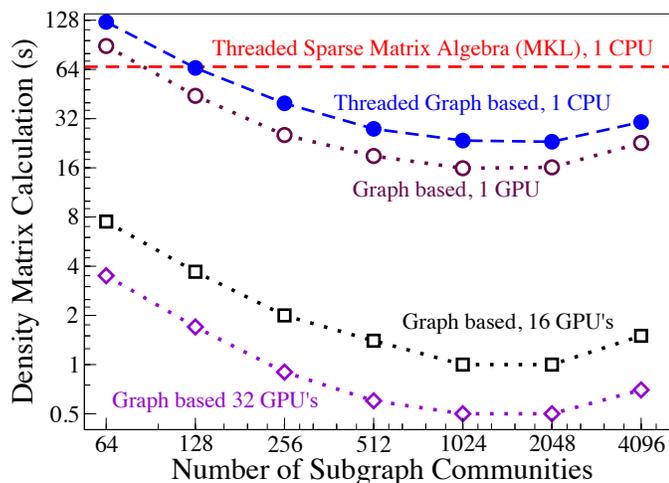


Figure 1 Time to calculate the density matrix within density functional tight-binding theory for a system of polyalanine in water (19,945 atoms) as a function of the number of partition-optimized subgraph communities using linear scaling sparse matrix algebra in comparison to our highly scalable graph-based electronic structure theory.

**FWP # LANL2014E8AN:
Next Generation First Principles Molecular Dynamics**

PI: Anders M.N. Niklasson

Publications Acknowledging this Grant in 2011-2015

- 1) A.M.N. Niklasson and M.J. Cawkwell, Generalized extended Lagrangian Born-Oppenheimer molecular dynamics, *J. Chem. Phys.* **2014**, 141, 164123.
- 2) P. Souvatzis and A.M.N. Niklasson, “First principles molecular dynamics without self-consistent field optimization”, *J. Chem. Phys.* **2014**, 140, 044117.
- 3) E. H. Rubensson and A.M.N. Niklasson, “Accelerated density matrix expansions for Born-Oppenheimer molecular dynamics”, *SIAM J. Sci. Comput.* **2014**, 36, B147-B170.
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COMPUTATIONAL AND THEORETICAL CHEMISTRY PROGRAM

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The work described in this report was enabled by our algorithms for constructing quasi-diabatic representations of adiabatic potential energy surfaces (PESs) coupled by conical intersections, for both bound (used in our treatments of nonadiabatic photoelectron spectroscopy) and dissociative (used to treat nonadiabatic photodissociation) systems.

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

WORK COMPLETED.

A. Representing PESs coupled by conical intersections for molecules comprised of 10 to 15 atoms: $C_6H_5OH(\tilde{X}) + hv \rightarrow C_6H_5OH(\tilde{A}) \rightarrow C_6H_5O(\tilde{X}, \tilde{A}) + H$

The photodissociation of phenol, $C_6H_5OH(\tilde{X}^1A') + hv \rightarrow C_6H_5OH^* \rightarrow C_6H_5O(\tilde{X}^2B_1, \tilde{A}^2B_2) + H$ is a problem of considerable current interest. Our goal in this project was to enable nonadiabatic dynamics of unprecedented accuracy by constructing coupled diabatic state representations of the relevant adiabatic potential energy surfaces and their nonadiabatic interactions using exclusively electronic structure data, energies, energy gradients and derivative couplings of the highest quality. During the current performance period we have accomplished this goal, completing construction of a coupled diabatic state representation of the S_0, S_1, S_2 , states of phenol capable of describing the above noted photodissociation processes.¹ *Ab initio* electronic structure data for the 1,2,3,4¹A states was obtained exclusively from a multireference single and double excitation configuration intersection (MRCISD) expansion comprised of over 88 million configuration state functions (CSFs). Electronic structure data at ~7300 nuclear configurations was required to construct the H^d . In a subsequent paper² we showed how

the accuracy of the existing coupled diabatic surfaces could be improved by small shifts of two of the diabats. The shifts improved the energetics in the Franck-Condon region, the $T_0(S_1)$ is within 55 cm^{-1} of an accurate experimental value, without degrading the representations elsewhere. This representation of a three electronic state photodissociation process in a molecule with 33 degrees of freedom based exclusively on electronic structure data obtained from accurate MRCISD wave functions is unique and will provide unprecedented opportunities for studying nonadiabatic photodissociation.

In this regard, this representation is currently being used by Hua Guo's group at University of New Mexico to study the photodissociation process using fully quantum mechanical reduced dimensionality models. Studies incorporating the geometric phase effect in the adiabatic representation are also beginning.

Work in Progress/Future Work

A. Nonadiabatic Photoelectron Spectra

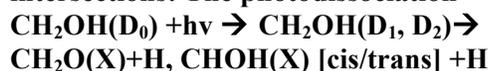
We are continuing our work in the area of nonadiabatic photoelectron spectroscopy investigating the photoelectron spectrum of cyclopentoxide which has been measured in Continetti's UC San Diego laboratory.³

Cyclopentoxide

During the previous performance period we established that cyclopentoxide, which can be viewed as a substitutional isomer of methoxy whose ground state is a Jahn-Teller distorted 2E state, has a low-lying excited state coupled to the ground state by a conical intersection seam.⁴ This, previously unanticipated, low-lying seam is expected to complicate considerably the description of the electron photodetachment spectrum of the precursor anion, cyclopentoxide. During the current performance period, we have advanced closer to our goal of simulating the low energy photoelectron spectrum of cyclopentoxide,

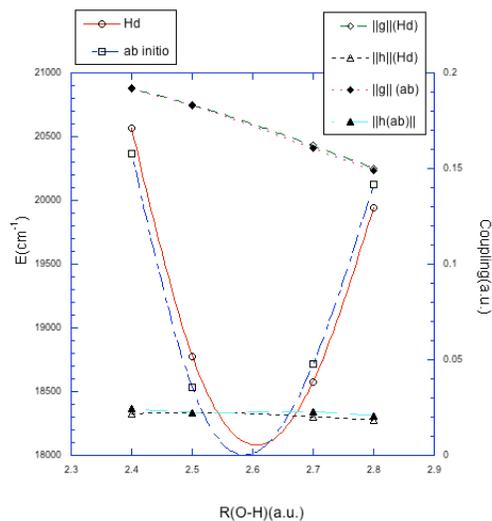
complementing the work of Continetti. Using an expansion of greater than 19 million CSFs, based on cc-p-VTZ basis sets on carbon and oxygen, and cc-p-VDZ basis sets on hydrogen, we are constructing a coupled diabatic state representation of the adiabatic potential energy surfaces and their nonadiabatic interactions in the full 39-dimensional internal coordinates space

B. Multichannel PESs coupled by conical intersections: The photodissociation



The captioned nonadiabatic photodissociation has been studied experimentally in Reisler's USC laboratory.⁵ The accurate simulation of this photodissociation process, requires construction of a coupled diabatic state representation of the adiabatic potential energy surfaces and their nonadiabatic interactions. This is a particularly challenging problem. Not only are three electronic states involved but three product channels, corresponding to the production of CH₂O or CHOH(cis/trans) must be simultaneously described.

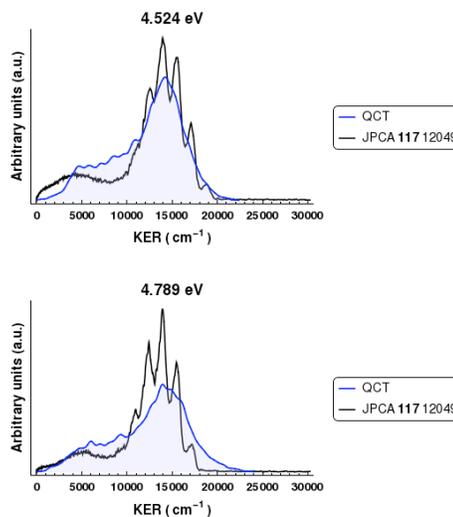
We are extending our previously published initial full 9 dimensional, 3 quasi diabatic state, representation of the D₀ and D₁ states⁶ to include D₂. The description is based exclusively on an MRCISD expansion of ~67 million CSFs which is capable of describing all channels in the above captioned reaction.



Conical intersections are key to the description

of the dissociation process providing valuable mechanistic insights into the nonadiabatic events. The figure above compares the *ab initio* and \mathbf{H}^d determined D₀ – D₁ seams in the vicinity of the minimum energy crossing point in the CH₂O-H dissociation channel. *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 a₀) was so included. The agreement between the \mathbf{H}^d and *ab initio* determined energies is seen to be excellent. Similarly good agreement is found for the \mathbf{g} and \mathbf{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,⁵.



in which CH₂O + H is the principal product. Note that each figure is based on five thousand trajectories which would not be possible using direct dynamics. An analysis of the trajectories shows that the slow hydrogens are produced in an indirect or quasi-statistical manner, with a hop to D₀ preceding a significant residence on D₀ prior to H dissociation. On the other hand, the fast hydrogens are produced by trajectories that, while they may oscillate on D₁ prior to a surface hop, following transfer to D₀ the H dissociates directly.

Representing Adiabatic Potential Energy Surfaces coupled by conical intersections

We close this report with a description of the algorithm we have developed, as part of this² and other funded research,⁷ 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 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 obtained from MRCISD wave functions using analytic gradient techniques. Using a recently reported² diabatic shifting approach energies obtained using the most accurate wave functions available can be incorporated into the fit.

(ii) The incorporation of energy gradient and derivative coupling 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-diabatic representations and provides for an accurate representation of the neighborhood of a conical intersection seam 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 representations for which 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.

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PUBLICATIONS ACKNOWLEDGING (EXCLUSIVELY) CURRENT DOE SUPPORT (2013-2016)

1. *Seams of Conical Intersections Relevant to the Quenching of $\text{OH}(A^2\Sigma^+)$ by Collisions with H_2* . Joseph Dillon and David R. Yarkony, J. Phys. Chem. A, 117, 7344-7355 (2013)

2. *On the Mechanism for the Nonadiabatic Reactive Quenching of $\text{OH}(A^2\Sigma^+)$ by $\text{H}_2(^1\Sigma_g^+)$. The Role of the 2^2A State*. Joseph Dillon and David R. Yarkony, J. Chem. Phys. **139**, 064314 (2013).

3. *On the Photoionization Spectrum of Propyne. A fully ab initio Simulation of the Low-Energy Spectrum including the Jahn-Teller Effect and the Spin-Orbit Interaction*. Sara Marquez, Joseph Dillon and David R. Yarkony, J. Phys. Chem. A. 117, 12002-12010 (2013)

4. *Full-dimensional quantum state-to-state non-adiabatic dynamics for photodissociation of ammonia in its A-band*. Changjian Xie, Jianyi Ma, Xiaolei Zhu, Dong Hui Zhang, David R. Yarkony Daiqian Xie and Hua Guo, J. Phys. Chem. Lett. **5**, 1055-1060 (2014).

5. *On the Electronic Structure of the Ground State of Cyclopentoxy. The Case for a Two Coupled State Description*

Christopher L. Malbon, David R. Yarkony and Xiaolei Zhu, *J. Mol. Spec.*, 311, 36-41 (2015)

6. *On the Nonadiabatic Photodissociation of the Hydroxymethyl Radical from the 2^2A State. Surface Hopping Simulations Based on a Full Nine Dimensional Representation of the $1,2,3^2A$ Potential Energy Surfaces Coupled by Conical Intersections*

Christopher L. Malbon and David R. Yarkony, *J. Phys. Chem. A* 119, 7498-7509 (2015)

7. *On the Elimination of the Electronic Structure Bottleneck in On the Fly Nonadiabatic Dynamics for Small to Moderate Sized (10-15 atom) Molecules Using Fit Diabatic Representations Based Solely on ab initio Electronic Structure Data: The Photodissociation of Phenol*

Zhu, X.; Yarkony, D. R. *J. Chem. Phys.* 144, 024105 (2016)

8. *An Improved Quasi-Diabatic Representation of the $1,2,3^1A$ Coupled Adiabatic Potential Energy Surfaces of Phenol in the Full 33 Internal Coordinates.*

Xiaolei Zhu, Christopher L. Malbon and David R. Yarkony, *J. Chem. Phys.* 144, xxxx (2016)

Molecular Dynamics Simulation on a Light-Harvesting Molecular Triad in Explicit Tetrahydrofuran Solvent Using Polarizable Force Fields

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Abstract

A light harvesting molecular triad is a synthetic molecule with covalent bonding between pyrrole-fullerene (C_{60}), diaryl-porphyrin (P), and carotenoid polyene (C) components. It is a donor-acceptor supramolecule that absorbs incident light in the visible region[1]. Charge separation upon electron excitation generates a giant dipole moment of ~ 150 Debye with a lifetime of ~ 300 ns[2]. However, its malleable conformation in solution prohibits its use for real-world applications. *The long-term goal of our research is to understand the relation between the distribution of the conformations of molecular triad that depends on solvent and its overall efficiency in charge transfer.*

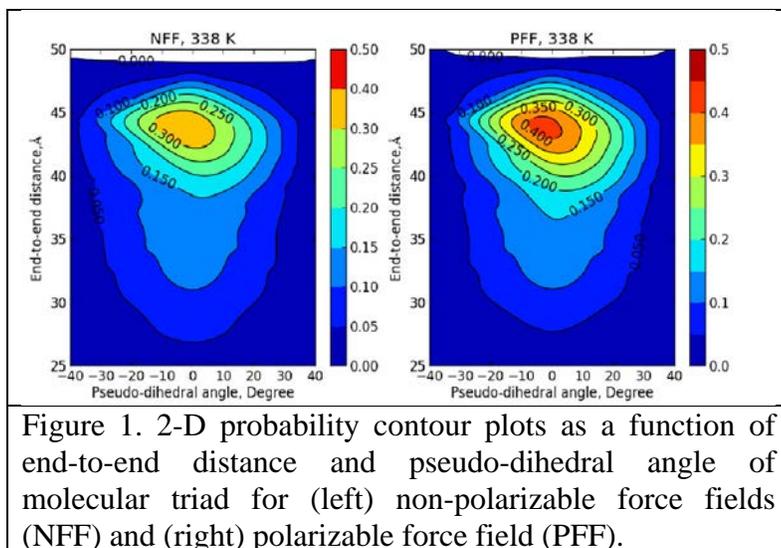


Figure 1. 2-D probability contour plots as a function of end-to-end distance and pseudo-dihedral angle of molecular triad for (left) non-polarizable force fields (NFF) and (right) polarizable force field (PFF).

Our group employed molecular dynamics simulations with non-polarizable force fields showed the structural stability of the triad for the ground and excited states [3-5]. Although the simulations with non-polarizable force fields describe the thermodynamics and structural properties of the triad well, they lack the effect of induced polarization that is critical to the charge transfer properties of organic photovoltaic (OPV) materials. This past year, we parameterized the polarizable force fields[6] for the individual component of the molecular triad as well as the THF solvent by matching their ensemble properties from simulations against the experimental measurements. We employed the Replica Exchange Molecular Dynamics simulations (REMD) to enhance the sampling of this very large system. We plotted the 2-D distribution plot with the end-to-end distance and the pseudo-dihedral angle of a molecular triad in Fig 1. The distribution of the triad from the simulations using the polarizable force fields is noticeably sharper than the non-polarizable ones. After the structural analysis, we found that the induced polarization stabilizes the rotational isomerization of the polyene chain that gives a sharp peak in Fig1.

Our next step is to develop the polarizable models for the excited states that dictate the efficiency or pathways of charge transfer in collaboration with Profs Barry Dunietz and Eitan Geva. The effect of the induced polarization and solvent chemical structure on the triad conformational landscape will be studied in details. The size of our simulations is exceptionally large that takes extraordinarily long time to converge. In order to expedite the simulation, we plan to compile the AMBER12 program with OpenACC to tap into the newly installed accelerators on the high performing computers from NERSC.

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Grant Numbers and Grant Titles

DE-SC0004832 Multiscale Investigation of Thermal Fluctuations on Artificial Photosynthetic

Postdoc: Oleg Starovoytov

1. G. Su, A. Czader, D. Homouz, G. Bernardes, S. Mateen, M.S.Cheung, "Multiscale simulation on a light-harvesting molecular triad", *J. Phys. Chem. B*. **116**, 8460–8473 (2012).
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4. O. Starovoytov, M.S. Cheung, "Simulations of molecular triad with polarizable force fields" to be submitted soon.

Koblar A. Jackson

Polarizability trends in clusters: measures of metallicity

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Abstract

Our research explores the physics and chemistry of atomic clusters, with a particular interest in cluster-based catalyst systems. Clusters are ultra-small particles containing up to only a few hundred atoms. At this sub-nanometer scale, nearly all the atoms are on the cluster surface and can participate in catalytic reactions. In contrast, most atoms in larger particles are locked away in the interior where they are unavailable for reactions. This makes clusters extremely “atom efficient” as catalysts, which can be valuable for expensive catalysts such as Pd and Pt. Another important feature of clusters is that their properties are size dependent. For example, Au and Ag are chemically inert as bulk metals but become catalytically active at small cluster sizes. The main thrusts of our program are therefore 1) to explore the evolution of cluster properties as a function of size and 2) to investigate the reactivity of model cluster-based catalyst systems and especially how that differs for smaller and larger clusters.

Recent work in our group has focused on the polarizability of clusters, *i.e.* the response of clusters to an applied electric field. We study this using density functional theory (DFT) calculations and a scheme for partitioning the response into charge transfer (metallic) and local dipole (dielectric) contributions. We find that clusters of metal atoms have a per atom charge transfer response that is identical to that of the corresponding bulk metal even at sizes as small as 10 atoms, with minor fluctuations at specific sizes that are related to electronic shell closings. This behavior appears universal, as it describes a range of metals including Na, Al, Cu, and Zn. This is remarkable since other properties of the clusters are far from being bulk-like, most notably the HOMO-LUMO gap which can be very large in small clusters.

Current work on Si_N over sizes ranging from $N = 2$ to 147 shows that these clusters are much more polarizable on a per atom basis than the semiconducting bulk solid. The figure below shows a plot of the per atom total polarizability and its charge transfer and local dipole contributions vs $N^{-1/3}$ for these clusters. ($N^{-1/3}$ scales like $1/R$ for a spherical cluster, where R is the cluster radius). The dipole and charge transfer contributions follow linear trends that are easily extrapolated to the bulk size limit where the dipole part vanishes and the charge transfer part has a value of approximately $31 \text{ Bohr}^3/\text{atom}$. The latter is much larger than $25 \text{ Bohr}^3/\text{atom}$, the per atom polarizability of bulk silicon, and close $32 \text{ Bohr}^3/\text{atom}$, the value for a

metal with the same volume per atom as silicon. The behavior of the dipole term is exactly the same as seen in clusters of metal atoms, providing additional evidence of metallic behavior in the clusters. It can be shown to stem from induced dipoles in the atoms at the cluster surface. Also consistent with metallic behavior is the fact that the interiors of the clusters are strongly screened from the external field. An intriguing question that arises from this study is “At what size does Si_N begins to show a dielectric response?”.

Other work in our group involves studies of Cu_MPd_N clusters and their reactivity toward H_2 . Our future plans include cluster-size studies of polarizability in insulating clusters and the impact of the residual self-interaction of electrons in DFT on calculated results for cluster-based catalyst systems.

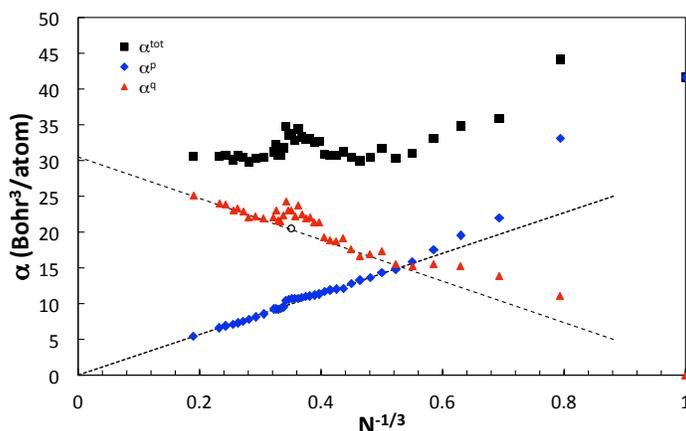


Fig. 1 Per atom total (black), charge transfer (red), and dipole (blue) polarizabilities of Si_N vs. $N^{-1/3}$. The dotted lines reflect trends. The large size limit for the charge transfer contribution is 31 Bohr³/atom.

Grant Numbers and Grant Titles

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

Postdoc: None

Students: Ritaban Chowdhury and Kushantha Withanage

Publications:

- 1) *Local spin density treatment of Substitutional Defects in Ionic Crystals with Self-Interaction Corrections*. K. Jackson, *Advances in Atomic, Molecular, and Optical Physics* **64**, 15 (2015).
- 2) *Site specific atomic polarizabilities in endohedral fullerenes and carbon onions*. R. Zope, S. Bhusal, T. Baruah and K. A. Jackson, *J. Chem. Phys.* **143**, 084306 (2015).
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Density functional simulations in the presence of environment

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Project scope: The project aims to improve the scalability of our electronic structure software for investigation of ground and excited state properties of molecular systems in the presence of an environment. The code (<http://quantum.utep.edu/?q=node/3>), which has a number of unique features, implements Kohn-Sham formulation of density functional theory using Gaussian basis sets and employs an optimal variational mesh. The code was parallelized nearly two decades ago using MPI within a master-slave paradigm which allowed routine simulations of systems containing about 200 atoms with basis functions of the order of 4000 basis functions with 2 million grid points. The project goal is to improve its scalability to study the ground and excited state properties of organic systems in the presence of explicit environment.

Technical progress and future work: To improve the scalability in memory, two approaches were used. The largest memory consuming part in the code is the storage of Hamiltonian and Overlap matrices, followed by the storage of the eigenvectors. The storage of the Hamiltonian and Overlap matrices was already minimized by using the packed storage format. As the systems size increases the reduced overlap between the basis functions on distant atoms results in increase in the sparsity of these matrices. The first approach to reduce memory demand exploits the sparsity to store only the nonzero elements using sparse storage formats. This allowed simulations of the systems containing up to 23000 basis functions using all available processors on the nodes of hopper (2Gb/node). To go beyond these system sizes, we used distributed storage of arrays using the block cyclic distribution. In this case the Hamiltonian, Overlap, and the eigenvectors are distributed in the block cyclic fashion. Since each processor holds only a small part of matrix, much larger systems could be studied. This approach also allowed us to speed up the construction of Hamiltonian and Overlap matrices significantly faster compared to the original master-slave paradigm. For example, 20% speed up was noted for a test calculation of reaction center in photosystem 1 performed on Hopper (at NERSC) using 312 processors and using 6-311G** basis set. This performance further improves with basis set size. In the same calculation of reaction center with a basis set roughly twice as large (NRLMOL/Pederson-Porezag basis set) 60% speed up was obtained. As the system size gets larger, the Hamiltonian and Overlap matrices become sparse. While this implementation is very useful as it eliminates memory bottleneck, there are some disadvantages. As a consequence, in building Hamiltonian matrix some tasks may not

have sufficient work to do resulting in load imbalance. Another disadvantage is that storing the eigenvectors in block-cyclic fashion results in a lot of communication when these eigenvectors are needed for construction of density matrix or Kohn-Sham orbitals. Future work is planned to overcome these issues by using hybrid programming by means of new shared memory features in the MPI-3 and to speed up part of codes by rewriting them to make use of these developments. We also plan to incorporate environment effects by means of simplified models such as using effective fragment potential method or PCM model.

Applications: The resultant code was applied to investigate the electronic structure of carotene-porphyrin-fullerene triad in the presence of a polar solvent. The experimental estimate of the charge transfer excitation energy is about 1.2 eV in dimethyl tetrahydrofuran which is lower than the theoretical value calculated using the perturbative delta-SCF method. To investigate the effect of solvent on the energetics, we performed molecular dynamics simulation of the triad in water. Due to the availability of good quality force field parameters, water was chosen to represent the polar solvent. The triad was immersed in 15866 water molecules and kept frozen in the molecular dynamics simulations. The intermolecular interaction in water was described using CHARMM-TIP3P potential. The simulations were performed for 10 nanosecond with time steps of 1 femtosecond. From the molecular dynamics trajectory of the last 9 nanoseconds, 41 snapshots were selected for density functional theory (DFT) calculations. The DFT calculations were performed in different charge states to obtain the ionization energies and electron affinities. This was done in three different ways.

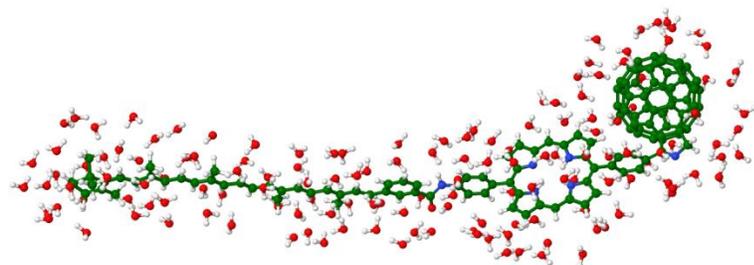


Figure 1 Porphyrin-Fullerene-Carotenoid triad in explicit water

In the first case, all water molecules were represented by point charges in all 41 DFT calculations in three charge states. In the second case, an average electrostatic potential of all snapshots was used in the DFT calculation. In this case, only one DFT calculation is needed for each charge state which results in substantial computational saving at the expense of accounting for the solvent effect in an average fashion. In the third case, the water molecules closest to the triad were explicitly included in the DFT calculations. This results in about 148-155 water molecules in the DFT part of the calculation. Using the default NRLMOL basis set, the number of basis functions ranged between 17000-18000 in the case of explicit calculations. The first two cases give very

similar results with increase in ionization of energy by 0.07 eV and increase in electron affinity by 0.03 eV. The average values of the ionization energy and electron affinity obtained from the calculations with explicit water are somewhat different. In this case the change in electron affinity is very small (0.01 eV) while the ionization energy increases by about 0.2 eV. These simulations show that the fundamental gap increases by 0.1eV in the triad frozen in water with respect to its gas phase value. The energy of the charge transfer excited state was also calculated for a triad in the average electrostatic potential of water configurations from the snapshots. The calculated charge transfer energy in this case was 2.51 eV, about 0.1 eV larger than the gas phase value. The excited state dipole in this model was 7 debye smaller than the gas phase value of 180 Debye possibly due to missing solvent polarization effects. The future plan is to carry out the CTE calculations with explicit water molecules. We are rewriting the excited part of the code so that these calculations can become feasible.

Publications acknowledging this grant:

- 1) *Density functional study of the electronic structure of dye-functionalized fullerenes and their model donor-acceptor complexes containing P3HT*, T. Baruah, A. Garnica, M. Paggen, L. Basurto and R. R. Zope [J. Chem. Phys. 144, 144304 \(2016\)](#).
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Interfacial Charge transfer and transport through organic semiconducting interfaces

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Abstract

Computational models are developed and employed to contribute to the design of materials used in energy conversion applications. In one direction we investigate photoinduced electron transport and transfer in organic semiconductor materials and interfaces relevant to photovoltaic functionality. In the second direction we study thermoelectric functionality of molecular bridges.

Our first-principles based approach is based on range separated hybrid functionals that achieve physically relevant description of key properties including ionization energies and charge transfer state energies. Importantly we have used our electronic structure approach to calculate rates of charge transfer processes employing a fully quantum mechanical approach. We achieve excellent agreement with available experimental measurements. We investigate structure functional relationships of several photovoltaic related systems.

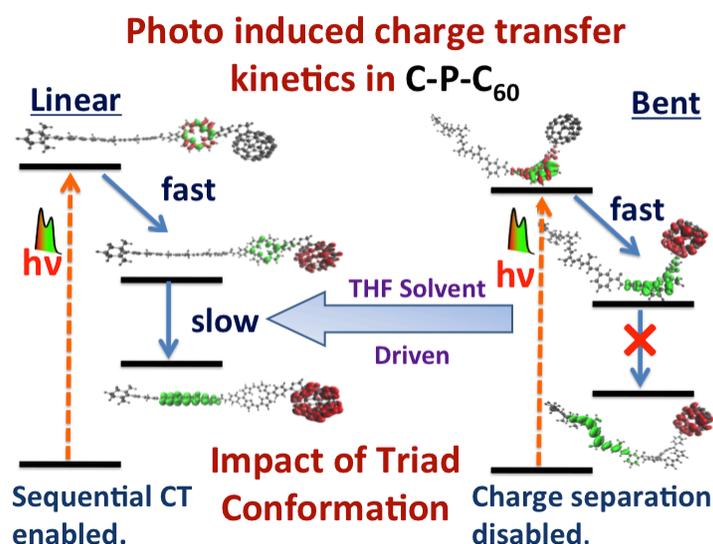
For example, in Figure 1 we summarize our study on a molecular triad system, where the nature of the CT process and the relationships of the molecular conformation are resolved. In Figure 2 we summarize the success of our electronic structure approach to reproduce measured vibrational and electronic spectra that is associated with a widely studied tri-metal complex. (The complex consists of a central Pt ion bridging Fe ions through cyano ligands). Our novel interpretation of the solvated complex reassigns the oxidation numbers and the nature of the CT process.

We are pursuing in collaboration a hierarchy of methodologies that combine molecular dynamics simulations, electronic structure calculations and quantum dynamics method development. The triad system will be targeted as a benchmark system in the development of our comprehensive computational scheme.

More specifically, interfacial structure and distributions of donor-acceptor geometries will be achieved using reliable and predictive MD simulations. Excited state energies, charge distributions, distortions of equilibrium geometries and electronic coupling coefficients for the relevant donor-acceptor geometries are determined using proper electronic structure techniques. Finally, simulating CT dynamics, as well as its dependence on and sensitivity to donor-acceptor geometry are implemented following feasible, robust and transferable quantum dynamics theory and simulation techniques.

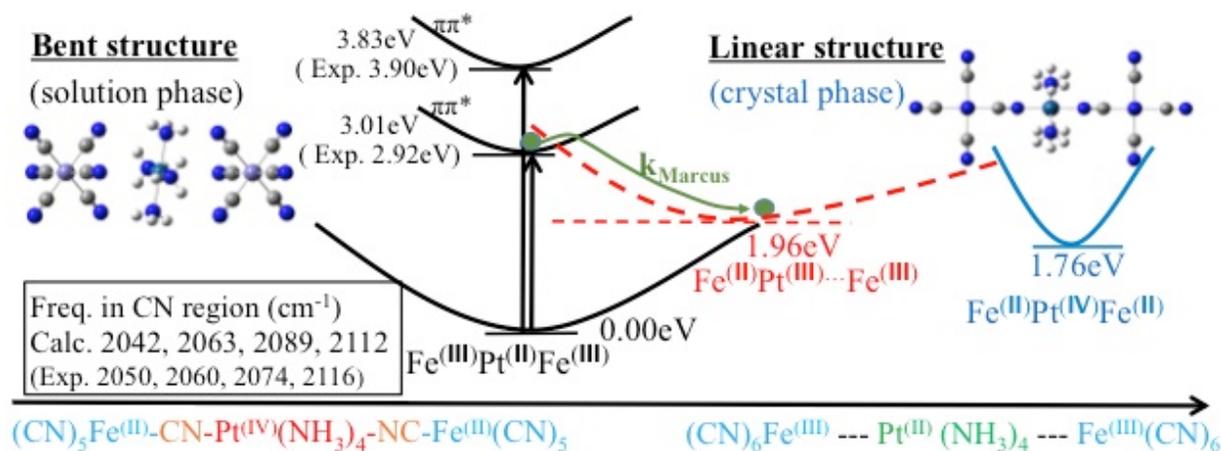
We have also implemented our approach to study chemical means to tune the properties of molecular bridges that affect thermoelectric conversion efficiencies. Our calculations provide valuable insight on experimented systems to assist in the design of the follow up experiments . We develop further our first-principle approach to study electron transport in potential biased molecular systems. In this direction we consider limitations of widely used functionals and analyze models of the molecular bridges to avoid computational artifacts. We have provided a prediction for a thermal valve where magnetic fields can be used to control heat transfer across molecular bridges.

Figure 1. CT process in a molecular triad – relating structural flexibility to charge separation



(Manna et al, J. Phys. Chem. Lett. 6, 1231–1237, 2015)

Figure 2. Charge polarization and conformation in a trimetal complex



(Zheng et al, J. Am. Chem. Soc. 136, 16954–16957, 2014)

Grant Numbers

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Postdocs: Arun K. Manna, Zilong Zheng, Qinquo Feng

Graduate Students: Heidi, Phillips, Srijana Bhandari

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Discontinuous methods for massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles

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Abstract

Lithium-ion (Li-ion) batteries have revolutionized consumer electronics and promise to do the same for transportation in plug-in hybrids, all-electrics, and aircraft, as well as electrical distribution in local storage and load leveling. In order to realize this promise, however, energy/power density, lifetime, and safety must be significantly improved. A key factor in all of these is the solid-electrolyte (SEI) interphase layer between anode and electrolyte, a product of electrolyte decomposition. A thin, stable layer with low electrical conductivity and high ionic conductivity is ideal.

In this work, we seek to understand for the first time the detailed chemistry and dynamics at this critical interface by performing quantum molecular dynamics simulations of anode/SEI/electrolyte systems at unprecedented scale; and in so doing, enable fundamental advances in device performance, lifetime, and safety. To reach the necessary length and time scales, we develop two new methodologies in collaboration with the SciDAC FASTMath Institute: the Discontinuous Galerkin (DG) and Pole Expansion and Selected Inversion (PEXSI) methods. The DG methodology significantly reduces the size of basis needed to solve the required quantum mechanical equations by representing global solutions in terms of local eigenfunctions in chosen subdomains (elements), while allowing systematic convergence by increasing the number of eigenfunctions per element. The PEXSI methodology enables the direct computation of densities, energies, and forces without diagonalization via Fermi operator expansion, thus eliminating the $O(N^3)$ scaling bottleneck with number of atoms of standard diagonalization based approaches, while retaining systemic improvability and applicability to metals and insulators alike.

In this presentation, we discuss our recent progress in the understanding of these anode/SEI/electrolyte systems, and in the development of electronic structure methodologies to make that understanding possible.

In studies of Li solvation and diffusion in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and mixed EC/EMC electrolytes [1], we find that Li prefers tetrahedral coordination in all electrolytes considered. Furthermore, we find that the stronger and more enduring the solvation structure, the lower the diffusivity; so that Li diffusion coefficients are significantly smaller than those of more weakly solvated PF₆ counter-ions in all electrolytes considered.

In collaboration with the SciDAC SDAV Institute (www.sdav-scidac.org), we carried out relative angle analysis of ion trajectories in EC, EMC, and EC/EMC electrolytes [2]. We find complex, non-Brownian dynamics over a range of time scales, with more strongly solvated Li ions manifesting more complex dynamics and more weakly solvated counter-ions showing more diffusive behavior. At time scales on the order of 2 ps, we find peaks in the relative angle distribution consistent with caging of Li, while at much shorter and longer time scales, we find transitions to ballistic and Brownian motion, respectively.

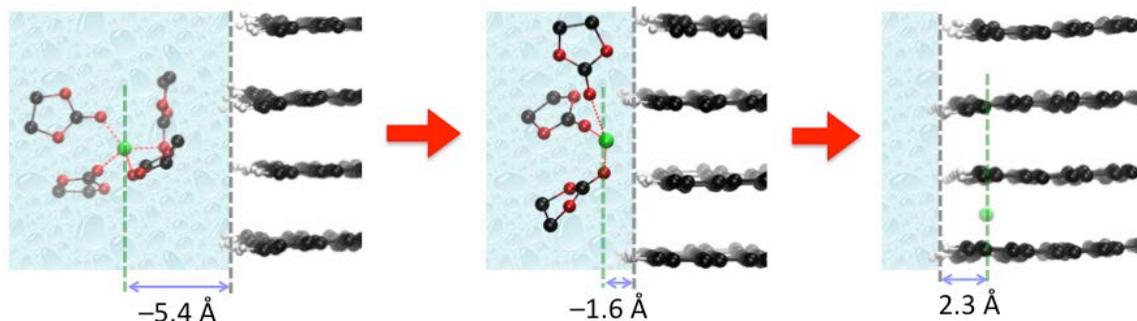


Figure 1: QMD simulation of solvated Li intercalation into graphite. (Surrounding solvent not shown.)

In constrained molecular dynamics simulations of anode-electrolyte interfaces, we find that Li sheds its first solvation shell as it approaches the graphite anode to intercalate (Fig. 1). Considering H, H/OH, and O edge terminations, we find that O termination presents the largest barrier to intercalation due to electrostatic interactions with Li. Extensive calculations mapping out the potential energy surface as Li approaches the anode suggest intercalation pathways. These detailed energy surfaces show a substantial effect in the choice of termination for a given anode.

Going forward, as the new DG and PEXSI methodologies allow, we plan to scale up to larger, more complex interfaces, including model SEI layers in order to understand the intercalation of Li from electrolyte into SEI and from SEI in to anode, with different edge orientations and external potentials. A detailed understanding of the chemistry and dynamics at both interfaces stands to open the way for fundamental advances in device performance, lifetime, and safety.

In collaboration with the SciDAC FASTMath Institute (www.fastmath-scidac.org), we have developed, implemented, and applied new DG and PEXSI electronic structure methodologies to reach the length and time scales needed to capture the necessary complexity of Li-ion anode-electrolyte systems.

In order to study smaller systems as the new DG and PEXSI methodologies have been developed, we have further developed and applied the Qbox planewave code to a range of electrolyte and small-interface systems. In order to efficiently treat metallic systems, we developed a new Projected Preconditioned Conjugate Gradient (PPCG) eigensolver [3], which has accelerated both Qbox and Quantum Espresso codes two-fold in such calculations.

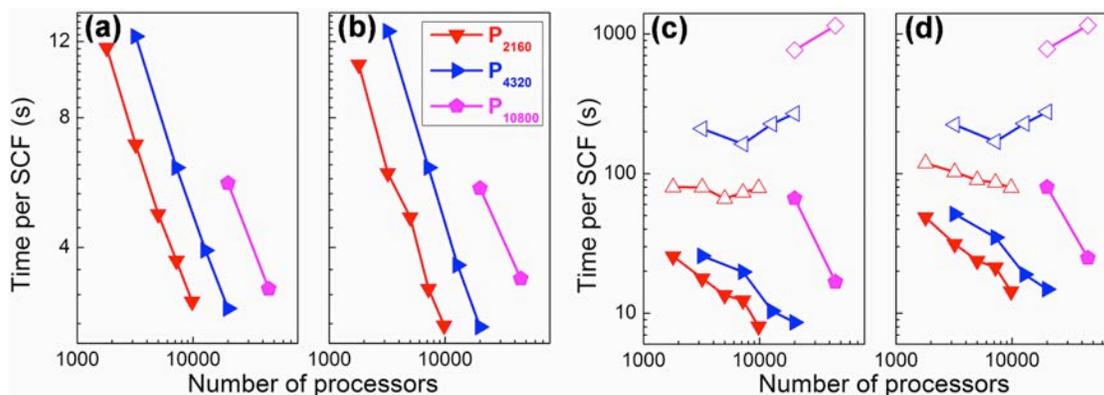


Figure 2: Wall clock times for DG-PEXSI calculations of phosphorene nanoribbon systems of 2160, 4320, and 10800 atoms [4]. (a) Basis generation. (b) Hamiltonian construction. (c) Density, energy, and force evaluation. (d) Total. Hollow markers correspond to diagonalization, solid markers to PEXSI.

We have developed and implemented accurate, systematically improvable energy and force expressions in the DG basis [5], and have carried out static and dynamic calculations on a range of systems [5-7]. To reach the largest system sizes, the PEXSI methodology [8-10] was employed to eliminate the need for diagonalization (Fig. 2). The DG and PEXSI codes have now scaled to over 10,000 atoms and 100,000 processors on leadership class supercomputers at LLNL and LBL.

Most recently, in order to treat three-dimensional Li-ion interface systems of 1,000–5,000 atoms efficiently, we implemented Chebyshev filtered subspace iteration to compute the occupied subspace of the DG Hamiltonian. This has proven particularly effective by virtue of the small size and limited spectral width of the DG Hamiltonian. In recent calculations of a 4,244-atom Li-ion interface, the current Chebyshev implementation was able to compute the occupied subspace in about 29 seconds on LBL Edison using 17,280 processors, with the ability to scale to more processors as available.

In order to reach up to 10,000-atom simulations, as required to model mixed anode/SEI/electrolyte systems, further advances in both Chebyshev and PEXSI methodologies will be required. For Chebyshev filtering, the current ScaLAPACK based subspace diagonalization becomes the bottleneck beyond ~5,000 atoms. For PEXSI, sparse-direct factorization and selected inversion become bottlenecks, particularly in 3D systems. Better scaling alternatives to these are the focus of current development.

Grant Numbers and Grant Titles

DOE SCW1357 Discontinuous methods for accurate, massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles

Postdocs: Mitchell T. Ong, Mathias Jacquelin, Wei Hu, Amartya Banerjee

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

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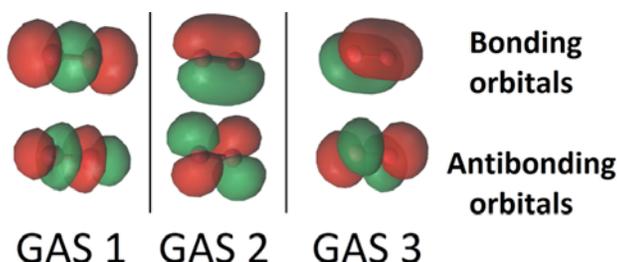
Multireference Methods for Excited States and Transition-Metal Containing Systems

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Abstract

The electronic structure of multireference molecular systems cannot be described to a good approximation by only a single way of distributing the electrons in the orbitals of a single Slater determinant. In this lecture I will describe our latest developments of Multi-Configuration Pair-Density Functional Theory, aimed at treating multireference systems using middle to large-size active spaces. This is achieved by generating the initial wave function using the generalized active space, GAS, concept. Results of calculations on excited states of organic molecules and systems containing transition metals will be presented.



An example of three GAS subspaces used in calculations on dioxygen, O₂

Grant Numbers and Grant Titles

Grant Numbers and Grant Titles

DE-SC0012702 Inorganometallic Catalyst Design Center, an Energy Frontier Research Center.

Postdoc(s): S. Odoh, V. Bernales, K.

Student: S. Stoneburner, J. Borycz

DE-SC0008666 Scientific Discovery through Advanced Computing (SciDAC).

Postdoc(s): A. Sand, K. Vogiatzis

Student(s): C. Hoyer

DE-FG02-12ER16362 Nanoporous Materials Genome Center.

Postdoc(s): S. Odoh, K. Vogiatzis

Student(s): J. Borycz

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Variational Monte Carlo for Excited States

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Abstract

Predicting spectroscopic properties is one of the key applications of electronic structure theory, with important uses in combustion, photochemistry, and materials science. However, modeling excited states has historically been more challenging than ground states due to the lack of a robust and efficient variational principle analogous to minimizing the ground state's energy. Using a new Monte Carlo approach, we have developed an efficient method for minimizing functions of the wave function whose global minima are excited states, much as the energy minimum is the ground state. This excited variational principle (EVP-QMC) allows a wave function ansatz to be fully optimized for an individual excited state, greatly increasing accuracy compared to typical approaches today that require sharing elements of the wave function between different states. Further, it is systematically improvable in exactly the same manner as the ground state variational principle, as we have demonstrated in the carbon dimer with configuration interactions of increasing length (grey and green curves in lower figure). In this case, a multi-Slater Jastrow ansatz with less than 100 variables, thanks to the individual state tailoring possible in EVP-QMC, matches or exceeds the accuracy of 4,000-variable coupled cluster and million-variable density matrix renormalization group approaches. Especially notable is that EVP-QMC has proven reliable for both single and double excitations, while the vast majority of excited state methods used today fail qualitatively when modeling double excitations.

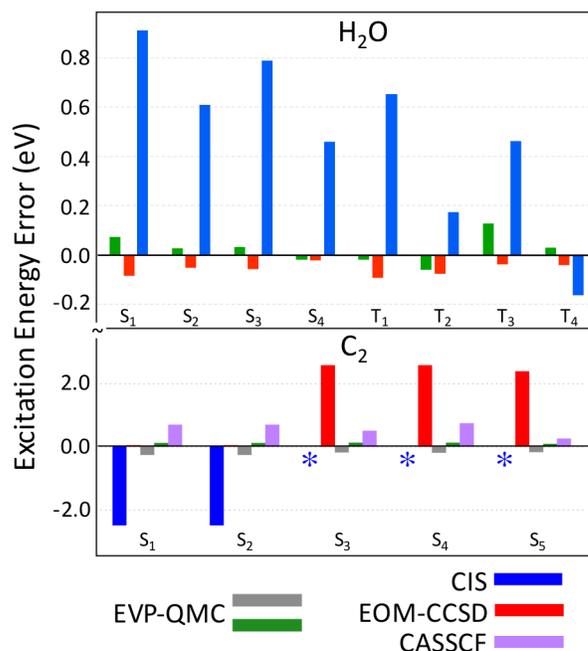


Figure: Benchmarking of excited state methods in water and the carbon dimer. The * symbols mark double excitations. Our variational Monte Carlo approach outperforms equation of motion coupled cluster, is more parallel, and has better cost scaling.

Current work focuses on extending EVP-QMC to the linear response regime and the solid state, for which the formalism is equally applicable. Preliminary data, such as those displayed for water, show the linear response approach to be competitive with the current gold standard molecular excited state method, equation-of-motion coupled cluster. EVP-QMC is also more parallel, more reliable for double excitations, and has a lower cost scaling than coupled cluster. Indeed, the ability of ground state QMC to model 100+ atom systems, the applicability of EVP-QMC to molecules and the solid state, and the rigorous guarantee of systematic improvability portend a bright future for high-accuracy spectroscopic predictions.

Grant Numbers and Grant Titles

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Postdoc(s): N/A

Student(s): Luning Zhao

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

N/A

Using Quantum Mechanics and Monte Carlo Simulations to Optimize Copper-Zinc-Tin-Sulfide (CZTS) Solar Cells

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Abstract

Program Scope

$\text{Cu}_2\text{ZnSnS}_{4-x}\text{Se}_x$ (CZTS), a quaternary chalcogenide compound, is a promising substitute for state-of-the-art silicon solar cells. It features an appropriate (1.0-1.5 eV) and direct band gap tunable via different levels of Se addition. Compared to other thin-film photovoltaic materials, such as CdTe and $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS), CZTS contains no expensive or toxic elements and thus is more economically and environmentally friendly. However, its record solar energy conversion efficiency is too low (~12%), mainly limited by its unexpectedly low open-circuit voltage compared to its ideal theoretical band gap. The voltage loss is considered to be related to the unstable Cu/Zn sublattice of CZTS, which produces a fluctuating band structure. Our computational studies elucidate the origins of the band fluctuation and to provide practical synthesis guidelines for possible improvements.

Progress (Abstract for Poster)

We studied the structure of the CZTS lattice using Monte Carlo (MC) simulations based on first principles data in order to understand the physical origin of the lattice disorder and to quantify its impact on the band structure of CZTS. Specifically, we built an energy model to describe the disordered lattice of CZTS, based on a cluster expansion formula. The model was trained using data from density functional theory (DFT) + U calculations, where the values of U were derived *ab initio*. The MC simulations utilizing this model predicted an order-disorder phase transition temperature of CZTS in excellent agreement with experiment. MC-generated structures were then fed to DFT + U calculations to derive the temperature dependence of CZTS's electronic structure. We found significant band gap shrinking as the annealing temperature increased, caused by local band fluctuations in the disordered lattice. The shrinking band gap is directly connected to the low open-circuit voltage observed in experiments. Through these studies, we determined intrinsic thermodynamic limits on the band gap of disordered CZTS, a difficult problem to circumvent at high annealing temperatures. We therefore suggest that a low-temperature annealing procedure is necessary to restore the order of the Cu/Zn sublattice in CZTS, such that higher efficiency can be achieved for CZTS-based solar cells.

Beyond the perfectly stoichiometric material, we further investigated the impact of Cu vacancies (V_{Cu}) on the CZTS band gap. A unique band gap opening behavior was found in samples containing vacancies, with a significant magnitude of ~0.2 eV. This band gap opening effect of V_{Cu} does not exist in the ordered material and is related to the disordered nature of the Cu/Zn sublattice. The free holes introduced by V_{Cu} aggregate in nano-meter-sized traps created by the disordered lattice. The Coulomb potential of the aggregated holes effectively damps the

band fluctuation, thus opening the band gap (Figure 1). This finding explains the important role of V_{Cu} and the reason for using Cu-poor synthesis conditions to produce the best-performing CZTS solar cells.

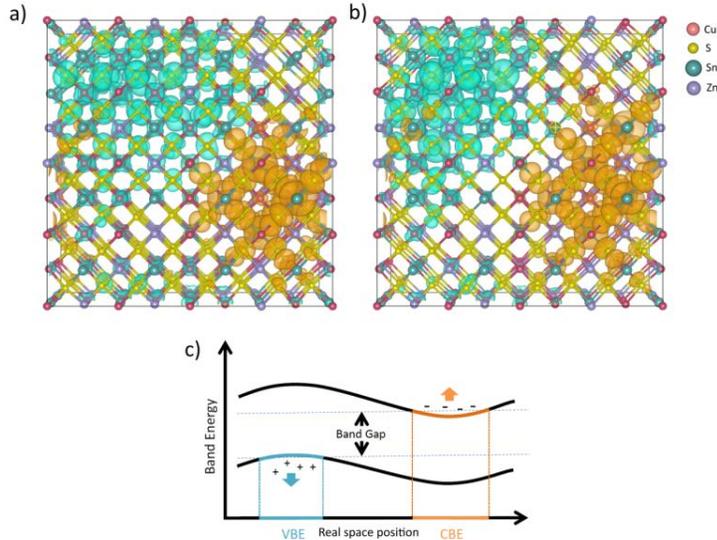


Figure 1. Fluctuating band edges in the disordered phase of CZTS: spatial distributions of the valence band edge (cyan) and the conduction band edge (orange) of (a) a stoichiometric CZTS supercell and (b) a nonstoichiometric CZTS supercell with 5% Cu vacancies, as well as (c) a schematic plot to demonstrate the band fluctuation in the disordered lattice and the band opening effect.

To explore the possibility of introducing more free holes by introducing more defects (particularly, V_{Cu}), we extended our cluster expansion model to study non-stoichiometric samples. Via MC simulations, we were able to determine the accessible regions of the CZTS compositional phase diagram under a particular synthesis condition (*i.e.*, temperature and sulfurization condition). These results provide guidelines to search for the optimal elemental ratio for CZTS synthesis, in order to introduce a maximum concentration of carriers while avoiding formation of secondary phases. We predict that a higher level of V_{Cu} can be introduced in more reactive sulfurization environments (high sulfur chemical potential). We therefore suggest that, at least from a thermodynamic perspective, a more reactive sulfurization condition should lead to CZTS products with larger band gaps and higher efficiencies.

Future Plans

It will be important to generalize our models to include selenium since all of our calculations were performed using pure sulfide. The best-performing CZTS cell was fabricated with a high level of Se addition, so it is important to understand the effects of Se in disordered CZTS. Ag doping was also proposed to improve the stability of the Cu/Zn sublattice, the effects of which need to be investigated. New models are required to study such Ag/Se doped systems, which is one of our future research directions. We also plan to further investigate the properties of charged defects with localized states (such as Sn_{Zn} , Sn_{Cu} , *etc.*) that perturb the band structure significantly and may induce non-radiative carrier recombination in CZTS. The development of a new generation of embedding theory is ongoing, enabling us to study such charged structures within an extended crystal environment.

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Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications

Principal Investigator: Emily A. Carter

Postdoc: Kuang Yu

Graduate Student: Nima Alidoust

Selected publications acknowledging this grant in the last three years

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LATE NEWS POSTER:

Ab-initio based approach for the efficient sampling of multidimensional cluster potential energy surfaces: application to $(\text{H}_2\text{O})_{20}$ and $(\text{H}_2\text{O})_{25}$.

Sotiris Xantheas

PNNL

Interfacial Electrocatalysis from First Principles

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Abstract

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 three major topic areas that related to structural and mechanistic analyses of electrochemical phenomena and water/catalyst interfaces (we have also been investigating several side projects that could mature into longer-term research directions, but those will not be described here). The first major area of interest relates to the electronic, structural, and catalytic properties of continuous ultrathin oxy/hydroxide films at the interface between precious metals and aqueous solutions. We have, in the past two years, developed methods that exploit basic van der Waals and self-interaction corrections to DFT-GGA calculations to determine the structure and oxidation states of these films on Pt(111) substrates; these structural and chemical properties are determined as a function of the local pH and applied voltage of the aqueous solutions. Beginning with the specific case of a continuous nickel oxy/hydroxide films on Pt(111), we also developed a model of so-called three-phase boundaries between the film, the precious metal substrate, and the surrounding aqueous phase.

Building upon this progress, we have recently developed models of explicit water molecules near the nickel/platinum three-phase boundary and have elucidated the effect of the explicit aqueous environment on water dissociation, a step that is critical in the production of hydrogen in alkaline electrolyzers. The results suggest that inclusion of explicit water molecules is essential to obtain a realistic result but that the calculated barriers converge quickly with respect to the amount and density of water molecules that are included. The determined barriers further suggest a unique synergy between the partially oxidized base metal nickel film and the underlying precious metal substrate; the barrier to activate water at these boundaries is dramatically lower than what is found on either the substrate or the film in isolation, suggesting a powerful new strategy for developing alkaline electrocatalysts of high activity. We have also generalized this work to show how permutation of elemental composition of the substrate and film can tune the dissociation barriers.

Concomitantly with the above work, we have developed strategies to generalize the structural analyses, described above, to identify the most thermodynamically stable oxidation states, structures, edge terminations, and shapes of oxy/hydroxide nanoislands on precious metal substrates. Such islands are naturally formed during deposition of base metals in alkaline solutions, and as our results on Ni/Pt indicate,

the molecular details of their structures have an important impact on their electrocatalytic properties. We have found a general approach that combines screening over many film/substrate lattice matches, an exhaustive list of edge directions and terminations with variable oxidation states, and the energies of different corner and cluster structures to produce comprehensive phase maps of the shape, edge properties, and oxidation states of 2D nanoislands as a function of applied electrochemical conditions (Figure). The resulting structures form a natural basis for calculation of properties of interest, ranging from magnetic structures of these dot-like islands to catalysis at the three-phase boundaries. These techniques have been coupled with ab-initio molecular dynamics-motivated approaches to provide accurate estimates of the aqueous solvation energies of both the clean edge structures and adsorbates on these edges. Although full AIMD simulations over nanoseconds for each of the many considered structures would provide the best statistics, we have, to economize on computational resources, employed a simplified scheme involving multi-ps AIMD runs, frequent quenching, use of Born-Haber cycles to evaluate solvation energies, and statistical averaging of the results. The results to date suggest that solvation corrections can vary significantly as a function of the edge geometry and can have an important impact on the thermochemistry of the reactions.

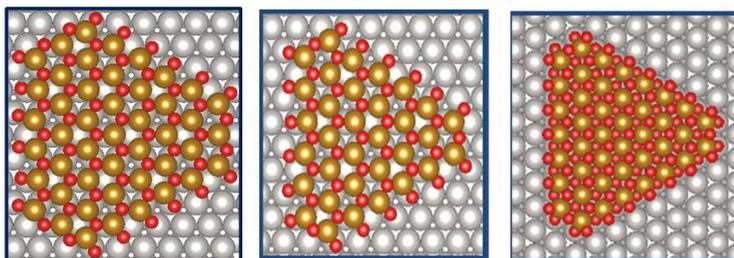


Figure. Effect of increasing applied voltage (left to right) on the shape and oxidation state of Pt(111)-supported FeO nanoislands.

To couple some of the structural considerations, described above, with rigorous analysis of electrocatalytic rates and mechanisms on transition metal surfaces and defects, we are developing a comprehensive reaction mechanism for selected nitrogen-cycle electrochemical processes on both low-index and defected platinum surfaces. We have selected the electroreduction of NO_x species as a model chemistry for which to develop efficient strategies to treat the complexities of the electrocatalytic environment. In the previous year, we elucidated several highly active pathways for NO electroreduction on smooth Pt(111) surfaces, as well as identifying a highly unusual solution-mediated pathway for formation of N_2O products. Very recently, we have extended this analysis to defected (stepped) platinum surfaces and have found a significant sensitivity of structure for the chemistry. We have further, in collaboration with the group of Karoliina Honkala at the University of Jyväskylä in Finland, developed a new strategy to combine the results of rigorous DFT-based electrochemical energy calculations with kinetic Monte Carlo simulations to predict the dynamic evolution of NO electroreduction currents as a function of applied electrochemical voltage. This technique, which we believe to be the first of its kind for electrochemical systems, accounts directly for interactions between adsorbates, is capable of reproducing experimentally predicted currents and potential dependence to within voltage ranges of 0.05V, and provides rigorous insight into kinetically significant steps in the overall reaction network ; we are currently generalizing this method for other Pt surfaces. Finally, we have made progress in developing and benchmarking more rigorous double layer models near Pt surfaces to study charge transfer between solvated protons in solution and NO_x species on the catalyst surface.

Finally, we are beginning to exploit the various electrochemical modeling techniques described above, including surface structure determination, solvation structures near flat and defected metal surfaces, the effect of aqueous solvents on surface stability, dynamical modeling of reaction networks, and double layer models of charge transfer, to more mechanistically complex processes. To this end, we have initiated a study

of ethanol electrooxidation. This chemistry, which has received significant experimental attention but is poorly understood at the mechanistic level, is central to the development of fuel cells that can exploit renewable resources, and the methods that we have been developing place us in a strong position to answer long-unresolved questions in the field.

Future Plans

We will continue to generalize the results of our thin film and three-phase boundary studies to other fundamental electrocatalytic processes. We are particularly interested in exploring CO electrooxidation, a crucial chemistry in fuel cells that has been shown to be promoted by bifunctional effects such as are seen at these boundaries. We are likewise applying our detailed thin film models to analyze another fundamental puzzle in chemical catalysis, known as the strong-metal support interaction, which we theorize results from wetting of metal surface with thin oxide films. We will further refine our aqueous models with extended ab-initio molecular dynamics runs and with statistical evaluations of entropy effects, which have not, to our knowledge, been rigorously calculated at electrified metal/liquid interfaces with electronic structure calculations. We will apply this and related techniques to consider a new fuel cell-crucial chemistry, ethanol electrooxidation, which will be treated in unprecedented detail with these methods. Finally, we will explore the applicability of detailed Quantum Monte Carlo calculations, on which we are collaborating with Argonne and Oak Ridge National Laboratories, to rigorously benchmark our DFT+U/VdW treatments of thin metal films on precious metal substrates.

Grant Numbers and Grant Titles

DE-BES-CTC Interfacial Electrocatalysis from First Principles

Postdoc(s): Zhenhua Zeng

Student(s): Hee-Joon Chun, Joseph Kubal

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

1. Z. Zeng and J. Greeley, "Characterization of oxygenated species at water/Pt(111) interfaces based on consistent DFT energetics and XPS simulations." *submitted*.
2. J. Greeley, "Theoretical Heterogeneous Catalysis: Scaling Relationships and Computational Catalyst Design." *Annual Review of Chemical and Biological Engineering*, *accepted*.
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Abdelkader Kara

Interface characteristics between organic molecules and metal surfaces: role of van der Waals and building a database

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Abstract

As Nobel Prize winner H. Kroemer said, “*The interface is the device*”. The physical and chemical phenomena that occur at the interface between materials or a material and its environment, at the nanoscale, are critical for the understanding of the key parameters and their correlations relevant to the atomic and electronic properties of the interface between organic materials and metal surfaces. To this end, we have employed density functional theory (DFT) with the inclusion of van der Waals (vdW) interactions to study a variety of molecules on several transition metal (TM) surfaces with varying degrees of chemistry and orientation. A great deal of the work consists of screening some of the functionals developed lately in conjunction with the self-consistent implementation of vdW interactions into DFT; while another body of the work results from collaborations with experimental groups on the atomic and electronic properties of organic materials on metal surfaces.

In a system where organic molecules are adsorbed on a metal surface, several types of bonding co-exist and an accurate description of the system should treat all the part of the system on the same footing. If the interaction between the molecules in the system is week and of vdW type; that between atoms of the substrate is strong and of covalent type. The bonding between a molecule and the metal substrate can vary between week physisorption to strong chemisorption. The week interaction between molecules, in the absence of the substrate has been described by several models based on vdW interactions, while TMs have been studied very successfully using DFT without the inclusion of vdW interactions. The challenge is to describe the molecule/metal system with at least the same accuracy as that for isolated molecules and substrate. A recent review by Klimes and Michaelides, presented a classification of the inclusion of vdW interactions into DFT in the form of a “stairway to heaven” (J. Chem. Phys. **137**, 120901 (2012)). At the top level of accuracy, we find the many-body theory, the random phase approximation, and other highly accurate methods. However, these methods are computationally exorbitant and can not be used for large systems for the present times. In the level just below, we find a *self-consistent* implementation of vdW into DFT (vdW-DF) (see J. Chem. Phys. **137**, 120901 (2012) and references therein.) We have used this high level, yet computationally affordable, implementation to study a variety of molecule/metal surface systems and extracted many interface characteristics. As several functionals have been proposed for the vdW-DF implementation, we have screened five of them. For several systems and functionals, we have gathered a great deal of information that we would like to share with the community. We would like to propose to create a web-hosted database of all the molecule/metal surface systems that we have studied and target the inclusion of available information on work done by other groups. Here, we present a few systems that we have studied during the last four years on the subject.

Adsorption of Pentacene on Cu(110): 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 adsorption⁶. The adsorption of Pn introduces several changes: i) lowering of the workfunction, ii) a charge transfer of nearly 1 electron from Cu(110) to Pn, and a significant charge redistribution iii)

appearance of a new interface state, iv) a population of the LUMO. In figure 1a, 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 photoemission spectroscopy⁶. 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 High-Resolution Surface X-Ray Diffraction¹⁰ (figure 1b).

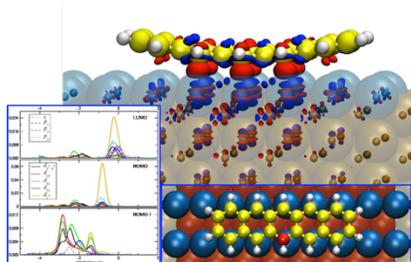


Figure 1a) Pentacene on Cu(110) adsorption geometry, projected densities of states and charge redistribution

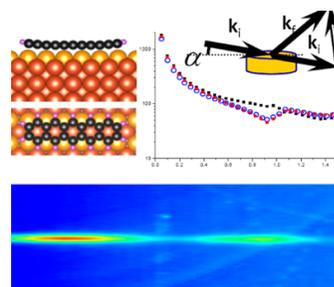


Figure 1b) Pentacene on Cu(110) XRD: comparison between experimental and computational data

Adsorption of Benzene on (111) and (110) metal surfaces: screening of vdWs

Benzene adsorption on the (110)³ and (111)⁹ of seven transition metal surfaces is studied to explore the performance of the several 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 the optB88 functional shows systematically good agreements.

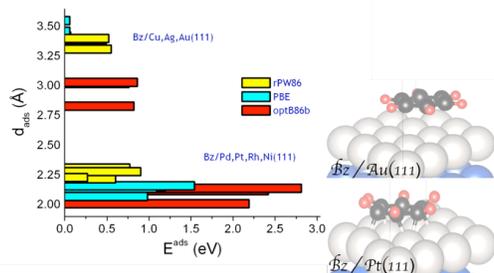
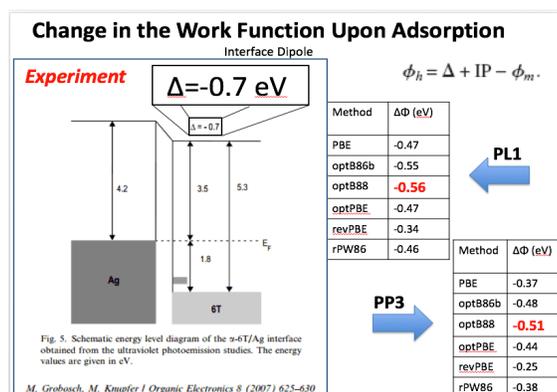


Figure 2: Benzene on M(111) adsorption geometry, Adsorption heights vs adsorption energies for 3 functionals.

Adsorption of Sexithiophene on Ag(110)



In good agreement with the experimental observation, we found that sexithiophene molecules adsorb, parallel (PL) and perpendicular (PP) to the Ag(110) channels, with similar adsorption energies⁵. The inclusion of the vdW interactions induced a substantial increase in the binding energy (0.8 eV for PBE vs 4.4 eV for optB86b). We found an interface dipole of 0.56 eV in good agreement with the 0.7 eV experimentally reported one.

Figure 3: Comparison between experimentally observed and computed interface dipole.

Experimental data on the adsorption characteristics, such as binding energies, for relatively large molecules on metal surfaces is rather scarce. In order to improve the accuracy of the bonding description and yet keep the computational cost at a manageable level (i.e. using vdW-DF) one needs guidance from higher-level calculations. We are planning to perform several calculations for prototype molecules (benzene, thiophene and pyridine) on a few metal surfaces, at high level of accuracy such as the random phase approximation. We also plan to continue screening available and new coming functionals as well as improvements of the vdW-DF, and increasing the number of molecule/substrate to our portfolio. All the gathered information will be stored and made available to the public as a web-hosted database. This database will contain all the details about a given system, including starting and optimized atomic positions and input information (energy cut-offs, k-points, etc). All published figures and table will be stored as well. In the figure below, we give schematics of an example page.

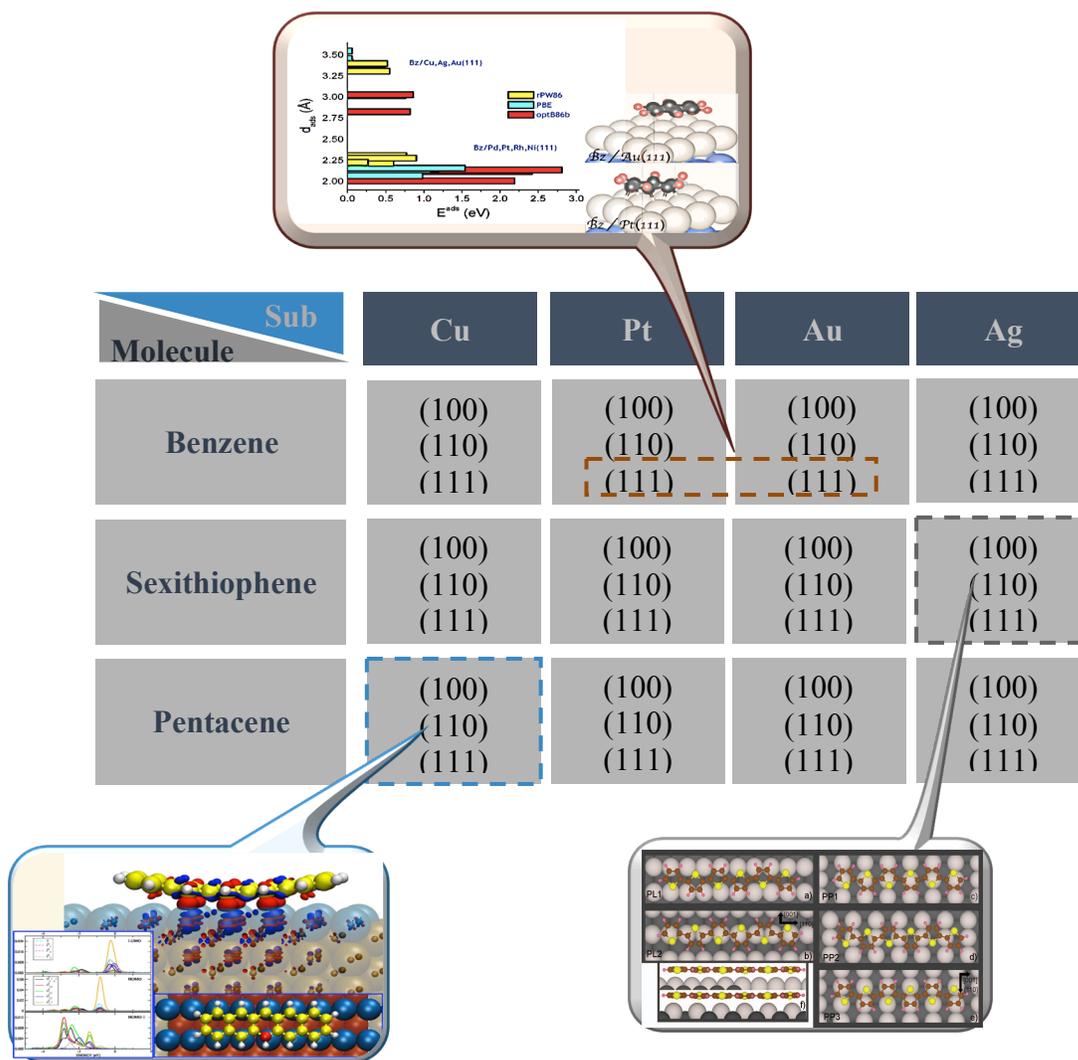


Figure 4: Schematic of a proposed database for molecule/surface systems.

Grant Numbers and Grant Titles

DE-SC0007045: Adsorption and Growth of Organic Materials on Metal Surfaces

Postdoc(s): Handan Yildirim

Student(s): PhD: James Westover, Tomas Rojas, Jeronimo Matos, Walter Malone; Undergraduate: Valentina Zaffino.

Publications:

1. K. Müller, J.C. Moreno-López, S. Gottardi, U. Meinhardt, H. Yildirim, A. Kara, M. Kivala, M. Stöhr: Cyano-Functionalized Triarylaminines on Coinage Metal Surfaces: Interplay of Intermolecular and Molecule–Substrate Interactions, *Chemistry–A European Journal* **22**, 581 (2016). DOI: 10.1002/chem.201503205
2. H. Yildirim, J. Matos and A. Kara: Role of Long Range Interactions for the Structure and Energetics of Olympicene Radical Adsorbed on Au(111) and Pt(111) Surfaces, *J. Phys. Chem. C* **119**, 25408 (2015). DOI: 10.1021/acs.jpcc.5b08191
3. J. Matos, H. Yildirim, A. Kara, Insight into the Effect of Long Range Interactions for the Adsorption of Benzene on Transition Metal (110) Surfaces, *J. Phys. Chem. C* **119**, 1886 (2015). DOI: 10.1021/jp511268s
4. J. Jia, A. Kara, L. Pasquali, A. Bendounan, F. Sirotti, and V.A. Esaulov, On the Sulfur Core Level Binding Energies in Thiol Self-Assembly and Alternative Adsorption Sites: an Experimental and Theoretical Study, *J. Chem. Phys.*, **143**, 104702 (2015). <http://dx.doi.org/10.1063/1.4929350>
5. J. Matos, T. Rojas, H. Yildirim, A. Kara, On the role of long range interactions for the adsorption of sexithiophene on Ag (110) surface, *J. Chem. Phys.*, **140**, 144703 (2014). <http://dx.doi.org/10.1063/1.4870459>
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7. S. Gottardi, K. Muller, J.C. Moreno-Lopez, H. Yildirim, U. Meinhardt, M. Kivala, A. Kara, M. Stöhr. Cyano-functionalized triarylaminines on Au(111): competing intermolecular and molecule/substrate interactions. *Adv. Mater. Int.*, **1**, 1300025 (2014). DOI: 10.1002/admi.201300025
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Structural Changes in Gold and Silver Nanoparticles after Photoexcitation

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Abstract

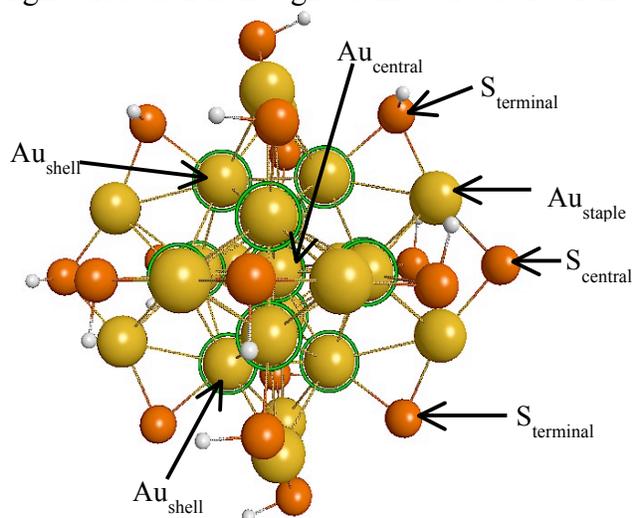
Gold and silver nanoparticles are of interest as possible sensitizers in photocatalysts and photovoltaic devices. Recently, thiolate-stabilized gold nanoparticles with 1-2 nm diameters have been employed to yield increased photocatalytic efficiencies. Visible light excitation is thought to first excite electrons in the nanoparticle before subsequent electron transfer to a semiconductor. However, very little is known yet about the changes that occur within a nanoparticle upon photoexcitation.

In this work, photoexcitation in the $\text{Au}_{25}(\text{SR})_{18}^-$, $\text{Ag}_{25}(\text{SR})_{18}^-$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{22}(\text{SR})_{16}$ nanoparticles will be discussed using time-dependent density functional theory methods.

The ground-state geometric and electronic structure of the $\text{Au}_{25}(\text{SH})_{18}^-$ nanoparticle (shown at right) have been well-characterized previously. The inner core of this nanoparticle is approximately icosahedral, and it is

surrounded by six SR-Au-SR-Au-SR motifs. The highest occupied molecular orbitals (HOMOs) in this system are approximately triply degenerate (with a splitting ≤ 0.03 eV), with an approximately doubly degenerate set (splitting = 0.01 eV) of lowest unoccupied molecular orbitals (LUMOs). Upon excitation, the Au-Au and Au-S bonds in the system on average expand slightly (by about 0.02 Å and 0.01 Å, respectively). However, the bonds do not expand uniformly. Two of the Au-Au bonds in the icosahedral shell increase by 0.25 Å, while four of the bonds increase by 0.10 Å. The shell becomes less symmetrical, which causes an increased splitting among the three HOMO orbitals and the two LUMO orbitals. In addition, the energies of the LUMO orbitals decrease. In consequence, relatively small geometrical changes in the structure lead to significant changes in the electronic structure, and the HOMO-LUMO gap decreases by almost 0.5 eV (from 1.27 eV to 0.78 eV). Strong Stokes shifts are also predicted for longer ligands.

Similar geometrical and electronic changes are also predicted for other nanoparticles including $\text{Ag}_{25}(\text{SR})_{18}^-$ and $\text{Au}_{38}(\text{SR})_{24}$. Relatively small geometrical changes upon photoexcitation lead to significant changes in the electronic structure of these nanoparticles, and large Stokes shifts are predicted in agreement with experiment. Of the systems examined in this work, the $\text{Au}_{22}(\text{SR})_{16}$ nanoparticle has the largest degree of structural flexibility. This nanoparticle is known to have the strongest luminescence quantum yields, so this flexibility may contribute to its quantum yield. However, this is also the only nanoparticle examined here for which a crystal structure is not known, so this flexibility may instead indicate that the previously predicted structure is not optimal. Additional work must be undertaken to determine the role of structural flexibility in quantum yield for these systems.



Grant Numbers and Grant Titles

DE-SC0012273 Understanding Electron Transfer in Plasmon-Enhanced Photocatalysis using Nonadiabatic Electron Dynamics

Postdoc(s): Andre Z. Clayborne

Student(s): K. L. Dimuthu M. Weerawardene, Ravithree Senanayake, Natalia V. Karimova

Manipulating Light with Transition Metal Clusters, Organic Dyes, and Metal-Organic Frameworks

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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, implementation, and benchmarking of many-body Green's function methods (GW approximation and the Bethe-Salpeter equation) to examine excited-state properties of transition metal / transition-metal-oxide clusters and organic molecules that comprise the building blocks of dyes and metal-organic frameworks (MOFs).
- Applications of time-dependent density-functional theory and many-body perturbation methods to examine the electronic and optical properties of MOFs to shed light on whether they can be utilized as materials for light-harvesting applications. In particular, we focus on MOF-5 and other IRMOFs, and their building units, and perform a systematic study of how their optical properties evolve from their sub-units. These studies are expected to lead to significant insights for future design of alternative photovoltaic and photocatalytic materials based on MOFs.

RECENT PROGRESS

We are near completion with our project in collaboration with two groups (Chelikowsky at UT Austin and Louie at UC Berkeley, in synergy with their SciDAC effort) to benchmark the accuracy of GW and GW-BSE computations on a test set of six aromatic molecules (benzene, naphthalene, thiophene, 1,2,5-thiadiazole, benzothiazole, and tetrathiafulvalene). These benchmarks include excitations from and between orbitals of diverse character (sigma, pi, lone pair, and continuum / Rydberg), and require the simulation of unbound orbitals (with negative

electron affinities). This work focuses on (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 real-space (localized) basis compared to a plane-wave basis.

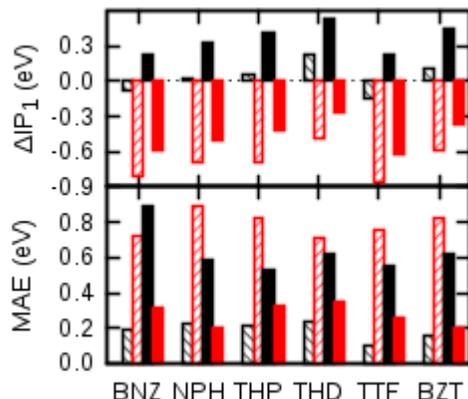


Fig. 1: Error in the first ionization potential (top) and mean absolute error over all ionization potentials less than 15 eV. The black striped bars correspond to perturbative G_0W_0 , red striped bars correspond to perturbative $G_0W_0\Gamma_{LDA}$ (inclusion of LDA-derived vertex), black solid bars are quasiparticle self-consistent GW, and red solid bars are quasiparticle self-consistent $GW\Gamma_{LDA}$.

We find that real-space simulation cells as small as 12 bohr (for single-ring molecules) or 14 bohr (for two-ring molecules) can be used when simulating low-lying localized excitations. Cancellation between vertex effects and self consistency is observed, such that G_0W_0 and quasiparticle self-consistent $GW\Gamma_{LDA}$ have the best agreement with reference values for ionization potentials (Fig. 1), and $G_0W_0\Gamma_{LDA}$ and quasiparticle self-consistent GW give predictions that are closest to reference values of electron affinities. For the vertical singlet excitation energies, TDDFT with LDA exchange-correlation and self-consistent GW+BSE (Fig. 2) are found to give better agreement with reference values, while perturbative GW (using an initial DFT-LDA electronic structure) exhibits a red-shift in the absorption spectra.

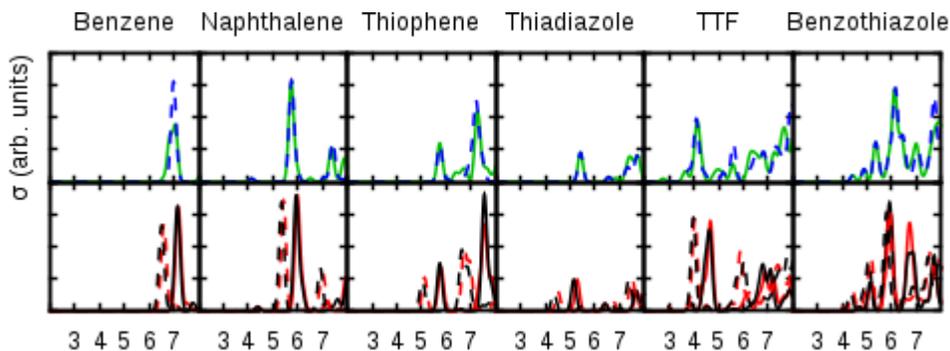


Fig. 2: Absorption cross section of aromatic molecules as predicted by TDDFT or GW+BSE using various flavors of GW. The top panels show the TDDFT spectra at two sizes of unit cell (radius of 12 or 14 bohr for the blue dashed lines and 20 bohr for the green solid lines) to indicate spatial convergence of the spectra. GW+BSE calculations performed in the smaller simulation cell are shown in the bottom panels. Black dashed lines correspond to perturbative G_0W_0 +BSE, red dashed lines correspond to perturbative $G_0W_0\Gamma_{LDA}$ +BSE, black solid lines are quasiparticle self-consistent GW, and red solid lines are quasiparticle self-consistent $GW\Gamma_{LDA}$ +BSE.

We are also completing our GW+BSE benchmark study of transition-metal atoms (Cu, Zn, Ag, and Cd) and their monoxide molecules. Accurate experimental reference values are available for absorption and ionization energies, and the group IB and IIB atoms and ions also provide a GW and GW+BSE test set that includes states with s , p , and d symmetries. We collaborate with Fabien Bruneval (CEA, France) to compare the real-space basis of RGWBS with the atom-centered basis sets used in MolGW. We find that GW self-energies of orbitals with d symmetries converge significantly slower than those of s and p symmetries, regardless of the basis set used; we explore extrapolation schemes for the two different basis sets (Fig. 3). We furthermore benchmark GW and GW+BSE while including the LDA-derived vertex correction.

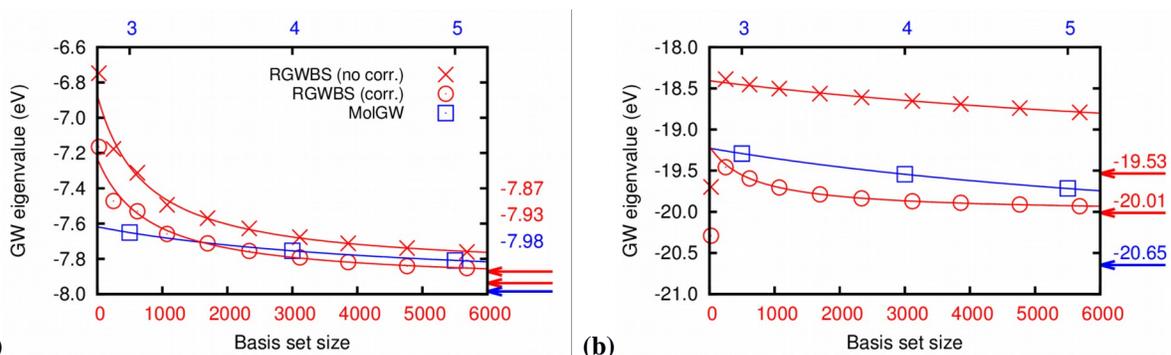


Fig. 3: Comparison of convergence of G_0W_0 self energy as a function of the the number of states in the GW sum-over-states for (a) the Cu+ LUMO, which has s character, and (b) the Cu+ HOMO, which has d character. RGWBS calculations with (red circles) and without (red crosses) a static remainder correction are compared to MolGW calculations using aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets.

Finally, we continue our collaboration with the group of Leor Kronik (Weizmann Institute, Israel) and Anna Krylov (USC) on investigating the electronic structure of copper-oxide clusters (Cu_xO_y , $x = 1-2$, $y = 1-4$) using DFT, hybrid functionals, equation-of-motion coupled-cluster methods, as well as the GW method at various levels of theory. These show that hybrid functionals are better at predicting the binding energy of states with primarily d -character compared to semi-local exchange-correlation functionals, as they largely eliminate the self-interaction errors. However, standard semi-local functionals such as PBE outperform hybrid functionals at predicting the binding energy of peaks with more p -type character. We are currently working to achieve a fundamental understanding of these general findings.

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 and electronic properties of CuO_2 -based nanocrystals
- Investigations into the optical properties of MOFs using TDDFT and GW-BSE

PUBLICATIONS ACKNOWLEDGING THIS GRANT

- 1) Hung, L.; Baishya, K.; Ogut, S. First-principles real-space study of electronic and optical excitations in rutile TiO₂ nanocrystals. *Phys. Rev. B* **2014**, *90*, 165424.

James P. Lewis

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

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Program Scope

We have successfully developed and implemented a non-adiabatic molecular dynamics (NAMD) algorithm within FIREBALL (a local orbital density functional theory code) 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. The benefits of our simulation methodology yields two primary benefits over other non-adiabatic molecular dynamics codes. *Firstly*, we can 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. It is fruitful to explicitly calculate the NACVs, for instance, in order to search for conical intersections or avoid crossing regions. Our *exact* expression for the NACVs enables us to efficiently investigate photo-isomerization processes in large systems. *Secondly*, the efficiency of our NAMD approach means that we can also explore significantly statistical ensembles of excitation processes. For example, in our photo-isomerization studies, we explore between 500-1,000 trajectories. We then explore the properties of entire ensembles rather than individual trajectories (*photo-isomerization is a probability event*). Recently, we have extended the non-adiabatic molecular dynamics formalism to investigate photo-isomerization, photo-reactions, and plasmonic excitations in metal nanoparticles. In our approach, we consider an ensemble of simulations (a few hundred simulations) and investigate the properties of the system for the entire ensemble.

RECENT PROGRESS

Azo-functional Linkers for Porous Coordinated Polymers

More recently, we have been investigating the photo-isomerization processes in azo-functional organic linkers through simulations utilizing non-adiabatic molecular dynamics. We are exploring the impact of functional groups (*e.g.* CH₃, NH₂, *etc.*) on the optical properties, isomerization reaction time, and quantum yield. We find that the photo-isomerization properties are *strongly dependent* on the functional groups attached to the azobenzene derivative. 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.

The main conclusion of our most recent manuscript is that we have demonstrated that we can successfully elucidate more information about the pathway towards relaxation and isomerization by studying the projections of the non-adiabatic coupling vectors onto individual atoms in the molecular systems. In all our initial case studies (shown in Fig. 1), we found that the central CNNC atoms contribute the most to the non-adiabatic 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 azobenzene system.

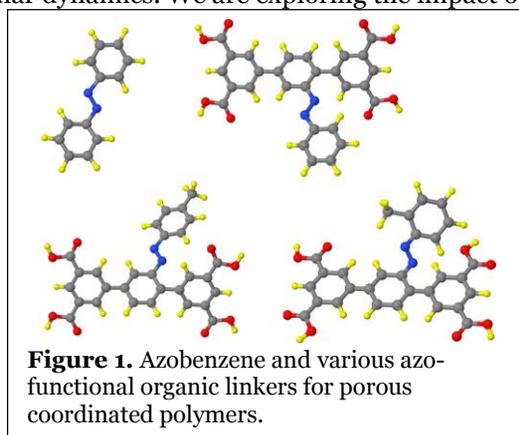


Figure 1. Azobenzene and various azo-functional organic linkers for porous coordinated polymers.

In all our initial case studies (shown in Fig. 1), we found that the central CNNC atoms contribute the most to the non-adiabatic 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 azobenzene system.

Table 1. Ensemble averages for values of modulus of projection on the central atoms CNNC atoms of the non-adiabatic coupling vectors and absolute value of the non-adiabatic 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	
	$ \mathbf{d}_{ij} (\text{\AA}^{-1})$	$ \mathbf{d}_{ij}\cdot\mathbf{V} (\text{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

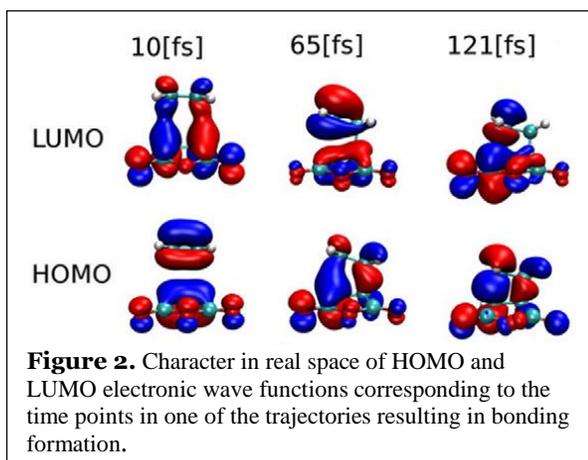
In all four systems, we found that the nitrogen atoms possessed the non-adiabatic coupling vectors and terms with the largest magnitude compared to other atoms in the system. The magnitude of the nitrogen coupling terms are about the same for all four linker systems, but the magnitude of the nitrogen 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 non-adiabatic 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 non-adiabatic 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.

Photo-Induced Reactions

One of the greatest challenges in simulation methodology is to accurately and efficiently interpret photo-induced reaction mechanisms which are critically important in many chemical processes, such as vision, photodamage, UV absorption, photosynthesis, photography, *etc.* Recently, we have pursued simulations of photo-induced reactions; more specifically, we have published results on the [2 + 2] cycloaddition of ethylene with maleic anhydride and on the [2 + 2] photo-induced polymerization reaction of two C_{60} molecules. We have identified different deactivation channels of the initial electron

excitation, depending on the time of the electronic transition from LUMO to HOMO, and the character of the HOMO after the transition. We recently reported DFT–NAMD simulations of the prototypical photo-cycloaddition (PCA) reaction of maleic anhydride ($C_2O_3H_2$) with ethylene (C_2H_4), forming cyclobutane-1-2-dicarboxylic anhydride ($C_4O_3H_6$). The reaction is generated by a single electron excitation induced by the interaction with light; the two π bonds perish and two σ bonds arise, thus 4 bonding electrons are involved in the reaction process. The formation of a molecular complex by the two reactants leads to four linear combinations of the frontiers orbitals. The HOMO orbital is formed by the overlap of π bonds of opposing signs, which gives rise to the intermolecular anti-bonding character of the HOMO orbital. Consequently, the intermolecular anti-bonding character of the HOMO orbital inhibits a thermally activated reaction. In contrast, the LUMO orbital shows intermolecular bonding characteristics. Thus, a photo-induced electron excitation from the HOMO to the LUMO induces an additional attractive force which facilitates the PCA reaction, as discussed below.

We performed, in total, 50 independent DFT–NAMD simulations, each with total time of 2 ps; in each simulation, a single electron was initially promoted from the HOMO to the LUMO state of the molecular



complex ($C_2H_4 + C_2O_3H_2$). The same initial positions and velocities were applied for each trajectory to show clearly the stochastic nature of the MDET algorithm. Electron transitions were allowed only amongst Four frontier orbitals (HOMO-1, HOMO, LUMO, LUMO + 1) were propagated in time.

We were able to identify three different deactivation channels of the initial electron excitation according to our simulations: (i) a direct addition reaction of ethylene and the anhydride; (ii) a direct non-reactive de-excitation; and (iii) an intermediate transient state with subsequent de-excitation leading to an addition/dissociation process. According to our simulations, 15, of a total 50, simulations produced the addition reaction forming cyclobutane diacid anhydride; thereby our simulations give an estimated yield of the addition reaction as $\approx 30\%$. A direct addition reaction of reactants was observed in 12 cases. A detailed analysis of the reaction pathway for one of these cases is presented in Fig 2 which represents the character in real space of the HOMO and LUMO electronic wave functions at different times along the simulations for one of the trajectories. More details regarding the time evolution of the energy spectrum for the four frontiers molecular orbitals with their temporal occupancies are provided in the manuscript.

Plasmonic Excitations in Au Nanoparticles

The investigation of plasmonic excitations as a means to energetically catalyze reactions is a fast-growing interest in photocatalytic chemistry. Recently, we have also applied our non-adiabatic molecular dynamics approach to investigate the relaxation of excited electronic (plasmon) states in Au

nanoparticles (more specifically Au_{55}). Five plasmon states in Au_{55} were identified based on their proximity to vacuum level and based on the nature of their electron densities (states are *nearly free* electronic states and project out of the nanoparticle) as shown in Fig. 3. The energies of the HOMO state (S_{303}) and LUMO state (S_{304}) were found to be -3.85 eV and -3.25 eV, respectively. To simulate the relaxation of an electron from the plasmon state, an electron was removed from the HOMO state and placed it in one of the 5 plasmon states. The excited electron relaxes during the non-adiabatic molecular dynamics simulation which lasted 10,000 time steps at 300 K. The total simulation time was 30 ps (time step size is 3 fs). The electron hopping probability depends explicitly on the non-adiabatic coupling between the classical motion of the nuclei and the electronic quantum state. Throughout the simulations, we observe up and down electron transitions among the electronic energy states during the NAMD simulations; the electron progressively relaxes back to the ground (HOMO) state.

The electron population of each electronic energy state between the initial plasmon state and HOMO state were extracted for all the 50 NAMD trajectories and the average of the populations of each electronic state for all trajectories were plotted. For an example, there were 36 energy states involved in electron relaxation from the initial S_{338} (plasmon state) to S_{303} (HOMO state). Figure 4 shows the variations of average population of all the energy states which were involved for the electron relaxation from each plasmon state. The maximum average population of each energy states (except HOMO state and plasmon state) were plotted as a function of

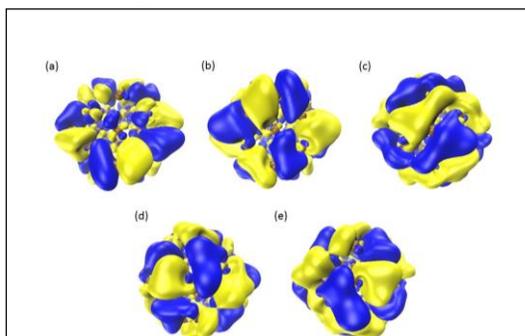


Figure 3. Electron density of plasmon state (a) S_{338} , (b) S_{339} , (c) S_{341} , (d) S_{342} and (e) S_{343} .

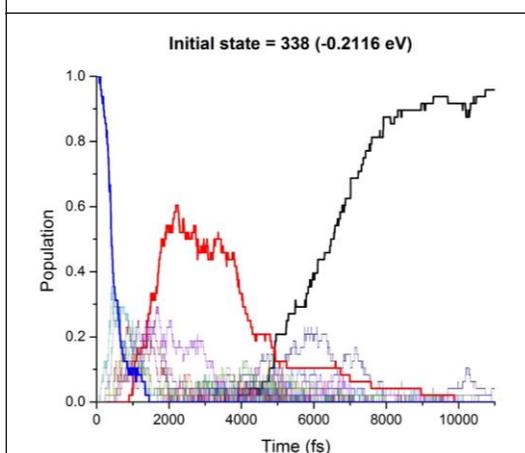


Figure 4. The populations of all the states between HOMO state and initial plasmon state for initial plasmon state (a) S_{338} , (b) S_{339} , (c) S_{341} , (d) S_{342} , (e) S_{343} . The HOMO state in black color, initial plasmon state in blue color and state S_{331} in red color can be seen. The populations of the other states were faded for clarity of the major states.

state number. According to the Fig. 4, state S_{331} at -0.8148 eV shows the dominant maximum average population compared to the other states regardless of the energy of the initial plasmon state. We further investigated the populations of the state S_{331} and found that the population remained above 0.4 for more than 1 ps during the relaxation regardless which of the 5 initial plasmon states. Also, we clearly identify the average population variation of highly populated long living state S_{331} in red. The average population variation of initial plasmon state, S_{303} (HOMO state) and state S_{331} showed a similar pattern among all the 5 initial plasmon states. No other energy state demonstrated such a long-living population during the complete relaxation. The overall relaxation can be identified as a 3 step process. First, excited electron was relaxed in to the state S_{331} from initial plasmon state in ~ 1 ps regardless of the energy of the initial plasmon state. Then, it stayed in state S_{331} for ~ 3 ps and after that it gradually relaxed to the HOMO state. The lack of a conical intersection between state S_{331} and state S_{330} in first ~ 4 ps may be the reason for the long-living population of the electron at state S_{331} during the relaxation process. The full relaxation from the plasmon state to the HOMO ~ 11 ps for all the 5 initial plasmon states.

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

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An Expert Ab Initio Transition-State-Theory-Based Master Equation Code

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Abstract

Program Scope

The goal of this project is to develop expert codes for accurately predicting the kinetics of gas phase chemical reactions. The ab initio transition state theory based master equation (AITSTME) approach provides the basic framework for this effort. The code development effort is designed to facilitate all aspects of the implementation of the AITSTME approach while also increasing its utility through further advances in its theoretical underpinnings. A successful code package will be widely used in the modeling of key reactions in combustion chemistry, atmospheric chemistry, astrophysics, and chemical vapor deposition, for example.

Recent Progress

We have continued to develop and expand our general-purpose AITSTME software package, termed PAPR (Predictive Automated Phenomenological Rates). The central element is a new master equation system solver (MESS) for complex-forming chemical reactions with multiple wells and multiple bimolecular products. The code includes a variety of features for (i) solving the master equation, (ii) incorporating advanced treatments for the transition matrix, and (iii) for examining the outcome of the kinetics. Currently, the solution features include parallel direct diagonalization of the transition matrix, a low-eigenvalue method for low temperatures, well truncations as appropriate, and limited use of quadruple precision for problem cases. The transition matrix allows for multidimensional quantum and semiclassical treatments of torsions, anharmonic treatments of umbrella modes, IR radiative transitions, inclusion of external reactants, automated connectivity, a variety of collisional energy transfer kernels, and a number of “standard” statistical models. The output features include automated merging of species, evaluation of product energy distributions, hot reaction probabilities, and time dependent species populations. Many of these features are only available in the MESS code. Considerable effort was devoted over the last year to increasing the stability, utility, and efficiency of this code.

Various ancillary codes, that are directly coupled to the MESS code and are part of the PAPR package, provide a number of additional features. For example, the VaReCoF code allows for the parallel implementation of direct variable reaction coordinate transition state theory, the DiNT code implements Direct Nonadiabatic Trajectory simulations, the OneDMin code estimates Lennard-Jones parameters from detailed intermolecular potentials, and a python script generates PLOG modified Arrhenius fits for all reaction channels over a complex potential energy surface.

The MESS code is proving to be of great value for studying the kinetics of complex systems. For example, Alexander Mebel, a world leader in the exploration of potential energy surfaces for PAH forming reactions, recently spent a sabbatical at Argonne with the express purpose of learning to use the PAPR package of codes. As a first step, Alex used the codes to predict the temperature and pressure dependent kinetics of the reactions involved in the conversion from phenyl to naphthalene via the HACA mechanism. This analysis demonstrated the key importance of treating the pressure dependence, which has been ignored in all prior combustion modeling studies. These results have led Alex and our group to initiate a long term collaboration to predict the temperature and pressure dependent kinetics of all the main pathways involved in the conversion from one to two or three

aromatic rings. Such an analysis, which would not be feasible without the PAPR software package, should significantly improve the fidelity of PAH formation mechanisms used in combustion models.

We have also continued our work on coupling the two-dimensional master equation (2DME), in energy E and angular momentum J ,

with accurate calculations of collision induced E and J transfer rates. This work has involved further code development, together with a new application to $H + O_2 (+M) \rightarrow HO_2 (+M)$, which is the most important recombination reaction in combustion. The resulting predictions are in remarkably good agreement with the extensive experimental data (cf. the Figure), and allow for a more accurate description of the dependence of the kinetics on various colliders. Interestingly, the results indicate a much more gradual approach to the low-pressure limit than was previously assumed on the basis of the one-dimensional master equation calculations.

In another recent application, we predicted the kinetics of the $O + C_2H_4$ spin-forbidden reaction by incorporating a nonadiabatic statistical treatment of intersystem crossing in the ME approach. This method is sometimes called “nonadiabatic transition state theory,” as the operating equations have similarities to conventional transition state theory. The weak nonadiabatic coupling was modeled using the Landau-Zener expression, which was validated against a more detailed multidimensional approach in our earlier work. The resulting a priori product branching was found to agree well with available room temperature experimental results and with an earlier empirical ME calculation. However, the results of the a priori and empirical ME calculations differ from one another at elevated temperatures (where no experimental results are available), thus emphasizing the usefulness of fully a priori predictions.

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Software Release

The PAPR web-site (chm.wls.chm.anl.gov/papr) now provides free access to our package of kinetics codes. There are four primary codes that we are releasing at this time (MESS, VaReCoF, DiNT, and OneDMin), together with a number of ancillary scripts.

MESS: Master Equation System Solver is our new master equation code featuring the strategies detailed in Y. Georgievskii, J. A. Miller, M. P. Burke, S. J. Klippenstein, *J. Phys. Chem. A*, **117**, 12146-12154 (2013).

DiNT: Direct Nonadiabatic Trajectories. A molecular dynamics program for adiabatic and nonadiabatic chemistry, version 1.1; A. W. Jasper, C. M. Oana, and D. G. Truhlar, Sandia National Laboratories and University of Minnesota (2013).

VaReCoF: Variable Reaction Coordinate Flux is our direct transition state theory code for predicting the kinetics of barrierless reactions. Y. Georgievskii, L. B. Harding, S. J. Klippenstein, *Phys. Chem. Chem. Phys.* **8**, 1133-1147 (2006).

OneDMin: A code for calculating Lennard-Jones parameters from detailed intermolecular potentials; A. W. Jasper and J. A. Miller, Sandia National Laboratories (2013).

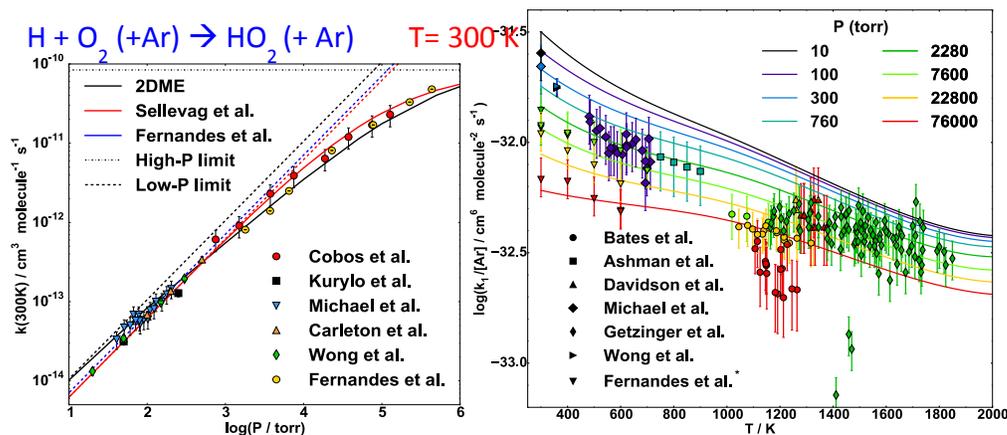


Figure Caption: Temperature and pressure dependent a priori predictions for the $H + O_2$ recombination rate coefficient compared with experiment.

Future Plans

Future efforts will continue to expand our suite of released codes, including new codes for locating crossing seams, sampling crossing seams, and calculating nonadiabatic fluxes. We will also incorporate our previously published Monte Carlo sampling schemes into our transition state theory codes to allow for more complete a priori treatments of vibrational anharmonicity. Other codes, such as our 2DME code, will be made available as manuals are written for them and as they become more stable.

We have a vision of expanding to treat whole classes of kinetics via large-scale simulations of many reactions. Continued progress in the automation of the kinetic predictions will require further consideration of the coupling to ab initio electronic structure evaluations. Scripts will be provided for these couplings. Further work on more general programming of the 2DME and more direct coupling to trajectory simulations of energy and angular momentum transfer is also planned. Another topic of interest involves the development of coupled master equations that treat a succession of reactions without the presumption of thermalization at each stage.

A systematic study of intersystem crossing for several O + alkene and alkyne reactions is underway. This study will make use of several of the codes newly developed for this project, allow us to quantify the accuracy of the ME approach when applied to spin-forbidden reactions, and will result in the development of improved strategies for treating intersystem crossing.

Grant Numbers and Grant Titles

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Postdoc(s): Marco Verdicchio, Xiaohu Li

Ten Publications

1. S. J. Klippenstein, *From Theoretical Reaction Dynamics to Chemical Modeling of Combustion*, Proc. Combust. Inst., plenary paper, submitted (2016).
2. X. Li, A. W. Jasper, J. Zador, J. A. Miller, S. J. Klippenstein, *Theoretical Kinetics of O + C₂H₄*, Proc. Combust. Inst., submitted (2015).
3. A. M. Mebel, Y. Georgievskii, A. W. Jasper, S. J. Klippenstein, *Temperature- and Pressure-Dependent Rate Coefficients for the HACA Pathways from Benzene to Naphthalene*, Proc. Combust. Inst., submitted (2015).
4. A. W. Jasper, *Multidimensional Effects in Nonadiabatic Statistical Theories of Spin-Forbidden Kinetics: A Case Study of O(³P) + CO → CO₂*. J. Phys. Chem. A, **119**, 7339-7351 (2015).
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New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States

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I. Program Scope

This research program focuses on the development, dissemination, and applications of new generations of *ab initio* electronic structure approaches and computer codes exploiting the exponential wave function ansätze of single- and multi-reference coupled-cluster (CC) theories, which can provide an accurate description of chemical reaction pathways and potential energy surfaces involving closed- and open-shell species, molecular electronic excitations characterized by one- as well as many-electron transitions, including challenging cases of electronic near-degeneracies, and properties other than energy. The overall goal is to design and apply methods that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, light harvesting, and photochemistry. The emphasis is on approaches that offer high accuracy, ease of use, and lower computational costs compared to other quantum chemistry techniques that aim at similar precision, so that one can study complex molecular problems with dozens or hundreds of non-hydrogen atoms, in addition to smaller systems, in a predictive and systematically improvable manner, supporting ongoing experiments or in the absence of experimental information. Methods pursued in this program can utilize modern multi-node, multi-core computer architectures and are well suited for pursuing novel coding strategies, such as automated and parallel implementations. The most promising electronic structure approaches developed in this program are shared, at no cost, with the community through the GAMESS package. Some methods discovered in this program, in the original or modified form, are also available in the NWChem, Q-Chem, and MRCC codes.

II. Recent Progress (2013 – 2015 and January 1 – March 1, 2016)

Our research in the reporting period has consisted of two distinct and yet closely related parts, namely, (1) development of new *ab initio* electronic structure approaches and many-body theories for fermionic systems exploiting the exponential CC ansatz, which has been accompanied by substantial programming effort and benchmark calculations, and (2) applications of new and existing quantum chemistry approaches to ground and excited-state molecular potential energy surfaces, singlet-triplet and singlet-singlet gaps in biradicals, multi-photon ionization experiments, structural, electronic, and catalytic properties of transition metal nanoparticles and complexes, and photochemistry of bioinorganic systems.

In the area of new *ab initio* methods, we have extended the idea of the active-space equation-of-motion (EOM) CC methods to the doubly electron-attached (DEA) and doubly ionized (DIP) formalisms, which are applicable to open-shell species with two electrons outside the closed-shell cores, particularly to the electronic spectra of biradicals and single bond breaking, without invoking complicated steps of genuine multi-reference CC theories. In particular, we reported the development of the state-of-the-art, full and active-space, DEA- and DIP-EOMCC methods with up to 4-particle–2-hole (4p2h) and 4-hole–2-particle (4h2p) excitations [1,6]. By examining bond breaking in F₂ and low-lying singlet and triplet states in CH₂, (HFH)⁺, and trimethylenemethane, we demonstrated that the DEA- and DIP-EOMCC methods with an active-space treatment of 4p2h and 4h2p excitations reproduce the results of the analogous full calculations at a tiny fraction of the computer effort, allowing us to determine the singlet-triplet and singlet-singlet gaps in these biradical systems to within fractions of kcal/mol [1,6]. We also showed that the DEA- and DIP-EOMCC approaches with the full and active-space treatments of 4p2h and 4h2p excitations provide results which are practically insensitive to the choice of the underlying molecular orbital (MO) basis, including orbitals of the target *N*-electron species and their (*N*−/+2)-electron counterparts [6]. This should be contrasted with the DEA/DIP EOMCC methods truncated at 3p1h/3h1p excitations, which are less accurate and more sensitive to the choice of MO basis [6]. We have also continued working on

the EA- and IP-EOMCC methodologies. For example, we used the scalar relativistic IP-EOMCC approaches, correlating valence and semi-core electrons and including up to 3h2p terms in the ionizing operator, to provide an accurate and complete assignment of peaks and shoulders in the experimental photoelectron spectrum of Au₃⁻ [8] for the first time. We demonstrated that one has to correlate semi-core electrons, in addition to the valence ones, use larger basis sets, and include the higher-order 3h2p effects to obtain meaningful results. We showed that geometry relaxation during electron ejection from Au₃⁻ contributes to the peak widths, in addition to multiple electronic states behind a given spectral feature.

We have continued developing the generalized form of the previously proposed biorthogonal moment energy expansions, which in the past resulted in the left-eigenstate completely renormalized (CR) CC and EOMCC approaches, exploited, for example, in Refs. [2,4,5,7,9,10], and, most recently, in the discovery of the CC(*P;Q*) formalism, which we will work on in the future. We recall that the CC(*P;Q*) theory enables one to contemplate a wide variety of novel, computationally efficient *ab initio* schemes for high accuracy calculations of ground- and excited-state potential energy surfaces. Among them is the CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy, in which energies obtained in the active-space CC/EOMCC calculations, such as CCSDt/EOMCCSDt or CCSDtq/EOMCCSDtq, which recover much of the non-dynamical and some dynamical electron correlation effects, are corrected for the higher-order, primarily dynamical, correlations, such as certain classes of triples ('3') or triples and quadruples ('3,4') missing in the active-space CC/EOMCC considerations. In the reporting period, we extended the previously developed CC(t;3) approach, which provides ground-state potential energy surfaces, reaction profiles involving biradical transition states, and singlet-triplet gaps in biradical systems that agree with the parent full CCSDT data to within small fractions of a millihartree for total and relative energies at a fraction of the cost, to the virtually exact CC(t,q;3) and CC(t,q;3,4) models including connected quadruple excitations. By examining the double dissociation of water, the insertion of Be into H₂, and the singlet-triplet gap in the strongly correlated (HFH)⁻ system, we demonstrated that the CC(t,q;3) and CC(t,q;3,4) methods, especially the latter one, offer significant improvements in the active-space CCSDtq results, reproducing the exact (full CI) or virtually exact (CCSDTQ) total energies to within small fractions of a millihartree, at a tiny fraction of the computer effort involved in the CCSDTQ calculations, even when the electronic quasi-degeneracies become substantial. Our first paper about these findings is presently in preparation and our work on the excited-state extension of the CC(t;3) scheme is in progress.

We have also continued developing and testing the older CR-CCSD(T) and CR-EOMCCSD(T) and the more recent CR-CC(2,3) and CR-EOMCC(2,3) approaches. In particular, we examined vertical excitation energies for a comprehensive test set of about 150 singlet excited states of 28 medium-size organic molecules to benchmark two variants of the approximately size-intensive CR-EOMCCSD(T) method, abbreviated as δ -CR-EOMCCSD(T), and the analogous two variants of the newer, rigorously size-intensive, δ -CR-EOMCC(2,3) approach based on the biorthogonal method of moments of CC equations against the previously published CASPT2, CC3, and EOMCCSDT-3 results as well as the suggested theoretical best estimate (TBE) values [9]. We demonstrated that the non-iterative triples corrections to the EOMCCSD excitation energies defining the relatively inexpensive, single-reference, black-box δ -CR-EOMCC approaches provide significant improvements in the EOMCCSD data, while closely matching the results of the iterative and considerably more expensive CC3 and EOMCCSDT-3 calculations and their CASPT2 and TBE counterparts, demonstrating the utility of the cost effective δ -CR-EOMCC methods in applications involving molecular electronic spectra [9]. Our δ -CR-EOMCC approaches were also used to identify and characterize about 50 additional excited states, including several states having substantial two-electron excitation components, which have not been found in the previous work on the same molecules and which can be used in future benchmark studies [9]. We uncovered a simple mathematical relationship between the reduced excitation level diagnostic obtained in EOMCCSD calculations, introduced by our group in 2005, and the magnitude of the triples δ -CR-EOMCC corrections to the EOMCCSD excitation energies [9]. This may allow us to estimate the effect of the triples on the EOMCCSD results solely on the basis of relatively inexpensive EOMCCSD calculations.

We have continued applying our CR-CC and CR-EOMCC methods to important chemical problems, especially those relevant to catalysis and photochemistry. In particular, we reported the unprece-

mented scalar relativistic CR-CC(2,3) computations for the aerobic oxidation of methanol to formic acid on the Au₈⁻ nanoparticles [4]. Not only did we obtain a definitive description of the relevant catalytic reaction pathway, but we also used the CR-CC(2,3) results to benchmark representative density functional theory (DFT) approaches, demonstrating that most of them fail. In the same spirit, we used parallel CCSD(T) codes in GAMESS based on our algorithms developed in the early 2000s to evaluate performance of various DFT functionals in the examination of reaction mechanisms of Cu(I)-catalyzed indole synthesis and click chemistry of iodoalkynes and azides. We also reported the unprecedented δ -CR-EOMCC(2,3) computations showing that the previously postulated doubly excited state of azulene below the ionization threshold and mediating the 1+2' multi-photon ionization that leads to a clear Rydberg fingerprint exists [2], proving a crucial role of doubly excited states in the Rydberg fingerprint spectroscopy. Furthermore, we applied CR-EOMCC(2,3) and its ground-state CR-CC(2,3) counterpart to several singlet and triplet potential energy surfaces corresponding to the dissociation of the water molecule into OH and H, showing that the black-box CR-CC(2,3) and CR-EOMCC(2,3) methods are as accurate as the most sophisticated, expert, multi-reference CC approaches [7]. Our preliminary analysis indicates that further (in fact, spectacular) improvements in the CR-EOMCC(2,3) excited-state data for the water molecule can be made if we replace the CR-EOMCC corrections by their aforementioned CC(t;3) extensions, which will be developed in the near future. We also performed the unprecedented active-space CCSDt/EOMCCSDt and CR-CC(2,3)/CR-EOMCC(2,3) computations for the low-lying singlet and triplet states of the challenging organic biradical, 1,2,3,4-cyclobutanetetraone, which present substantial problems to the existing single- and multi-reference wave function and DFT approaches [10].

Some additional algorithmic advances in the reporting period include the development of efficient parallel numerical derivatives for fast geometry optimizations and vibrational frequency calculations at any level of CC/EOMCC theory through the utilization of modern multi-node, multi-core computer architectures. We used the resulting codes, combined with a parallel implementation of CCSD(T) in GAMESS, to optimize the geometries of the low-energy structures of the neutral Au₈ particle, answering one of the key questions in catalysis involving smaller gold nano-particles, which is their planar vs. non-planar shape [3]. We examined the effects of geometry relaxation at the high *ab initio* CCSD(T) level and of the combined effects of the basis set and core-valence correlations, comparing the results with MP2 and DFT. Our best CCSD(T) computations favor the planar configuration of Au₈, with the next three non-planar structures separated by 4–6 kcal/mol [3]. We also demonstrated the usefulness of our CR-CC ideas and algorithms, developed in the context of quantum chemistry, in extending the CC theory with singles, doubles, and a non-iterative treatment of triples to three-body interactions emerging in the nuclear structure considerations [5].

Finally, we have continued our work on the development and applications of the local correlation CCSD, CCSD(T), and CR-CC(2,3) approaches, and their multi-level extensions, which exist under the umbrella of 'cluster-in-molecule' (CIM) methods, extending them to open-shell approaches employing the ROHF references. The resulting CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods, and their CIM-MP n analogs enable high-accuracy calculations for closed- and open-shell systems with hundreds of correlated electrons. Our CIM-CC and CIM-MP2 codes in GAMESS were released in May 2013. They are characterized by the linear scaling of the CPU time with the system size, when a single-level CIM-CC or CIM-MP2 approach is used, memory requirements that do not grow with the size of the system, coarse-grain parallelism, which can be further enhanced by the fine-grain parallelism of each CIM subsystem calculation, and the purely non-iterative character of the local triples and other perturbative energy corrections. They enable one to fuse high- and low-level CC and MP n calculations without splitting large molecular systems into *ad hoc* fragments and saturating dangling bonds. Our plan is to further enhance our CIM-CC GAMESS codes, so that they can take full advantage of modern massively parallel, multi-node computer platforms, where each node has multiple cores.

III. Future plans

Our method development work in the next three years will concentrate on (i) extension of the recently formulated CC($P;Q$) hierarchy, which allows one to combine the active-space CC and EOMCC ap-

proaches with the moment energy expansions used in the completely renormalized CC/EOMCC computations, to excited potential energy surfaces along bond breaking coordinates, **(ii)** development of novel classes of single-reference CC methods for strongly correlated electronic systems by extending the approximate coupled-pair (ACP or ACC) theories, co-pioneered by the PI with Professor Josef Paldus about 25 years ago, to higher-order dynamical correlation effects the ACP/ACC approaches have difficulty with, such as connected triples, **(iii)** extension of the previously developed active-space variants of the electron-attached (EA) and ionized (IP) EOMCC methodologies, already in GAMESS, and their recently developed doubly electron attached (DEA) and doubly ionized (DIP) analogs, which enable precise determination of ground and excited states of open-shell species that differ by one or two electrons from the related closed-shell systems, to the triply electron attached (TEA) and triply ionized (TIP) cases, and **(iv)** work toward implementation of highly parallel, linear scaling, local correlation CC and ACP/ACC codes exploiting the previously developed CIM ideas and their multi-level extensions allowing one to mix different electronic structure theory levels in a single computation, which can take full advantage of modern massively parallel, multi-node computer platforms, where each node has multiple cores. We will also continue our recently initiated work on experimenting with the active-space DEA- and DIP-EOMCC algorithms aimed at a potentially substantial additional reductions of the computer costs involved, especially in the DEA case. As in the past, all of the proposed methodological and algorithmic advances will be accompanied by benchmark and realistic computations, especially those that can be tied to the ongoing experimental work. Among the applications to be completed in the near future are the photoelectron spectra of silver nanoparticles and copper oxide. We are also planning to continue our earlier work on the oxidation processes catalyzed by the gold nanoparticles and to start exploring photochemistry of inorganic complexes studied in the context of solar energy conversion schemes. Other applications, including small radical-molecule and radical-radical reactions relevant to combustion and properties of aluminum hydride clusters relevant to hydrogen storage, will be pursued as well.

IV. Ten selected publications of DOE sponsored research that have appeared in the past 3 years

- [1] J. Shen and P. Piecuch, "Doubly Electron-Attached and Doubly Ionized Equation-of-Motion Coupled-Cluster Methods with 4-particle-2-hole and 4-hole-2-particle Excitations and their Active-Space Extensions," *J. Chem. Phys.* **138**, 194102-1 – 194102-16 (2013).
- [2] P. Piecuch, J.A. Hansen, D. Staedter, S. Faure, and V. Blanchet, "Communication: Existence of the Doubly Excited State that Mediates the Photoionization of Azulene," *J. Chem. Phys.* **138**, 201102-1 – 201102-4 (2013).
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- [6] J. Shen and P. Piecuch, "Doubly Electron-Attached and Doubly Ionised Equation-of-Motion Coupled-Cluster Methods with Full and Active-Space Treatments of 4-particle-2-hole and 4-hole-2-particle Excitations: The Role of Orbital Choices," *Mol. Phys.* **112**, 868-885 (2014).
- [7] J.J.Lutz and P.Piecuch, "Performance of the Completely Renormalized Equation-of-Motion Coupled-Cluster Method in Calculations of Excited-State Potential Cuts of Water," *Comput. Theor. Chem.* **1040-41**, 20-34 (2014).
- [8] N.P. Bauman, J.A. Hansen, M. Ehara, and P. Piecuch, "Communication: Coupled-Cluster Interpretation of the Photoelectron Spectrum of Au₃⁻," *J. Chem. Phys.* **141**, 101102-1 – 101102-5 (2014).
- [9] P. Piecuch, J.A. Hansen, and A.O. Ajala, "Benchmarking the Completely Renormalised Equation-of-Motion Coupled-Cluster Approaches for Vertical Excitation Energies," *Mol. Phys.* **113**, 3085-3127 (2015).
- [10] J.A. Hansen, N.P. Bauman, J. Shen, W.T. Borden, and P. Piecuch, "Ab Initio Coupled-Cluster and Multi-Reference Configuration Interaction Studies of the Low- Lying Electronic States of 1,2,3,4-Cyclobutanetetraone," *Mol. Phys.*, in press; published online: 9 December 2015.

Active Space Decomposition for Exciton and Charge Dynamics

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Program Scope and Definition:

The objective of this program is to develop *ab initio* electronic structure theory for calculating highly accurate **diabatic model Hamiltonians for exciton and charge dynamics** relevant to solar energy conversion, such as singlet fission (a carrier multiplication process in organic semiconductors). The proposed approach is based on many-body wave functions and is systematically improvable. The model Hamiltonians could then be used in dynamics studies based on the quantum master equations to unravel the mechanisms of such processes. Furthermore, to study the importance of dynamics through conical intersections, it is proposed that we develop a computational tool to calculate **analytic nuclear energy gradients** (i.e., the slope of the potential energy surfaces) and non-adiabatic coupling matrix elements for these methods to allow for computing the conical intersection seams and simulating surface-hopping dynamics that explicitly treat the nuclear degrees of freedom.

Recent Progress: Active Space Decomposition. Under the sole support by this funding, we have developed the so-called active space decomposition (ASD) methods and implemented them into efficient parallel code in the BAGEL program package (Parker *et al.* JCTC 2014). The ASD ansatz decomposes the wave functions for molecular aggregates using their geometries,

$$\Psi = \sum_{IJ} C^{IJ} \Phi_I^A \Phi_J^B, \quad \langle \Phi_I^A \Phi_J^B | \hat{H} | \Phi_{I'}^A \Phi_{J'}^B \rangle = \Gamma_{\zeta}^{II'A} H_{\zeta,\eta} \Gamma_{\eta}^{JJ'B}$$

from which one can readily derive the diabatic model Hamiltonians for exciton and charge dynamics. This decomposition can be thought of as singular value decomposition (SVD) of a dimer wave function on the left-hand side. Our hypothesis was that the rank of SVD must be small when we choose the subsystems *A* and *B* based on molecular geometries, which have been tested numerically. Furthermore, this ansatz has been extended to multiple active subspaces using the DMRG algorithm (Parker *et al.* JCP 2014), revealing the profound connection between ASD and low-entanglement wave functions. The ASD-based model Hamiltonians for the singlet fission processes in pentacene and tetracene crystals (Parker *et al.* JPCC 2014) have been used as reference data by other computational chemists studying these processes.

Recently we have extended the ASD method so that it can be applied to covalently linked donor–acceptor pairs (Kim *et al.* JCTC 2015) by introducing the orbital optimization procedure. The orbital optimization corresponds to the **inverse problem** of the ASD decomposition above (i.e., determining the diabatic subspaces by optimizing the compression efficiency; note that the ASD method is variational). This new method has been applied to Closs' model systems for triplet transfer using

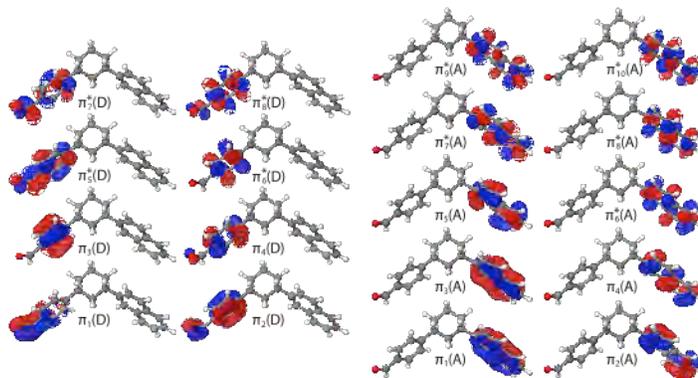


Figure 1: Orbital optimized ASD provides a way to determine the donor and acceptor active subspaces for covalently linked systems.

Marcus theory to give excellent agreements with the experimental rate constants.

Analytic Nuclear Energy Gradients for Multireference Theories.

Though recent studies have shown that one can reproduce the kinetics of the singlet fission processes in pentacene without considering the conical intersections, as opposed to earlier studies, there are still many questions to answer; for instance, are there any systems in which charge-transfer states are very high in energy and singlet fissions occur mainly through conical intersections? The key to answering these questions is to locate conical

intersection seams on the potential energy surfaces, and if possible, to perform on-the-fly dynamics simulations. For the first time since the CASPT2 method was developed in 1992, we have derived and implemented the equations for analytic nuclear energy gradients for fully internally contracted CASPT2 (MacLeod *et al.* 2015). The code is implemented in BAGEL. We demonstrated the efficiency of our code by optimizing the structure of a free-base porphyrin cation radical, which undergoes pseudo-Jahn–Teller distortion. We have recently parallelized the program using MPI3-RMA and are currently working on its extension to multiple state variants and non-adiabatic coupling matrix elements.

Future Directions: The ASD-DMRG method will be extended to higher-dimensional tensor networks (such as PEPS and MERA), which would allow us to compute the diabatic models directly for larger molecular aggregates. We will also investigate an ASD-like approach based on EOM-CC fragment wave functions, which would be not only useful for predictive applications but also interesting in the context of local correlation for excited states. These methods will be integrated in data-driven approaches for materials discovery as an intermediate layer between high-throughput computations and experiments.

Grant Number and Grant Title

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

Postdoc(s): Matthew MacLeod and Inkoo Kim (and, in part, Shane Parker and Jefferson Bates)

Student(s): (in part, Xiaotian Deng, Hai-Anh Le, and Ryan D. Reynolds)

Publications Acknowledging these Grant:

Parker, S. M.; Shiozaki, T. Quasi-diabatic states from active space decomposition. *J. Chem. Theory Comput.* **2014**, *10*, 3738–3744.

Parker, S. M.; Seideman, T.; Ratner, M. A.; Shiozaki, T. Model Hamiltonian analysis of singlet fission from first principles. *J. Phys. Chem. C* **2014**, *118*, 12700–12705.

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Kim, I.; Parker, S. M.; Shiozaki, T. Orbital optimization in the active space decomposition model. *J. Chem. Theory Comput.* **2015**, *11*, 3636–3642.

BAGEL: Brilliantly Advanced General Electronic-structure Library. <http://www.nubakery.org> under the GNU General Public License.

Molecule	H_{if} (meV)	k	$k(\text{exp})$
1,3-C-ee	0.863	7.0×10^9	7.7×10^9
1,4-C-ee	0.363	1.6×10^9	1.3×10^9
2,7-D-ee	0.076	6.9×10^7	9.1×10^7
2,6-D-ee	0.010	1.1×10^6	3.1×10^6

Figure 2: Marcus rates for triplet transfer computed by the ASD method agree well with the experimental data.

Presentation Title

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1101 University Ave, Madison, WI 53706

Abstract

The diversity of metal-organic framework (MOF) materials is immense. Nonetheless, only a small fraction of this potential diversity has been explored to date. Since the physical properties of MOFs vary strongly with their functionalization and structure, much of the excitement surrounding MOFs involves identifying or “designing” MOFs tailored for specific applications, either guided by computational results or via chemical intuition. Still, once a promising structure has been identified (either as a result of intuition or computational design), one key challenge remains: the resulting structure must be synthesized. This targeted synthesis remains an elusive goal, often requiring a delicate balance of reaction conditions (temperature, reactant concentrations, solvent / solvent mixtures...), typically discovered empirically by time consuming screenings over reaction conditions. Our present work aims to enable such targeted synthesis by developing comprehensive and predictive models of the fundamental processes occurring at the MOF-solution interface under synthetically-relevant conditions, including MOF interfacial structure and stability, crystal growth, nucleation, and post-synthetic modification.

We have focused initially on zeolitic imidazolate frameworks (ZIFs), a specific class of MOFs with divalent metal cations (typically Zn^{2+}) and bridging imidazolate (Im) linkers. This choice is motivated by the stability of ZIFs, their widespread applications, and their diverse crystal structure that are influenced by both functionalization and synthetic conditions. Our initial efforts have focused on the development of force fields suitable for the simulation of process at the ZIF-solution interface. These force fields must account for: (1) the relative strain / stability of the various ZIF structures; (2) the strong anisotropy of both the imidazole linker around the nitrogen atom (“lone pair”) and the common solvents used in ZIF synthesis (dimethyl formamide); (3) dative metal-ligand interactions during MOF formation. None of these criteria are satisfied by existing ZIF models (nor for any other MOF models).

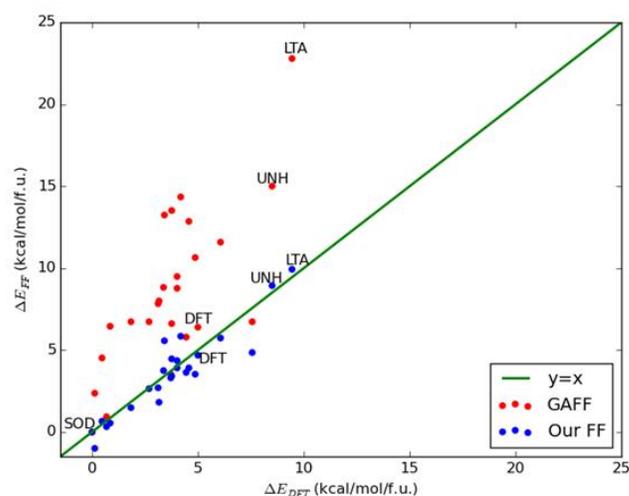
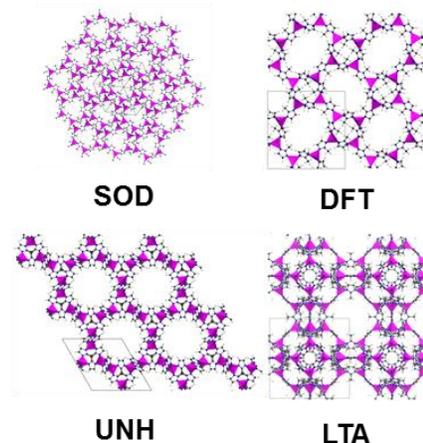


Figure 1. (Top) Illustration of several ZIF topologies; (Bottom) Comparison of initial GAFF ZIF force field with our optimized ZIF model.

We have made significant progress with regard to the first of these two requirements. We are developing a first-principles based “intra-molecular” ZIF force field that reproduces the stability of all known ZIF topologies. We utilized dispersion-corrected periodic density function theory calculations to calculate the relative energy of all known ZIF topologies. Since not all topologies are (currently) synthetically realizable with a given functionalization, we “mutated” the experimentally-observed crystal structures into a uniform (un-functionalized) imidazole reference, yielding a chemically-identical but topologically-diverse set of reference structures. The relative energy (per formula unit) of these structures can then be compared with the relative strain energy computed by a force field. Reproduction of this strain, along with basic structural motifs, is a key requirement for the simulation of interfacial properties. Figure 1 summarizes our current progress. Note that prior existing ZIF models (here, GAFF) have not been parametrized to reproduce the strain energy and exhibit both substantial systematic and random errors. In contrast, our optimized model displays substantial improvement in both strain energy and structure.

We have also made substantial progress in developing force fields for systems which exhibit atomic anisotropy, as is present in many MOF systems. In collaboration with Anthony Stone (Cambridge) and Alston Misquitta (Queen Mary College, London), we have developed a novel short-range functional form based on a simple Slater-like model of overlapping atomic densities and an iterated stockholder atom (ISA) partitioning of the molecular electron density. This Slater-ISA methodology yields a more accurate, transferable, and robust description of the short-range interactions at minimal additional computational cost as compared to standard Lennard-Jones or Born-Mayer approaches. This Slater-ISA approach also enables a straightforward generalization to atomically anisotropic systems (e.g. atoms containing lone pairs), also at minimal additional computational expense. These advances will be key in enabling our future studies of MOF interfacial systems.

This reporting period also spans the conclusion of our prior award, which focused on the development of methods for generating “physically-motivated” force fields from symmetry-adapted perturbation theory and the application of these methods to complex systems including MOFs. Recently, we used these force fields to critically assess “conventional” (empirically-parametrized) force fields for use in simulations of MOF gas uptake. Beyond MOFs, we demonstrated that our first-principles based approach can also be utilized to generate models for common organic liquids that are transferable from the gas-phase to the bulk, even in the absence of parameterization. In collaboration with Arun Yethiraj (Wisconsin), we used this approach to develop models for several ionic common ionic liquids, yielding what we believe are among the most accurate ionic liquid models, and reproducing structural, thermodynamic, and transport properties entirely from first principles. Yethiraj is now utilizing these models in studies of polymer-ionic liquid blends for polymer electrolyte applications.

Grant Numbers and Grant Titles

DE-SC0002152 Enabling Technologies for High-Throughput Screening of Nano-Porous Materials: Collaboration with the Nanoporous Materials Genome Center

DE-SC0014059 Crystal growth, nucleation, structure and dynamics at Metal Organic Framework/solution interfaces

Student(s): Tingting Weng
Xingyi Li
Mary Van Vleet

Recent Publications

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3. McDaniel, J. G.; Schmidt, J. R., Next-Generation Force Fields from Symmetry-Adapted Perturbation Theory. *Annu. Rev. Phys. Chem.* **2016**, in press.
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Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO₂ HydrogenationJingyun Ye¹, J. Karl Johnson¹¹University of Pittsburgh, Department of Chemical & Petroleum Engineering, Pittsburgh PA 15261

Abstract

Efficient conversion of CO₂ into chemicals has the potential to reduce net CO₂ emissions while generating high-energy density fuels and other valuable commodities. However, hydrogenation (reduction) of CO₂ is very challenging because of its kinetic and thermodynamic stability. Hence, reduction of CO₂ typically requires aggressive reaction conditions (high temperature and high pressure). Homogeneous catalytic conversion of CO₂ can be carried out under fairly mild conditions, but has the drawback catalyst recycling is extremely difficult. An ideal catalyst for large-scale industrial CO₂ hydrogenation would combine the advantages of homogeneous and heterogeneous catalysts. Moreover, if CO₂ capture could be combined in a single process with CO₂ reduction, then the economics could be significantly enhanced through process intensification.

We present first-principles calculations showing how it is possible to design catalysts computationally that have advantages of both homogeneous and heterogeneous catalysts. The catalysts we have designed are based on families of Lewis pair functional groups, which we have incorporated into a thermally and chemically stable metal organic framework (MOF) nanoporous materials.² We have developed design principles for optimizing catalyst performance based on a Sabatier analysis coupled with descriptors for the elementary reaction barriers for converting CO₂ to formic acid. The analysis was developed based on a series of 8 different Lewis pair functional groups that were incorporated into UiO-66. We denote these functionalized MOFs as UiO-66-X, where X denotes the functional group. Results of our Sabatier analysis are shown in Figure 1.¹ The Sabatier analysis allows us to screen functional groups in a computationally efficient way through computing the H₂ adsorption energies and hardness of the Lewis pair radical as surrogates for computing the full reaction barriers. Moreover, the calculations for H₂ adsorption barriers can be computed on the molecular catalytic Lewis pair moiety, making the calculations much more efficient than computing adsorption energies on the full periodic functionalized MOF.

We have developed a second generation family of functional groups based on the UiO-67 MOF, where we have incorporated the Lewis base site directly into one of the rings of the linker. One promising member

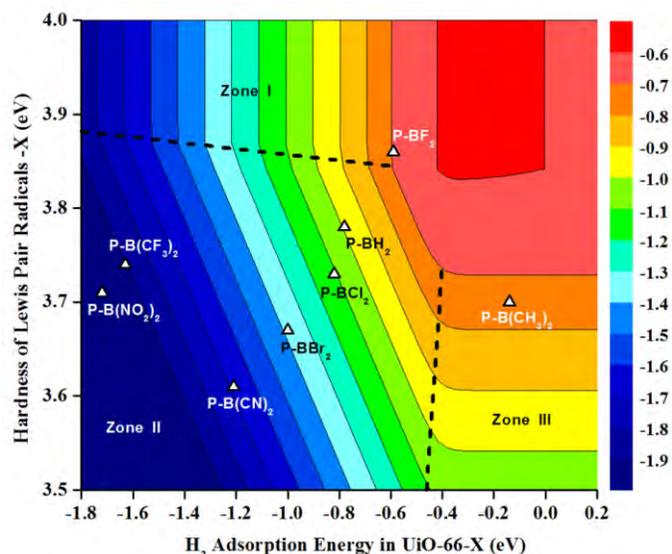


Figure 1. Contour plot of the Sabatier activity for the overall reaction rate for CO₂ hydrogenation at 298 K. The CO₂ hydrogenation barrier is given by a BEP relationship with the H₂ adsorption energy and the H₂ dissociation barrier is given by a relationship with the hardness of the LP radicals -X. Specific LP groups are labeled on the figure. Figure taken from Ye and Johnson.¹

of this family is identified as UiO-67-NBF₂, since it has two fluorine atoms bound to a boron atom, which is the Lewis acid site. We have investigated various loadings of the functional group within the UiO-67 primitive cell and have found that one can have at least four NBF₂ groups in the pore without significantly changing the kinetics of CO₂ hydrogenation to formic acid.³ More importantly, the multiple functional groups in a single pore makes it possible to convert CO₂ to methanol without transporting the reactants or products to other pores within the MOF. We have computed reaction pathways going from CO₂ to methanol within UiO-67-NBF₂. The UiO-67 framework and the UiO-67-NBF₂ functionalized material with one and four functional groups per pore are shown in Figure 2. We have identified various reaction pathways and found that for the most favorable pathway the rate limiting step for conversion of CO₂ to methanol is the dehydration of methanediol, CH₂(OH)₂, to formaldehyde, CH₂O. We have found that formic acid is a very effective catalyst for this dehydration reaction and that it functions as a proton shuttle. The reaction pathways are shown in Figure 3.

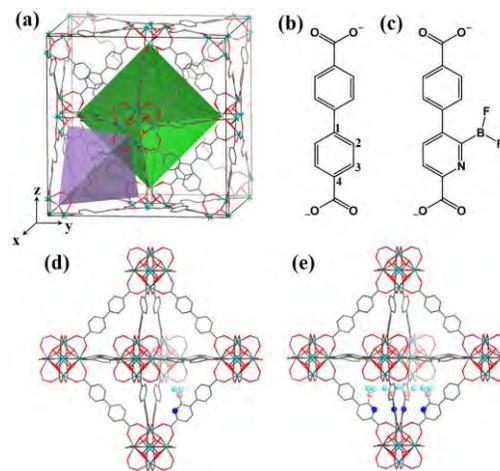


Figure 2. (a) Unit cell of UiO-67. (b) BPDC linker. (c) LP (N-BF₂), a modified BPDC linker. (d) UiO-67 with a single LP functional group per primitive cell. (e) UiO-67 with 4 LP functional groups per primitive cell.

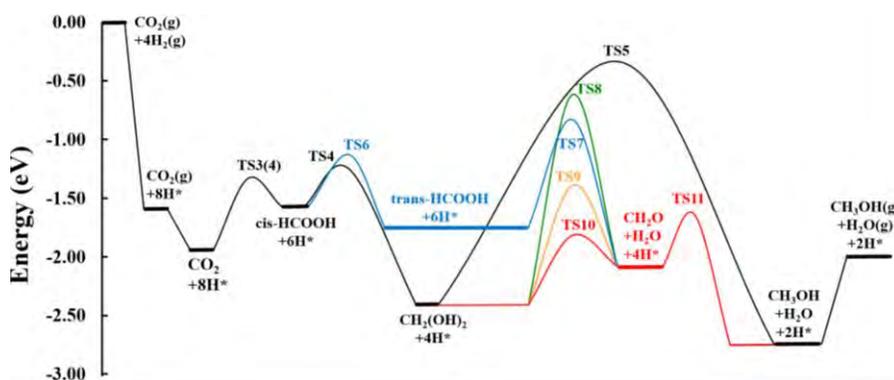


Figure 3. Potential energy profile for CO₂ hydrogenation to produce CH₃OH in UiO-67-(NBF₂)₄. Black: direct CH₂(OH)₂ hydrogenation to produce CH₃OH (all other pathways go through CH₂O as the intermediate to form CH₃OH); blue: cis-HCOOH→trans-HCOOH→CH₂O, green: self-decomposition of CH₂(OH)₂ to CH₂O; yellow: conversion of CH₂(OH)₂ to CH₂O catalyzed by H₂O; red: conversion of CH₂(OH)₂ to CH₂O catalyzed by HCOOH.

Another advantage of the UiO-67-NBF₂ catalyst over our previous generation of materials, UiO-66-X, is that the binding energy of CO₂ on the Lewis pair site is much weaker than the binding energy of H₂ in UiO-67-NBF₂. In contrast, the binding energy of CO₂ in UiO-66-X is comparable to or even greater than the binding energy of H₂, meaning that CO₂ competes for the catalytic sites and in the worst case could poison the activity of the catalyst at high CO₂ loading. The UiO-67-NBF₂ catalyst does not have this problem and will preferentially bind H₂ over CO₂, even at fairly high loadings of CO₂. This, we have identified a new family of catalysts with significant

advantages over the previous generation. Future work will focus on combining CO₂ capture with conversion and on developing more robust functional groups that do not bind intermediates or products strongly.

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- Ye, J.; Johnson, J. K., *Catalytic Hydrogenation of CO₂ to Methanol in a Lewis Pair Functionalized MOF in prepartion* **2016**.

Grant Numbers and Grant Titles

DE-FG02-10ER16165 Design of Stratified Functional Nanoporous Materials for CO₂ Capture and Conversion

Postdoc: Jingyun Ye

Publications

1. Jingyun Ye, J. Karl Johnson “Screening Lewis Pair Moieties for Catalytic Hydrogenation of CO₂ in Functionalized UiO-66”, *ACS Catalysis*, **5**, 6219–6229 (2015).
2. Jingyun Ye and J. Karl Johnson “Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO₂ Hydrogenation”, *ACS Catalysis*, **5**, 2921–2928 (2015).

Molecular modeling of multifunctional metal-organic frameworks

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The ability of controlling the physical and chemical properties of molecular assemblies at the nanoscale through the application of external perturbations is critical to the development of multifunctional materials, such as molecular switches, memory devices, and chemical sensors. By combining high porosity, large surface area, guest selectivity, and structural flexibility, metal-organic frameworks (MOFs) provide a promising platform for developing such stimuli-responsive materials. In particular, the incorporation of open-shell transition metals in the framework results in MOFs that can exhibit spin crossover (SCO), which is accompanied by distinct changes in the physical properties of the material (e.g., color, magnetism, and pore size).

A remarkable example of SCO behavior in MOFs is provided by the family of Hoffmann-type $[\text{Fe}(\text{pz})\text{M}(\text{CN})_4]$ MOFs (pz = pyrazine, and M = Ni, Pd, Pt). These materials display cooperative thermal- and light-induced spin crossover with transition temperatures ($T_{1/2}$) close to room temperature. Of particular interest is the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ framework that exhibits bidirectional chemo-switching between low-spin (LS) and high-spin (HS) states upon adsorption of chemically and structurally different guest molecules. Specifically, while the SCO transition for the empty framework occurs at ~ 290 K, the adsorption of protic solvents (e.g., alcohols and water) and bulky molecules (e.g., benzene and pyridine) stabilizes the HS state, shifting $T_{1/2}$ to lower values. In contrast, CS_2 molecules adsorbed in the MOF pores stabilize the LS state. No effect on the SCO transition is observed upon adsorption of small molecules such as CO_2 and N_2 . Importantly, the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ framework exhibits “memory” response, being able to retain a given spin state upon guest desorption. 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.

To characterize the SCO properties of MOFs at the molecular level, we have developed a unique hybrid Monte Carlo / molecular dynamics (MC/MD) method that builds upon the ligand field molecular mechanics (LFMM) model. Within LFMM, 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-based molecular orbitals. LFMM thus explicitly includes energy contributions that depend on both the instantaneous coordination geometry and the electronic structure of the metal centers. In our MC/MD method, the original LFMM model is combined with a Monte Carlo scheme based on the Metropolis acceptance/rejection criterion that is used to model spin-crossover transitions in systems with multiple metal centers in periodic boundary conditions.

We have applied our hybrid MC/MD method to investigate the SCO behavior of the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ MOF upon adsorption of a variable number of water molecules, from $N_w = 1$ to $N_w = 5$ molecules per unit cell. The magnetization values calculated from the hybrid MC/MD simulations indicate a progressive shift of $T_{1/2}$ to lower temperature as a function of water loading. However, the decrease of $T_{1/2}$ is not constant, suggesting that the sequential addition of water molecules in the pores induces different effects on the SCO properties of the $\{\text{Fe}(\text{pz})[\text{Pt}(\text{CN})_4]\}$ MOF. A distinct change in the material response occurs when two water molecules, on average, are adsorbed per unit cell, with $T_{1/2}$ decreasing more rapidly at higher loadings. The dependence of $T_{1/2}$ on the amount of water adsorbed in the MOF pores is directly

related to the variation of the structural parameters of the framework. In particular, the distance between the Fe(II) centers and the pyrazine linkers at low temperature, i.e., with the Fe(II) centers in the LS state, are significantly shorter than at high temperature when the Fe(II) centers are in the HS state. This is consistent with the weakening of the Fe-N bonds as a result of the occupation of the antibonding d-based molecular orbitals when the Fe(II) centers are in the HS state. Of particular interest is the variation of the Fe-N bond lengths in the LS and HS states as a function of N_w . When the Fe(II) centers of the framework are in the LS state the average Fe-N bond length increases by $\sim 0.4 \text{ \AA}$ as the number of water molecules adsorbed per unit cell increases from $N_w = 1$ to $N_w = 5$. In contrast, the average Fe-N bond length with the Fe(II) centers in the HS state remains essentially constant, independently of the amount of water adsorbed in the pores. The elongation of the Fe-N bonds in the LS state leads to an overall expansion of the framework, with a progressive destabilization of the LS state which directly correlates with the decrease of $T_{1/2}$ as the number of water molecules in the pores increases.

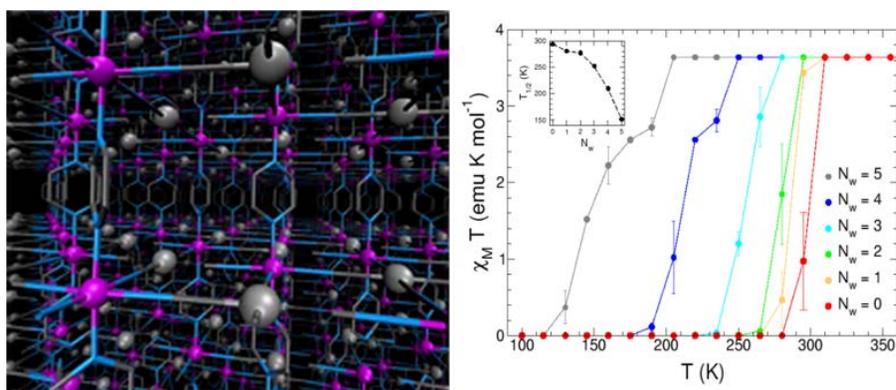


Figure 1. Left: Three-dimensional model of the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ MOF. Right: Calculated $\chi_M T$ (χ_M = molar susceptibility) of the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ MOF upon water adsorption. The modulation of the spin-crossover transition temperature is shown in the inset.

In parallel with the development of the hybrid MC/MD method, we are currently working on the extension of our many-body (MB) potential energy functions to guest molecules of interest for storage and separation in MOFs (e.g., CH_4 , CO_2 , and H_2). The implementation of MB potentials in our hybrid MC/MD approach will enable predictive, molecular-level simulations of adsorption, diffusion, and separation processes in MOFs.

Grant DE-FG02-13ER16387

Theoretical Studies of Spin Crossover Metal-Organic Frameworks

Postdocs: Jordi Cirera, Andreas W. Götz, C. Huy Pham

Students: Pushp Bajaj, Kevin Bao

Publications Acknowledging this Grant in 2013-2016

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

Terranova, Z.L.; Agee, M.M.; Paesani, F. Water Structure and Dynamics in Homochiral $[\text{Zn}(\text{1-L})(\text{X})]$ Metal-Organic Frameworks. *J. Phys. Chem. C* **2015**, *119*, 18239-18247.

Pham, C.H.; Cirera, J.; Paesani, F. Molecular Mechanisms of Spin Crossover in the $[\text{Fe}(\text{pz})\text{Pt}(\text{CN})_4]$ Metal-Organic Framework upon Water Adsorption. *J. Am. Chem. Soc.* **2016**, submitted.

Program Title: DE-SC0006863

First-Principles Spin-Dependent Many-Electron Dynamics: Dielectric Response and Dirac Formalism

Principal investigator: Xiaosong Li, Professor, Department of Chemistry, University of Washington, Seattle, WA 98195-1700, xsli@uw.edu

Postdoc(s): Franco Egidi

Student(s): Feizhi Ding, Joshua Goings, David Williams-Young

Presentation Title:

Time-Dependent Two-Component Relativistic Theory: Linear Response and Real Time

Program Scope: For heavy elements, as well as phenomena involving the electron spins, it is well known that accurate modeling of the excited states and molecular properties requires the inclusion of relativistic effects into the electronic wave function. Because relativistic theories of the electron are inherently spin multi-component, time-dependent ab initio models of spintronic, magnetic, and heavy element containing systems need the ability to handle situations where electron spin can freely evolve in space and time, moving about in any given direction. Most conventional methods employed in the modeling electronic dynamics, such as real-time time-dependent density functional theory (RT-TDDFT), are not flexible enough to handle the additional spin degrees of freedom. The primary problem lies in the so-called “spin collinearity constraint,” which requires that orbital spin is fixed in time. While this constraint is appropriate for a great variety of physical situations, it is inappropriate for many systems where relativistic effects are necessary, since within relativistic theory spin does not yield good quantum numbers, and specific interaction terms between pairs of electron spins and between the electron spins and their orbital motion. The goal of this research program is to develop new time-dependent relativistic methods that enable one to describe properties of the system such as the fine structure of absorption spectra, or transitions between states of different spin-multiplicities such as those observed in the case of phosphorescence.

Recent Progress: In order to address these problems, we recently have generalized both Hartree-Fock and density-functional based dynamics and response methodologies to what is known as a two-component spinor framework. This allows the spin magnetic moment to evolve freely in time under the influence of external fields. For example, using the real-time two-component spinor approach, it is possible to describe the spin flip of an electron under a strong magnetic field, and it becomes possible to describe electronic states where spin is not collinear, i.e. there isn't a preferred spin direction that is uniform in space. Recently, we have investigated the effect of utilizing a two-component spinor basis on both electronic and nuclear dynamics. For pure electronic dynamics, we have investigated the effect of weak magnetic fields on the evolution of the spin magnetic moment, obtaining the physical Larmor precession, a phenomenon that is at the basis of important magnetic spectroscopies. For mixed electronic/nuclear dynamics (in the Ehrenfest approach), we have observed that the two-component spinor approach can describe the spin decoherence during bond dissociation. Furthermore, the two-component spinor approach allows for the description of the correct qualitative dissociation of certain diatomic molecules. Additionally, we have explored the two-component framework for the description of excited states within the linear-response framework, which allows the modeling of absorption and emission spectroscopic processes in the most general framework.

Current and Future Plans: Given this groundwork, the next steps are to include the relativistic operators into the two-component Hamiltonian via the Douglas-Kroll-Hess (DKH) approximation or the eXact-Two-

Component (X2C) methods which, contrary to what happens in non-relativistic theories, always require at least a two-component method to be addressed given the fact that spin-orbit couplings are always present in the theory, and a non-collinear approach is mandatory. For time-dependent phenomena, we propose an efficient dual methodology to treat such effects in a two-component framework by exploiting either Linear Response (LR) theory, or the Real Time (RT) propagation of the wave function. A two-component formulation allows to rewrite the well known relativistic four-component Dirac equation in a form that can be solved using a machinery similar to the one employed in the non-relativistic calculations, but with the explicit presence of scalar and spin-orbit couplings in the Hamiltonian. The time-evolution of such a system subject to a perturbation can be well described using either LR or RT theory, each method having its own advantages and peculiarities. Compared to non-relativistic theory, the electron spin is free to evolve in any arbitrary direction, subject to the interaction with the other electrons and nuclei, as well as to the spin-orbit couplings, giving a much more complete description of the spin-dependent phenomena. This theory development will set the stage for a proper description of spin dynamics, which plays a crucial role in spintronics, catalysis, and quantum information processing.

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

1. J. J. Goings, F. Ding, E. R. Davidson, X. Li, "Approximate Singly Excited States from a Two-component Hartree-Fock Reference," *J. Chem. Phys.*, **2015**, *143*, 144106.
2. F. Ding, J. J. Goings, H. Liu, D. B. Lingerfelt, X. Li, "*Ab Initio* Two-component Ehrenfest Dynamics," *J. Chem. Phys.*, **2015**, *143*, 114105.
3. J. J. Goings, F. Ding, M. Frisch, X. Li, "Stability of the Complex Generalized Hartree-Fock Equations," *J. Chem. Phys.*, **2015**, *142*, 154109.
4. F. Ding, D. B. Lingerfelt, B. Mennucci, X. Li, "Time-Dependent Non-equilibrium Dielectric Response in QM/Continuum Approaches," *J. Chem. Phys.*, **2015**, *142*, 034120.
5. F. Ding, J. J. Goings, M. Frisch, X. Li, "*Ab Initio* Non-Relativistic Spin Dynamics," *J. Chem. Phys.*, **2014**, *141*, 214111.
6. J. J. Goings, A. Schimpf, J. W. May, R. Johns. D. R. Gamelin, X. Li, "Theoretical Characterization of Conduction-Band Electrons in Photodoped and Aluminum-Doped Zinc Oxide (AZO) Quantum Dots," *J. Phys. Chem. C*, **2014**, *118*, 26584.
7. J. J. Goings, M. Caricato, M. Frisch, X. Li, "Assessment of Low-scaling Approximations to the Equation of Motion Coupled-Cluster Singles and Doubles Equations," *J. Chem. Phys.*, **2014**, *141*, 164116.
8. A. Petrone, D. B. Lingerfelt, N. Rega, X. Li, "From Charge-Transfer to Charge-Separated State: A Perspective from the Real-Time TDDFT Excitonic Dynamics," *Phys. Chem. Chem. Phys.*, **2014**, *16*, 24457.
9. S. A. Fischer, D. B. Lingerfelt, J. W. May, X. Li, "Non-adiabatic Molecular Dynamics Investigation of Photoionization State Formation and Lifetime in Mn²⁺-Doped ZnO Quantum Dots," *Phys. Chem. Chem. Phys.*, **2014**, *16*, 17507.
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Computational Methods Based on Density Functional Theory for Reactions and Processes Involving Electronic Spin

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Abstract

Real-time time-dependent density functional theory (TDDFT) is routinely employed to calculate linear and non-linear optical adsorption spectra, charge transfer dynamics, as well as the simulation of time-dependent phenomena in molecular conductance. Despite this success, not much attention has been given to the dynamics of the spin degrees of freedom that are responsible for a wealth of important chemical and physical phenomena. Here, I will introduce our approach for the simultaneous time propagation of charge and spin density in molecular systems using the TDDFT formalism. Including the spin density in TDDFT simulations necessarily implies dealing with non-collinear magnetization to properly propagate both, charge and magnetization density vector, $n(t)$ and $m(t)$, respectively. I will show some proof-of-concept calculations for the linear H-He-H molecule and a bimetallic Cu complex where the low-frequency dynamics of the local magnetic moments from TDDFT can be directly compared to the classical spin precession from a Heisenberg-Dirac-van Vleck system. In this case it is possible to extract magnetic exchange couplings from the TDDFT simulations and compare to static methods such as the traditional energy differences or constrained linear-response methods. I will also discuss our ongoing efforts to develop analysis tools as well as modified dynamics technics.



DE-SC0005027: Computational Methods Based on Density Functional Theory for Reactions and Processes Involving Electronic Spin

Postdoc: None.

Student: To be hired.

Recent Progress

We have developed a computational scheme based on a time-dependent extension of noncollinear spin density functional theory for the simultaneous simulation of charge and magnetization dynamics in molecular systems.^[1] We have benchmarked the method

against the low-frequency spin dynamics of the H–He–H molecule and the bimetallic Mn complex BISDOW where the magnetization dynamics can be directly compared to the classical magnetization precession of a Heisenberg-Dirac-van Vleck Hamiltonian. We have also recently investigated the stability, maximum intercalation capacity, and voltage profile of alkali metal intercalated hexagonal BC₃ (M_xBC₃), for 0 < x < 2 and M=Li, Na, and K.^[2] We showed that these intercalation compounds are stable with respect to BC₃ and their bulk metal counterparts and that among all M_xBC₃ considered, the maximum stable capacity corresponds to an x value of 1.5, 1, and 1.5 for Li, Na, and K, respectively. These results were based on dispersion-corrected density functional theory and suggest that BC₃ can become a robust alternative to graphitic electrodes in metal ion batteries.

Future Plans

- Implement local spin analysis for static and TD-DFT and local spin Hessian analysis to identify unstable spin solutions and perform local spin analysis during dynamical simulations.
- Incorporate adaptive control time step size during the propagation part of the noncollinear spin TD-DFT code to deal with longer time evolutions and larger systems.
- Evaluate dynamic polarizabilities and optical spectrum for magnetic systems from noncollinear spin TD-DFT calculations.

Publications Acknowledging this Grant in 2012-2015

1. Peralta, J. E.; Hod, O.; Scuseria, G. E. Magnetization Dynamics from Time-Dependent Noncollinear Spin Density Functional Theory Calculations, *J. Chem. Theory Comput.* **2015**, 11, 3661–3668.
2. Joshi, R. P.; Burak, O.; Barone, V.; Peralta, J. E. Hexagonal BC₃: A Robust Electrode Material for Li, Na, and K Ion Batteries, *J. Chem. Phys. Lett.* **2015**, 6, 2728-2732.
3. Williams, B.; Barone, B.; Pate, B.; Peralta J. E. Gradient Copolymers of Thiophene and Pyrrole for Photovoltaics. *Comput. Mater. Sci.* **2015**, 96, 69-71.
4. Phillips, J. J.; Peralta, J. E. Magnetic Exchange Couplings from Noncollinear Perturbation Theory: Dinuclear Cu^{II} Complexes. *J. Phys. Chem. A* **2014**, 118, 5841-5847.
5. Peralta, J. E.; Barone, V.; Jackson K. A. Site-specific Polarizabilities from Analytic Linear-response Theory. *Chem. Phys. Lett.* **2014**, 608, 24-27.
6. Abate B. A.; Peralta J. E. The Performance of Density Functional Approximations for the Structures and Relative Energies of Minimum Energy Crossing Points. *Chem. Phys. Lett.* **2013**, 590, 227-230.

2016 CTC PI MEETING

ABSTRACT

- **Program Title:** Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies.
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- **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 with tunable band gaps. 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 that require stable magnetic moments.

Our comprehensive program starts 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 investigation of the transport properties of molecules of such motifs and efforts towards synthesis and properties of assemblies of such motifs. The program involves four interrelated areas of study, namely: A) 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) 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) studies of ligated cluster assemblies and supported ligated clusters to explore magnetic assemblies with tunable band gaps.; and D) develop computational tools to carry out electronic transport studies. The theoretical studies will be carried out in close collaboration with experimental groups.

- **Recent Progress :** Our recent work has proceeded along four different directions.
 - (1) An exciting recent development in nanoscience is the formation of materials with ligated chalcogenide motifs as primitive motifs. Roy et al. (*SCIENCE* **341**, 157 (2013)) have reported synthesizing cluster solids from an assembly of individually synthesized chalcogenide superatoms that exchange charge with counterions to form ionic solids. These assemblies built from different transition metal chalcogenides and counter ions offer potential for photovoltaics, spintronics, and single molecule electrical circuits. In fact, they have just reported formation of a van der Waals solid where C_{60} layers can be mechanically exfoliated. One such assembly $[Ni_9Te_6(PMe_3)_8][C_{60}]$ consists of $Ni_9Te_6(PET_3)_8$ clusters composed of a Ni_9Te_6 core decorated with 8 tri-ethylphosphine (PET_3) ligands attached to Ni sites. The cluster had previously been isolated as an intermediate species during the synthesis of the bulk NiTe from organometallic reagents serving as sources of Ni and Te. This is, however, the first time that $Ni_9Te_6(PET_3)_8$ is shown to form a rock-salt (NaCl) structure where ligated cluster acts as an electron donor when combined with C_{60} as an electron acceptor. More recent experiments indicate that the ionic solid is magnetic and undergoes a ferromagnetic phase transition at low temperatures (4K) while it exhibits Curie-Weiss behavior at higher temperatures (above 10K).

The SQUID measurements also indicate that the individual clusters behave as isolated localized magnets with a magnetic moment of around $5.4 \mu_B$ per functional unit. Additional magnetic measurements on $[\text{Ni}_9\text{Te}_6(\text{PMe}_3)_8][\text{C}_{60}]$ with tri-methylphosphine ligands and on $[\text{Ni}_9\text{Te}_6(\text{PET}_3)_8][\text{C}_{70}]$ brought out new features. Because of smaller ligand shell, $[\text{Ni}_9\text{Te}_6(\text{PMe}_3)_8][\text{C}_{60}]$ has a smaller superatom-to-superatom separation and it was found to increase the magnetic transition temperature (TM) to 7K. On the other hand, the large size of C_{70} leads to larger lattice parameter than in $[\text{Ni}_9\text{Te}_6(\text{PET}_3)_8][\text{C}_{60}]$ and was shown to reduce the TM to around 2.5 K. These observations raise several fundamental issues. The chalcogenide cluster Ni_9Te_6 has a high ionization potential of 5.88 eV. The PET_3 ligands also have a high ionization potential of 7.98 eV. How does then the addition of PET_3 ligands change the electronic feature of cluster to make it an electron donor? This is critical to the formation of the ionic assembly as C_{60} , with an electron affinity (EA) of 2.68 eV acts as an electron acceptor. On the magnetic side, an estimation of the exchange coupling within each individual cluster would clarify if the solid undergoes a paramagnetic or super-paramagnetic relaxations above 10K? In addition, the characterization of magnetic anisotropies of these solids is needed to understand the nature of the magnetic transition at low temperatures. The ferromagnetic phase and the hysteresis at 2K, require magnetic coupling between the superatoms. What is the origin of this coupling and are the MAE and coupling sensitive to the charge state of the clusters? These could provide an understanding of the change in TM as one modulates the superatom-superatom separation that could change the charged state of the clusters.

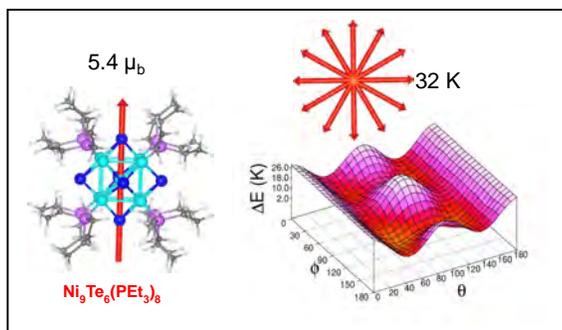
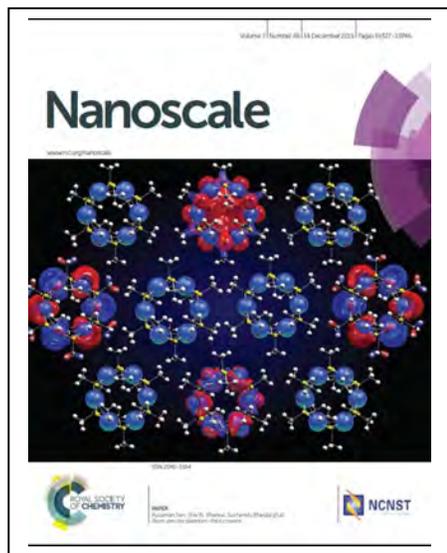


Fig. 1 Theoretical studies indicate that the ligated $\text{Ni}_9\text{Te}_6(\text{PMe}_3)_8$ cluster has a magnetic anisotropy energy of only 32K while it has a large exchange energy of 0.2 eV indicating that it is a superparamagnetic solid at ordinary temperatures.

Our First-principles theoretical studies provided an electronic and magnetic characterization of the $\text{Ni}_9\text{Te}_6(\text{PET}_3)\text{C}_{60}$ ionic material. We showed that while both the chalcogenide cluster and ligand individually have high ionization potentials, the ligated cluster has a charge transfer from ligands to the cluster. Consequently, the PET_3 ligands create an internal coulomb well that lifts the quantum states of the Ni_9Te_6 cluster lowering its ionization potential to 3.39 eV thus creating a superalkali motif. The metallic core has a spin magnetic moment of $5.3 \mu_B$ in agreement with experiment. However, the clusters are marked by low magnetic anisotropy energy (MAE) of 2.72 meV and a larger intra-exchange coupling exceeding 0.2 eV indicating that the observed paramagnetic behavior around 10K is due to superparamagnetic relaxations. The magnetic motifs separated by C_{60} experience a weak superexchange that stabilizes a ferromagnetic ground state as observed around 2K. The calculated MAE is sensitive to the charged state that could account for the observed change in magnetic transition temperature with size of the ligands or anion. Our findings, recently published in *JACS* **138** (6), pp 1916–1921 (2016) provide the first insight into the observed magnetic and electronic behaviors.

(2) We have continued our joint experimental/theory effort in the synthesis of novel assemblies containing transition elements. Here, the focus is to make new nanomaterials where the building blocks are atomically precise clusters, and where the band gap can be tuned. The eventual goal is to

synthesize magnetic materials with tunable band gaps. In one such study, ligand stabilized water soluble Pt nanoclusters were synthesized and characterized through electrospray ionization mass



spectrometry. Glutathione was used as the ligand, and assemblies based on $\text{Pt}_5(\text{SG})_{10}$, and $\text{Pt}_6(\text{SG})_{12}$ clusters were synthesized. Theoretical investigations found that these clusters do not possess a metal core, but rather are most stable in a ring structure. The clusters are stabilized through the thiol ligands forming a square planar structure around each Pt atom to form a ring. The structural elucidation was confirmed through UV/Vis and IR spectroscopy. Our work was featured in a cover page of Nanoscale.

In another effort we synthesized three alkaline earth metal (Ca, Sr and Ba, respectively) based coordination polymers using 3-amino-1, 2, 4-triazole-5-carboxylic acid (3-AmTrZAc). Structural analyses revealed that Ca- based structure $[\text{Ca}(3\text{-AmTrZAc})(5\text{-AmTrZAc})(\text{H}_2\text{O})]$ (1), is two-dimensional and Sr and Ba based $[\text{Sr}(3\text{-AmTrZAc})_2(\text{H}_2\text{O})]$ (2) and $[\text{Ba}(3\text{-AmTrZAc})_2(\text{H}_2\text{O})]$ (3) respectively, are three-dimensional. We also found that in the Ca-based $[\text{Ca}(3\text{-AmTrZAc})(5\text{-AmTrZAc})(\text{H}_2\text{O})]$ (1), structure, the 3-AmTrZAc reactant converts to 5-AmTrZAc. The relative stability of the two isomers was found to be controlled by the dipole-ion interaction between the triazole ring and the carboxylate ion. We measured the band gap energy and it was largest for the Ca-based structure while the Sr and Ba structures had smaller band gap energies. Density functional theoretical investigations find that internal electric fields generated by the alkaline earth counterions increases the gap in the 5-AmTrZAc anion, and lower it in the 3-AmTrZAc anion.

(3) Another outstanding problem in nano-magnetism is to stabilize the magnetic order in nanoparticles at room temperatures. For ordinary ferromagnetic materials, the reduction in size leads to a decrease in the magnetic anisotropy, resulting in superparamagnetic relaxations at nanoscopic sizes. The transition limits the use of nanoparticles for memory storage and other applications. We had earlier proposed that cobalt carbides could offer such a material where the mixing between the C p- and Co d-states could result in an enhancement of anisotropy. Following our first principal theoretical predictions, we have now extended these studies to mixed Fe-Co systems in a joint theory/experimental effort. In collaboration with experimental groups, we provided experimental evidence substantiating the synthesis of a novel cobalt iron carbide phase (CoFe_2C) of nanoparticles. Structural characterization of the new carbide phase was performed by transmission electron microscopy (TEM), electron diffraction (SAED-TEM) and energy electron spectroscopy (EELS). X-ray diffraction (XRD) was also performed as a complimentary analysis. Magnetic characterization of the carbide phase revealed a blocking temperature, T_B , of 790 K for particles with a domain size as small as 5 ± 1 nm. The particles have magnetocrystalline anisotropy of $4.6 \pm 2 \times 10^6 \text{ J/m}^3$, which is 10 times larger than that of Co nanoparticles. Such colossal anisotropy leads to thermally stable long range magnetic order. Moreover, the thermal stability constant is much larger than that of the commonly used FePt nanoparticles. With thermal stability and colossal anisotropy, the CoFe_2C nanoparticles have huge potential for enhanced magnetic data storage devices.

(4) We have continued our effort in developing electronic principles that govern the stability of metal silicon clusters to identify highly stable species. Our First principles studies on the geometric structure, stability, and electronic structure of WSi_n clusters, $n=6-16$, showed that the observed differing “magic sizes” for WSi_n clusters are associated with the nature of the growth processes. The

WSi₁₂ cluster, observed as a magic species in experiments reacting transition metal ions with silane, is not stable due to a filled shell of 18 electrons, as previously proposed, but due to its atomic structure that arrests further growth because of an endohedral transition metal site. In fact, it is found that all of these clusters, n=6-16, have filled 5d shells except for WSi₁₂, which has a 5d⁸ configuration that is caused by crystal field splitting. The stability of WSi₁₅⁺, observed as highly stable in clusters generated by vaporizing silicon and metal carbonyls, is shown to be associated with a combination of geometric and electronic features. Similar studies on FeSi_n clusters show that FeSi₉, FeSi₁₁, and FeSi₁₄ clusters exhibit enhanced local stability as seen through an increase in Si binding energy, Fe embedding energy, the gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), and the Ionization Potential (IP). The conventional picture for the stability of such species combines an assumption of electron precise bonding with the 18-electron rule; however, we find this to be inadequate to explain the enhanced stability in FeSi₁₁ and FeSi₁₄ because the d-band is filled for all FeSi_n clusters for n≥9. FeSi₁₄ is shown to be the most stable due to a compact and highly symmetric Si₁₄ cage with octahedral symmetry that allows better mixing between Fe 3d- and Si 3p- electronic states.

- **Future Plans:**

We are proceeding along several directions to identify potential magnetic building blocks and properties of their assemblies. We are currently exploring the potential of ligated clusters in photovoltaics by using ligands to create charge donors and acceptor units that can be used to separate electron and holes. In particular, we are studying ligated chalcogenide clusters where it has been possible to synthesize cluster assembled materials using C₆₀ and iron oxide cluster counter ions. We are studying metal silicon clusters supported on C₆₀ and their potential for photovoltaics following the recent experiments. We are also developing phenomenological models to predict the behavior of assemblies of superparamagnetic clusters in an effort to understand experiments on nano-assemblies. 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. “The Role of Alkaline-Earth Counterions on the Architecture, Band Gap Energy, and Proton Transfer of Triazole Based Coordination Polymers”, K. S. Asha, A. C. Reber, A. F. Pedicini, S. N. Khanna, and S. Mandal, *Eur. J. Inorg. Chem.* **2015**, 2085–2091 (2015).
2. “Experimental evidence for the formation of CoFe₂C phase with colossal magnetocrystalline-anisotropy for data storage technology”, Ahmed A. El-Gendy, Massimo Bertino, Dustin Clifford, Meichun Qian, Shiv N. Khanna, Everett E. Carpenter, *Appl. Phys. Lett.* **106**, 213109 (2015).
3. “Using graphene to control magnetic anisotropy and interaction between supported clusters” Sanjubala Sahoo, M Fhokrul Islam and Shiv N Khanna, *New J. Phys.* **17**, 053052 (2015).
4. “Making sense of conflicting magic numbers in WSi_n clusters”, M. B. Abreu, A. C. Reber, and S. N. Khanna, *J. Chem. Phys.* **143**, 074310 (2015).
5. “Geometry controls the stability of FeSi₁₄”, V. Chauhan, M. B. Abreu, A. C. Reber, and S. N. Khanna, *Phys. Chem. Chem. Phys.* **17**, 15718-15724 (2015).
6. “Controlling the magnetic anisotropy of Ni clusters supported on graphene flakes with topological defects”, S. Sahoo, S. N. Khanna, and P. Engel, *Appl. Phys. Lett.* **107**, 043102 (2015).
7. “Atom precise platinum-thiol crowns”, A. George, K. S. Asha, A. C. Reber, S. R. Bilek, A. F. Pedicini, A. Sen, S. N. Khanna, and S. Mandal, *Nanoscale* **7**, 19448-19452 (2015).
8. “Ni₉Te₆(PMe₃)₈C₆₀ Is a Superatomic Superalkali Superparamagnetic Cluster Assembled Material (S³-CAM)”, V. Chauhan, S. Sahoo, and S. N. Khanna, *Jour. Am. Chem. Soc.* **138**, 1961-1921 (2016).

Magnetic Order in Nanoassemblies with Metal-Chalcogenide and Metal-Carbide Building Blocks.

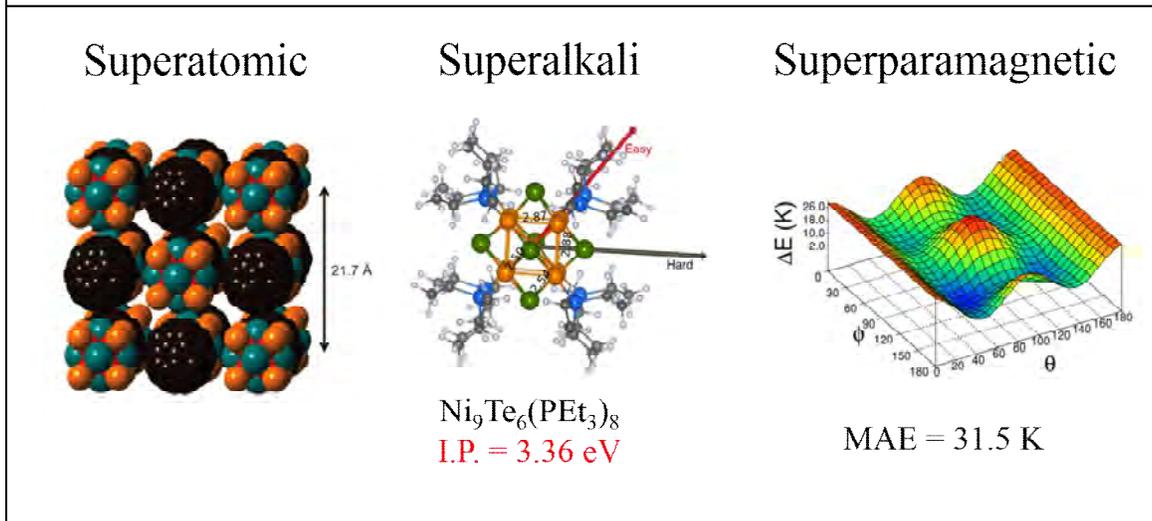
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A promising direction in the research on clusters is to design nanomaterials with size selected clusters or the nanoparticles as the building blocks. Since the properties of clusters/nanoparticles change with size and composition, nano-assemblies offer the unique prospect of designing nanoscale materials with controlled properties. The presentation will focus on our recent work on two different assemblies with different magnetic properties.

Nanostructured Metal chalcogenides are well known for their applications in efficient energy conversion and as non-linear optical and magnetic materials. It has recently been possible to synthesize atom precise nanoscale solids (Roy et al. (SCIENCE 341, 157 (2013))) from an assembly of individually synthesized chalcogenide superatoms that exchange charge with counterions to form ionic solids. These assemblies built from different transition metal chalcogenides and counter ions offer potential for photovoltaics, spintronics, and single molecule electrical circuits. One such assembly $[\text{Ni}_9\text{Te}_6(\text{PMe}_3)_8][\text{C}_{60}]$ consists of $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$ clusters with tri-ethylphosphine (PET_3) ligands as electron donors and exhibits interesting magnetic properties including ferromagnetic behavior at low temperatures and paramagnetic like behavior above 10K.

Fig. 1 $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8\text{C}_{60}$ is a Superatomic Superalkali Superparamagnetic Cluster Assembled Material ($\text{S}^3\text{-CAM}$)



I will present results of our First-principles theoretical studies that provided an electronic and magnetic characterization of the $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8\text{C}_{60}$ ionic material. We show that while both the chalcogenide cluster and ligand individually have high ionization potentials, the ligated cluster has a charge transfer from ligands to the cluster. Consequently, the PET_3 ligands create an internal coulomb well that lifts the quantum states of the Ni_9Te_6 cluster lowering its ionization potential to 3.39 eV thus creating a

superalkali motif. The metallic core has a spin magnetic moment of $5.3 \mu_B$ in agreement with experiment. However, the clusters are marked by low magnetic anisotropy energy (MAE) of 2.72 meV and a larger intra-exchange coupling exceeding 0.2 eV indicating that the observed paramagnetic behavior around 10K is due to superparamagnetic relaxations. The magnetic motifs separated by C_{60} experience a weak superexchange that stabilizes a ferromagnetic ground state as observed around 2K. The calculated MAE is sensitive to the charged state that could account for the observed change in magnetic transition temperature with size of the ligands or anion. Our findings, recently published in *JACS* **138** (6), pp 1916–1921 (2016) provide the first insight into the observed magnetic and electronic behaviors.

The second assembly relates to an outstanding problem in nano-magnetism, namely, stabilize the magnetic order in nanoparticles at room temperatures. For ordinary ferromagnetic materials, the reduction in size leads to a decrease in the magnetic anisotropy, resulting in superparamagnetic relaxations at nanoscopic sizes. The transition limits the use of nanoparticles for memory storage and other applications and one of the fundamental questions is if the anisotropy could be enhanced in reduced sizes. We had earlier proposed that cobalt carbides could offer such a material where the mixing between the C p- and Co d-states could result in an enhancement of anisotropy. Following our first principal theoretical predictions, we have now extended these theoretical studies to mixed Fe-Co systems that predict even higher anisotropy. In collaboration with experimental groups, we provided experimental evidence substantiating the synthesis of a novel cobalt iron carbide phase ($CoFe_2C$) of

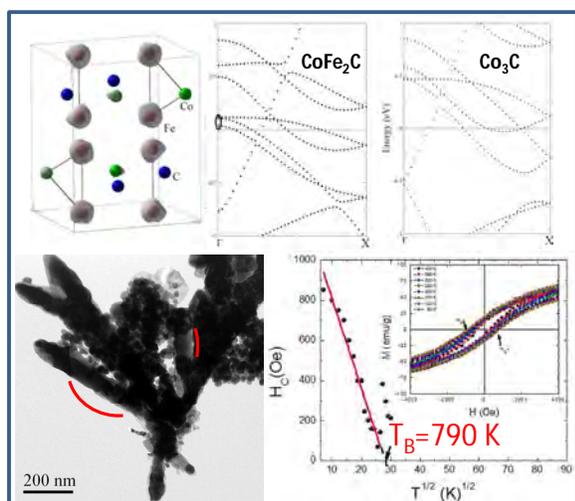


Fig.2. Atomic and electronic structure and magnetic characteristics of the new $CoFe_2C$ phase.

nanoparticles. Structural characterization of the new carbide phase was performed by transmission electron microscopy (TEM), electron diffraction (SAED-TEM) and energy electron spectroscopy (EELS). X-ray diffraction (XRD) was also performed as a complimentary analysis. Magnetic characterization of the carbide phase revealed a blocking temperature, T_B , of 790 K for particles with a domain size as small as 5 ± 1 nm. The particles have magnetocrystalline anisotropy of $4.6 \pm 2 \times 10^6$ J/m³, which is 10 times larger than that of Co nanoparticles. Such colossal anisotropy leads to thermally stable long range magnetic order. Moreover, the thermal stability constant is much larger than that of the commonly used FePt nanoparticles. With thermal stability and colossal anisotropy, the $CoFe_2C$ nanoparticles have huge potential for enhanced magnetic data storage devices.

We are now exploring the magnetic behavior of assemblies of magnetic nanoparticles and the use of ligated metal chalcogenide clusters as electron donors and acceptors by controlling the nature of ligands.

Grant Number and Grant Title

DE-SC0006420 Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies.

Post Doc: Vikas Chauhan
Sanjubala Sahoo (Partial)

Student: A. Pedicini (Summer)

Selected Publications:

1. "The Role of Alkaline-Earth Counterions on the Architecture, Band Gap Energy, and Proton Transfer of Triazole Based Coordination Polymers", K. S. Asha, A. C. Reber, A. F. Pedicini, S. N. Khanna, and S. Mandal, *Eur. J. Inorg. Chem.* **2015**, 2085–2091 (2015).
2. "Experimental evidence for the formation of CoFe₂C phase with colossal magnetocrystalline-anisotropy for data storage technology", Ahmed A. El-Gendy, Massimo Bertino, Dustin Clifford, Meichun Qian, Shiv N. Khanna, Everett E. Carpenter, *Appl. Phys. Lett.* **106**, 213109 (2015).
3. "Using graphene to control magnetic anisotropy and interaction between supported clusters" Sanjubala Sahoo, M Fhokrul Islam and Shiv N Khanna, *New J. Phys.* **17**, 053052 (2015).
4. "Making sense of conflicting magic numbers in WSi_n clusters", M. B. Abreu, A. C. Reber, and S. N. Khanna, *J. Chem. Phys.* **143**, 074310 (2015).
5. "Geometry controls the stability of FeSi₁₄", V. Chauhan, M. B. Abreu, A. C. Reber, and S. N. Khanna, *Phys. Chem. Chem. Phys.* **17**, 15718-15724 (2015).
6. "Controlling the magnetic anisotropy of Ni clusters supported on graphene flakes with topological defects", S. Sahoo, S. N. Khanna, and P. Engel, *Appl. Phys. Lett.* **107**, 043102 (2015).
7. "Atom precise platinum-thiol crowns", A. George, K. S. Asha, A. C. Reber, S. R. Biltek, A. F. Pedicini, A. Sen, S. N. Khanna, and S. Mandal, *Nanoscale* **7**, 19448-19452 (2015).
8. "Ni₉Te₆(PMe₃)₈C₆₀ Is a Superatomic Superalkali Superparamagnetic Cluster Assembled Material (S³-CAM)", V. Chauhan, S. Sahoo, and S. N. Khanna, *Jour. Am. Chem. Soc.* **138**, 1961-1921 (2016).
9. "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).
10. "Does the 18-Electron Rule Apply to CrSi₁₂?" M.B. Abreu, A.C. Reber, and S.N. Khanna, *J. Phys. Chem. Lett.* **5**, 3492-3496 (2014).

Many-Body Effects in Transport and Energy Transfer at Molecule-Metal Interfaces

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Abstract

Many-body effects are an important factor in prediction of responses of molecular nanodevices to external perturbations (bias, radiation, thermal gradient, etc.). My research mostly focuses on development of theoretical methodologies related to *the nonequilibrium atomic limit*, i.e. formulations employing many-body states of an isolated molecule, and their application to transport and energy transfer at molecule-metal interfaces [1]. Driven by experimental developments we study nonlinear optical spectroscopy of single-molecule devices [2,3], suggest a way for detection of intra-molecular dynamics in junctions on sub-picosecond timescale utilizing a variant of pump-probe spectroscopy [4], and describe effects of many-body transitions (measured in equilibrium molecular systems) on transport properties of nonequilibrium devices [5]. We also study foundations of quantum thermodynamics at nanoscale (crucial for characterization of nanoscale thermoelectric devices) [6-8], develop tools of the nonequilibrium atomic limit [9], and apply them to gain insight in non-adiabatic dynamics and electronic structure simulations [1,10]. In the presentation I will focus on some of our most recent advancements.

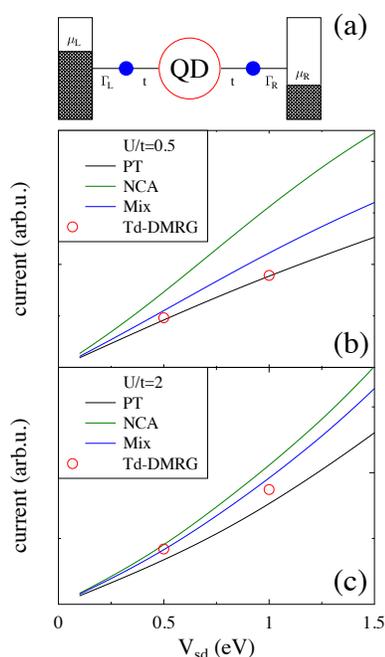
Optical spectroscopy of molecules chemisorbed at surfaces and interfaces. In the last decade optical spectroscopy measurements in current-carrying molecular junctions became possible. Traditionally theoretical studies of nonlinear optical spectroscopy rely on bare perturbation theory (PT) in molecular coupling to radiation field. Perturbative expansions yield terms characterized by double-sided Feynman diagrams, which are utilized for classification of separate optical processes in the system. The approach is well known and is widely and successfully applied in theoretical studies. At the same time bare PT is known to be a non-conserving approximation, which may fail qualitatively when applied to systems coupled to baths (such as, e.g., molecular junctions). We show that in the case of molecules attached to metallic surfaces and with radiation field treated quantum mechanically application of standard tools of nonlinear optical spectroscopy may become problematic. In particular, model simulations employing realistic parameters show that bare PT violates charge and energy conservation laws, and that the violation may be significant. With experimental developments leading to appearance of such fields as quantum nanoplasmonics the message on inapplicability of standard tools of nonlinear optical spectroscopy in junctions when radiation field has to be treated quantum mechanically is important and timely.

Nuclear dynamics at molecule-metal interfaces. The coupled electronic-nuclear dynamics in molecules positioned at and interacting with metal interfaces presents a fundamental problem that stems from the fact that in such systems the usual time scale separation between electron and nuclear dynamics does not necessarily hold. The problem has gained renewed interest in the context of nuclear dynamics in molecular conduction junctions, a presently active field of research because of its fundamental and practical importance. Full quantum-mechanical solution of electron-nuclear dynamics is possible only for relatively small systems. Thus, one has to rely on quasi-classical formulations. Among them, Ehrenfest dynamics and fewest switches surface-hopping (SH) algorithm are employed most often. SH schemes are an easy and efficient method for accounting for non-adiabatic nuclear motion. However, these schemes suffer from a fatal flaw: they were not derived as an approximation to some exact equations but instead postulated in a very intelligent but quite an *ad hoc* manner. In this they differ from other approximate dynamical schemes. The main achievement of our study is in that it provides, for the first time, such a derivation, showing that surface hopping dynamics can be derived as a well-defined approximation to exact equations of motion. Moreover, previous *ad hoc* considerations are obtained as limiting cases from our more general scheme.

Given the prominence of the surface hopping methodology in many applications of chemical dynamics, putting it on firm theoretical grounds is an important step forward. Derived expressions describe nuclear dynamics in the presence of non-adiabatic transitions in the molecule both due to optical processes and electron transfer between molecule and metallic contact(s). They reproduce original SH formulation in the limit of small metal-molecule coupling (where broadening of the molecular energy levels can be disregarded) and Ehrenfest dynamics (motion on the potential of mean force) information on the different charging states is traced out, which is relevant when this coupling is relatively strong.

Nonequilibrium diagrammatic technique for Hubbard Green functions. The Hubbard nonequilibrium Green functions (NEGF) method is an extension of the quantum master equation (QME) formulation of optical spectroscopy (the latter is utilized in most theoretical treatments) to Green function techniques. It is crucial in order to account for the system-bath correlations. Traditionally evaluation of multi-time correlation functions within QME treatment of optical scattering processes relies on the quantum regression theorem, which destroys system-bath correlation at each instance of radiation field interaction with the system. The main obstacle to employ the Hubbard NEGF is absence of diagrammatic technique similar to standard NEGF theory. We propose a variant of such technique based on generalization of previous equilibrium considerations. The resulting methodology allows expressing multi-time correlation functions of Hubbard (projection or molecular excitation) operators in terms of the Hubbard Green functions and simulation of nanodevices optical responses both in frequency and time domains. Moreover, our results show that previous efforts in this direction are not completely consistent with the proper perturbation theory. The proposed methodology introduces multi-time correlation functions analog of the real-time perturbation theory previously formulated only for time-local observables.

Nonequilibrium divide-and-conquer method for electronic structure simulations. One of the central



Nonequilibrium divide-and-conquer. Shown are model (a) and current vs. bias for $U/t=0.5$ (b) and $U/t=2$ (c).

challenges of quantum chemistry is accurate prediction of electronic structure of nanoscale systems and their response to external perturbations with the final goal to develop a molecular level understanding and reach quantitative level of theoretical prediction. Advancement of fabrication techniques at the nanoscale has led to a surge of experimental activity in constructing nanodevices, thus extending the challenge to theory into the realm of open systems far from equilibrium. Theoretical simulations of open non-equilibrium systems at nanoscale mostly employ single-particle basis (e.g. orbitals as in NEGF-DFT). These approaches allow treating systems of realistic sizes, but become inconvenient in treating strong system interactions. An alternative approach (nonequilibrium atomic limit) utilizes many-body states of the isolated system as a basis, which allows accounting for the system interactions, however applicability of such formulations is limited to relatively small systems. We propose a methodology, the non-equilibrium divide-and-conquer method, which will capitalize on strong sides of both approaches: the NEGF-DFT ability to treat big systems and the PP- and Hubbard NEGF ability to account for strong local interactions exactly.

Following ideas of the dynamical mean field theory we utilize the partitioning of the original system (either in real or state space) with the parts treated by either single-particle or many-body states approaches, thus extending the usual divide-and-conquer methodology to the realm of non-equilibrium systems and introducing analog of quantum chemistry active space in either real or state spaces.

Future Plans

1. Develop time-dependent approaches to light-matter interaction.
2. Go beyond perturbative consideration of the light-matter interaction.
3. Incorporate elements of quantum electrodynamics into description of the near field.
4. Include plasmon excitations and non-thermal distribution in contacts.
5. Incorporate intra-molecular, metal, and charge transfer light scattering.
6. Take into account light and bias induced dynamics.
7. Responding to experimental challenge to theory utilize both flux and noise simulations to elucidate information on junction dynamics available from combined optical measurements.
8. Study possibility for molecular optospintronics.
9. Implement theoretical developments in codes for *ab initio* simulations.

Grant Numbers and Grant Titles

DE-SC0006422 Many-body effects in transport and energy transfer

Postdoc(s): Gregory Bulnes Cuetara, Yi Gao, Maicol A. Ochoa

Student(s): Alexander J. White

Ten recent publications:

- [1] A. J. White, M. A. Ochoa, and M. Galperin, *Nonequilibrium atomic limit for transport and optical response of molecular junctions*. J. Phys. Chem. C **118**, 11159-11173 (2014) [**Feature Article**]
- [2] S. Dey, M. Banik, E. Hulkko, K. Rodriguez, V. A. Apkarian, M. Galperin, and A. Nitzan, *Observation and analysis of Fano-like lineshapes in the Raman spectra of molecules adsorbed at metal interfaces*. Phys. Rev. B **93**, 035411 (2016).
- [3] A. J. White, S. Tretiak, and M. Galperin, *Raman scattering in molecular junctions: A pseudoparticle formulation*. Nano Lett. **14**, 699-703 (2014).
- [4] M. A. Ochoa, Y. Selzer, U. Peskin, and M. Galperin, *Pump-probe noise spectroscopy of molecular junctions* J. Phys. Chem. Lett. **6**, 470-476 (2015).
- [5] A. Baratz, A. J. White, M. Galperin, and R. Baer, *The effects of electromagnetic coupling on conductance switching of a gated tunnel junction*. J. Phys. Chem. Lett. **5**, 3545-3550 (2014).
- [6] M. Esposito, M. A. Ochoa, and M. Galperin, *Quantum thermodynamics: A nonequilibrium Green's function approach*. Phys. Rev. Lett. **114**, 080602 (2015) [**Editors' Suggestion**]
- [7] M. Esposito, M. A. Ochoa, and M. Galperin, *Nature of heat in strongly coupled open quantum systems*. Phys. Rev. B **92**, 235440 (2015).
- [8] M. Esposito, M. A. Ochoa, and M. Galperin, *Efficiency fluctuations in quantum thermoelectric devices*. Phys. Rev. B **91**, 115417 (2015).
- [9] M. A. Ochoa, M. Galperin, and M. A. Ratner, *A nonequilibrium equation-of-motion approach to quantum transport utilizing projection operators*. J. Phys.: Condens. Matter **26**, 455301 (2014).
- [10] M. Galperin and A. Nitzan, *Nuclear dynamics at molecule-metal interfaces: A pseudoparticle perspective*. J. Phys. Chem. Lett. **6**, 4898-4903 (2015).

Fragment-Based Quantum Chemistry for Non-Covalent Interactions and Excitation Energy Transfer

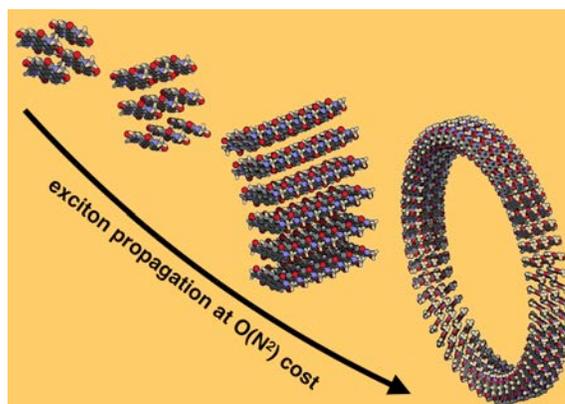
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Abstract

Project Scope

This project aims to develop and implement new fragment-based quantum chemistry algorithms for accurate yet efficient calculation of non-covalent interactions and energy transport in large systems composed of “soft” materials, *i.e.*, liquids, biomolecules, and organic semiconductors. These methods are tailored towards applications including quantitative description of ligand binding to biomaterials and/or nanoporous materials, the description of solvent effects on electronic excitation energies, and simulation of energy (exciton) transport in organic semiconductors. For applications of this type, these new methods rival the accuracy of traditional, post-Hartree-Fock electronic structure calculations, yet the natural parallelizability provided by the fragment-based approach makes these methods affordable even in large systems. We have, for example, demonstrated proof-of-principle calculations of excitation energy transfer in a 150-chromophore model of a self-assembling organic nanotube, a calculation that would involve the equivalent of more than 50,000 Gaussian basis functions, if carried out using traditional methods.



Recent Progress

For non-covalent interactions, we have developed an “extended” version of symmetry-adapted perturbation theory that we call “XSAPT”. The original SAPT is an old approach for energy decomposition analysis in non-covalent dimers, and has seen a revival of interest in recent years as a means to parameterize classical force fields in a physically-motivated way. XSAPT extends SAPT to many-body system, and recently we have introduced key improvements to the description of van der Waals interactions in XSAPT. These are in many ways the most challenging part of the interaction energy, and become increasingly important as system size grows. We have introduced empirical dispersion potentials (“XSAPT+D”) that can be parameterized using (expensive) 3rd-order SAPT calculations on small dimers then applied in many-body systems, and which greatly improve upon the accuracy of (more affordable) 2nd-order perturbation theory. However, the pairwise atom–atom approximation that is inherent in these “+D” corrections breaks down when the fragments are large, and for nanoscale materials one must implement non-additive corrections to the atomic C_6 and C_8 coefficients, which we have recently done in an *ab initio* way.

An alternative approach to describing non-covalent interactions in large systems is a generalized many-body expansion (GMBE). In the traditional MBE, which forms the basis of numerous fragment-based approaches including the popular fragment molecular orbital (FMO) method, the energy or other property of a large system is expressed in terms of calculations involving monomers, dimers, trimers, ... of subsystems. Recent benchmark calculations, for systems considerably larger than those examined heretofore, reveal that MBE/FMO-type methods require four-body terms (*i.e.*, tetramers) to achieve

quantitative accuracy. Unfortunately the sheer number of tetramers leads to catastrophic loss-of-precision problems once the number of fragments exceeds 30–40. In the GBME, we achieve quantitative accuracy using only a *two-body* expansion, by dividing up the supersystem into *overlapping* fragments and using set-theoretical ideas to avoid double-counting of interactions. Using this approach, we have recently demonstrated that accurate *ab initio* energy landscapes for proteins exceeding 1,000 atoms can be obtained by dividing up the protein into fragments consisting of 2–4 amino acids.

Excitation energy transfer represents another area in which fragment-based approaches prove fruitful, and in particular we have developed a fully *ab initio* version of the old Frenkel-Davydon exciton model, in which a collective excitation in a molecular crystal, aggregate, or other multi-chromophore system is described using an *ansatz* consisting of a linear combination of excitations that are localized on individual chromophores. The chromophores wave functions can be computed in a distributed way, and then we can compute the couplings between these basis states in a fully *ab initio* way without introducing common approximations such as dipole coupling or neglect of exchange interactions, both of which are dubious in closely-packed crystals and aggregates. Using this model, we have simulated exciton transport in models of a self-assembled organic nanotube, finding that very different dynamics are obtained in small model systems as compared to larger ones containing 50–100 chromophores. Although the small models are amenable to traditional quantum chemistry calculations, they suffer from an artificial heterogeneity of the site energies due to “edge effects” that become less important as the size of the aggregate is increased to better model the real organic semiconductor.

Along similar but not equivalent lines, exciton-type approximations can be applied to the basic equations of time-dependent density functional theory (TD-DFT), leading to tremendous reductions in cost (without significant loss of accuracy) for systems composed of multiple, weakly-coupled chromophores. A particularly efficacious use of this approach is for systems where the excitation is localized on only *one* chromophore, but in the presence of a large number of solvent molecules that remain in their ground states. Here, exciton-type approximations can be used to include full Coulomb and exchange interactions between chromophore and solvent, but distributed across processors such that the largest workload on any single processor consists in a TD-DFT calculation of the chromophore only. This approach can be used to obtain excitation energies that are converged with respect to a quantum-mechanical description of the solvent, at low computational cost and in a way that avoids the spurious charge-transfer-to-solvent states that arise in traditional TD-DFT calculations involving explicit solvent.

Future Plans

Future work on non-covalent interactions aims to extend the GBME to energy gradients, since most spectroscopic observables can be written in the form of a derivative of the energy with respect to a field, a nuclear displacement, or some other perturbation. This will facilitate calculation of vibrational spectra in macromolecules and, separately, the inclusion of solvent effects on high-level coupled-cluster calculations of optical properties and NMR spectra.

In the context of the *ab initio* Frenkel-Davydon exciton model, we plan to derive and implement gradients of the site–site couplings with respect to the nuclear coordinates. This is helpful in two ways: first, the derivatives of the couplings can be used to understand how various vibrational or phonon modes couple to energy transfer in organic photovoltaic materials; and second, these couplings are the key ingredient in the formulation of analytic energy gradients for the exciton model.

Grant Numbers and Grant Titles

DE-SC0008550 Development of Accurate and Affordable Electronic Structure Methods for the Condensed Phase

Postdoc(s): Jie Liu

Student(s): Ryan M. Richard, Ka Un Lao, Adrian F. Morrison, Kuan-Yu Liu, Ying Zhu, Saswata Dasgupta

Publications

1. J. Liu and J. M. Herbert, *Pair-pair approximation to the generalized many-body expansion: An efficient and accurate alternative to the four-body expansion, with applications to ab initio protein energetics*. *Journal of Chemical Theory and Computation* **12**, 572 (2016).
2. J. Liu and J. M. Herbert, *Local excitation approximations to time-dependent density functional theory for excitation energies in solution*. *Journal of Chemical Theory and Computation* **12**, 157 (2016).
3. J. Liu and J. M. Herbert, *An efficient and accurate approximation to time-dependent density functional theory for systems of weakly coupled monomers*. *Journal of Chemical Physics* **143**, 034106 (2015).
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5. K. U. Lao, R. Schäffer, G. Jansen, and J. M. Herbert, *Accurate description of intermolecular interactions involving ions using symmetry-adapted perturbation theory*. *Journal of Chemical Theory and Computation* **11**, 2473 (2015).
6. K. U. Lao and J. M. Herbert, *Accurate and efficient quantum chemistry calculations for noncovalent interactions in many-body systems: The XSAPT family of methods*. *Journal of Physical Chemistry A* **119**, 235 (2015).
7. A. F. Morrison, Z.-Q. You, and J. M. Herbert, *Ab initio implementation of the Frenkel-Davydov exciton model: A naturally parallelizable approach to computing collective excitations in crystals and aggregates*. *Journal of Chemical Theory and Computation* **10**, 5366 (2014).
8. R. M. Richard, K. U. Lao, and J. M. Herbert, *Aiming for benchmark accuracy with the many-body expansion*. *Accounts of Chemical Research* **47**, 2828 (2014).
9. R. M. Richard, K. U. Lao, and J. M. Herbert, *Understanding the many-body expansion for large systems. I. Precision considerations*. *Journal of Chemical Physics* **141**, 014108 (2014).
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High-throughput search for organic photovoltaic materials

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Abstract

Supported by this program, we are carrying out the largest-ever quantum chemistry experiment that we are aware of. This project consists in a high-throughput search of organic photovoltaic materials using distributed computing via the IBM World Community Grid. Our project has recently analyzed and released the data, and several groups around the world are using it for their predictions and for benchmarking of quantum chemistry methods and machine learning. We have focused on the following key aspects for this project. A) The development of a **robust calibration database** for experimental data. The Harvard Organic Photovoltaics 2015 (HOPV15) database is available for download and has been reported⁸. B) The development of **robust calibration methods** for the quantum chemistry data using Bayesian methods, specifically Gaussian Processes.⁷ The use and development of **machine learning** methods using deep networks for creating surrogate models for quantum chemistry (See Figure 1) D).²The public release of the data for more than 2.3 million molecules in the molecularspace.org website and data dumps.⁵ And most importantly, E) the development of **easy to synthesize** molecular candidate libraries tailored for specific experimental groups so that they are easily to test. In particular, we have focused on several replacement molecules for the ubiquitous PCBM molecule. The use of all these in combination has led to a revamp and optimization of our screening procedures that leads to accelerated discovery. In this presentation or poster, we will summarize these developments and also discuss other ongoing and future directions.

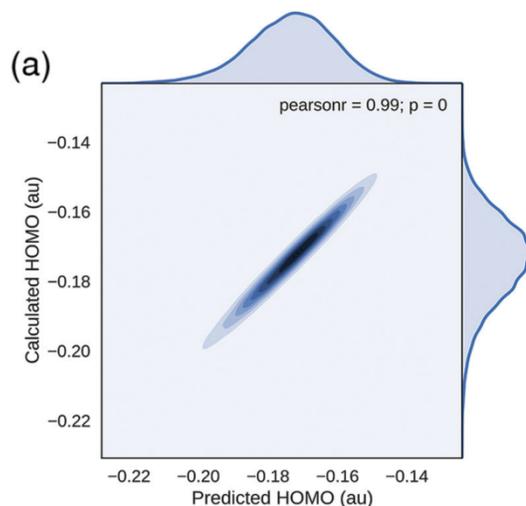


Figure 1 Use of a deep neural network for the prediction of organic photovoltaic properties. A calibration of the predicted HOMO vs the Calibrated HOMO for the Clean Energy Project Data Set. A deep network can evaluate a molecular property more than six orders of magnitude faster than quantum chemistry [E. O. Pyzer-Knapp, et al. Advanced Materials, 2015]

Grant Numbers and Grant Titles

DE—SC0008733

Towards 3rd Generation Organic Tandem Solar Cells with 20% Efficiency: Accelerated Discovery & Rational Design of Carbon-Based Photovoltaic Materials through Massive Distributed Volunteer Computing

Postdoc(s): Sule Atahan, Changwon Suh, Christopher Wilmer, Edward Pyzer Knapp, Takatoshi Fujita, Steven Lopez, Dmitriy Rappoport,

PI & Scientific Employees: Alan Aspuru-Guzik, Kai Treppe, Timothy Hirzel, Carlos Amador-Bedolla, Rossy Carolina Roman Salgado,

Student(s): Adrian Jinich, Martin Blood-Forsythe

Up to Ten Publications Acknowledging these Grants in the last 3-4 years

Publications

1. Edward O. Pyzer-Knapp, Changwon Suh, Rafael Gómez-Bombarelli, Jorge Aguilera-Iparraguirre, and Alán Aspuru-Guzik. What is High Throughput Virtual Screening? A Perspective from Organic Materials Discovery. *Annu. Rev. Mat. Res.* 2015, 45, 195-216.
2. Edward O. Pyzer-Knapp, Kewei Li, and Alan Aspuru-Guzik Learning from the Harvard Clean Energy Project: The Use of Neural Networks to Accelerate Materials Discovery *Adv. Funct. Mater.* 2015, 25, 6495-6502.
3. Eric Glowacki, Halime Coskun, Martin A. Blood-Forsythe, Uwe Monkowius, Lucia Leonat, Marek Grzybowski, Daniel Gryko, Matthew S. White, Alán Aspuru-Guzik, and Niyazi S Sariciftci. Hydrogen-bonded diketopyrrolopyrrole (DPP) pigments as organic semiconductors. *Organic Electronics* 15, no. 12 (2014): 3521-3528.
4. Ying Diao, Kristina M. Lenn, Wenya Lee, Martin A. Blood-Forsythe, Jie Xu, Yisha Mao, Yeongin Kim, Julia A. Reinspach, Steve Park, Alán Aspuru-Guzik, Gi Yue, Paulette Clancy, Zhenan Bao, and Stefan C.B. Mansfield. Understanding Polymorphism in Organic Semiconductor Thin Films Through Nanoconfinement. *Journal of the American Chemical Society* 136, no. 49 (2014): 17046-17057.
5. Johannes Hachmann, Roberto Olivares-Amaya, Adrian Jinich, Anthony L. Appleton, Martin A. Blood-Forsythe, László R. Seress, Carolina Román-Salgado, Kai Treppe, Sule Atahan-Evrenk, Süleyman Er, Supriya Shrestha, Rajib Mondal, Anatoliy Sokolov, Zhenan Bao, and Alán Aspuru-Guzik. Lead candidates for high-performance organic photovoltaics from high-throughput quantum chemistry – the Harvard Clean Energy Project. *Energy & Environmental Science* 7, no. 2 (2014): 698-704.
6. Hylke B. Akkerman, Stefan Mannsfeld, Ananth Kaushik, Eric Verploegen, Luc Burnier, Arjan Zoombelt, Jonathan Saathoff, Sanghyun Hong, Sule Atahan-Evrenk, Xueliang Liu,

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Excited and spin states of molecules with DFT

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Abstract

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. We have earlier demonstrated the ability of DFT to accurately predict the charge transfer excitations. It was shown that even using pure generalized gradient approximation (PBE) to exchange-correlation functionals such systems could be described both efficiently and accurately. This method is implemented in the NRLMOL code, which is a density functional theory code that uses localized Gaussian basis functions. We have applied this method to a range of systems from pentacene-TIPS crystals to large molecular complexes. The applications have shown that the method in general can be applied to systems with gaps.

One of the systems we have been studying is endohedral fullerenes. These fullerenes or carbon cages have an endohedral unit, which stabilizes the cage by electron transfer from the endohedral unit to the cage. Our previous work has demonstrated that the endohedral units are generally shielded by the carbon cage from external perturbations. This may serve as a model to isolate a magnetic core inside the carbon cage. We have carried out calculations on a number of transition metal oxide cubane structures encapsulated within various possible carbon cages. Our calculations show that Co_4O_4 encapsulated carbon cages show higher magnetization reversal barriers compared to units containing Mn atoms. This work is analyzed and written up.

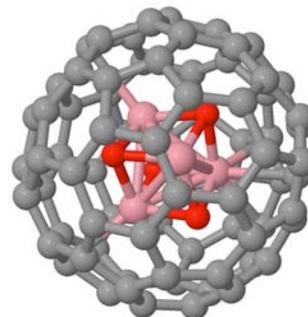


Fig.1: $\text{Co}_4\text{O}_4@C_{76}$ has a magnetic anisotropy barrier of 40K.

Another recent development is the incorporation of a large number of pure GGA and meta-GGA functionals, as implemented in LIBXC exchange-correlation library. Apart from these we have also implemented the newly published SCAN meta-GGA functional. The SCAN functional is strongly constrained that satisfies all the known 17 constraints for density functionals. One of the preliminary applications of the SCAN functional is on the spin state of the de-oxy heme molecule. The GGA functionals generally tend to stabilize the low-spin states, which is reversed with the meta-GGA functionals. However, we found that with TPSS functional the low-spin state is preferred. On the other hand the situation is rectified with the application of the SCAN functional. This is in excellent agreement with a recent application of self-interaction correction through Fermi-orbitals to the de-oxy heme molecule. However, another similar application to $\text{Fe}(\text{O}_2)_2$ species showed that the SCAN results do not compare with the multi-reference calculations. These results are being analyzed.

The immediate future goals are to test the SCAN functional for light harvesting systems, and extend the

calculations of the coupling constants with fragment orbitals.

DE-SC0002168 Density functional theory based methods for light-harvesting molecules

Postdoc(s): Yoh Yamamoto

Student(s): Kamal Nyaupane

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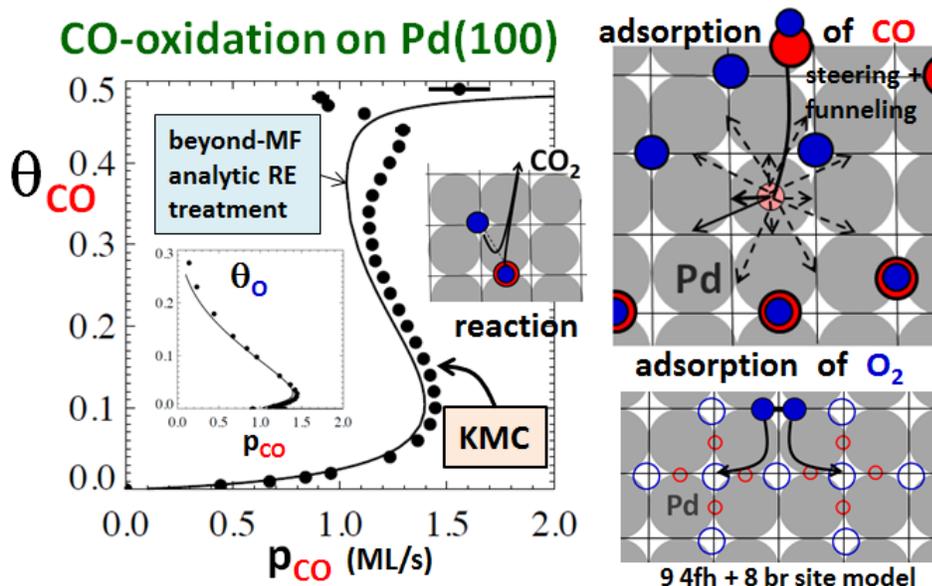
Predictive molecular-level and coarse-grained mesoscale modeling of chemisorption and catalytic reaction-diffusion processes on surfaces

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Abstract

One key goal of our project is the development of realistic and comprehensive molecular-level models for catalytic reaction-diffusion processes, e.g., predicting reaction yield in flow or batch reactors. Traditional mean-field (MF) rate or reaction-diffusion equation modeling of chemical kinetics can fail due to strong spatial correlations between reactants. For surface reactions, the origin of such correlations is usually thermodynamic at lower coverages and pressures (P) (reflecting ordering of mobile interacting adspecies), or kinetic at high coverages or P (due inhibited mobility). Our modeling must precisely describe (e.g., with ab-initio energetics) adlayer thermodynamics, well as local-environment-dependent kinetics of adsorption, desorption, diffusion, and reaction. We have utilized KMC simulation to analyze models for oxidation on metal(100) surfaces at low P, describing steady-state bifurcation diagrams, titration, and temperature programmed reaction kinetics. For deeper insight, we have developed beyond-MF rate equations accounting for adlayer ordering to describe these systems. For oxidation reactions at high P where the metal surface is often oxidized, non-MF reaction kinetics can be strongly impacted by kinetically-induced spatial correlations. We have also developed an analytic formulation successfully providing insight into these correlations. (There is some synergy between the latter and our distinct studies of catalytic conversion reactions in nanoporous materials where again limited mobility due to the narrow pores impacts reactivity.) Finally, in a separate body of work related to catalytic surface reactions, we consider the interaction of S with metal surfaces, noting that S act as a catalytic promoter or poison, and can induce surface rearrangement sometimes associated with metal-S complex formation.



DOE Grant DE-AC02-07CH11358: Ames Laboratory Chemical Physics Program

Lead PIs: James W. Evans, Mark S. Gordon; co-PI's: Theresa Windus, Klaus Ruedenberg
Staff Scientists: Da-Jiang Liu, Mike Schmidt, Federico Zahariev Student: Andres Garcia.

PROGRAM SCOPE

This theoretical Chemical Physics project at Ames Laboratory pursues 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*. The former includes quantum chemistry studies for large systems, homogeneous and heterogeneous catalysis, etc. The latter on which we focus here explores: (i) the interplay between anomalous transport and catalytic reaction in functionalized mesoporous materials in collaboration with Ames Lab experimentalists; (ii) chemisorption and heterogeneous catalysis on metal surfaces including: bifurcations in reactive steady-states; TPR and titration kinetics; connecting atomistic to spatiotemporal mesoscale behavior; (iii) statistical mechanics of reaction-diffusion processes exhibiting non-equilibrium phase transitions, metastability, critical phenomena, etc..

RECENT PROGRESS

Chemisorption and Catalysis on Extended Surfaces

Detailed and predictive multisite lattice-gas (msLG) models and efficient KMC simulation algorithms were developed to describe oxidation reactions on unreconstructed metal surfaces under lower-pressure (P) conditions.^{1,2} The msLG models account for multiple stable adsorption sites of some reactant species, and thus allow more accurate treatment of adlayer ordering and reaction configurations. Reactive steady-states are impacted not only by adlayer thermodynamics, but also by kinetics. Thus, guided by DFT analysis, we have developed 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 O₂ dissociation.^{3,4} 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.^{1,2} These interactions, together with the above refined adsorption models, were incorporated into msLG CO-oxidation models.¹⁶ 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.¹ In order to provide deeper insight into behavior controlling reactivity, we have also developed beyond-MF rate equation treatments for slightly simplified msLG models of CO-oxidation in selected metal(100) and metal(111) surface. These analytical formulations account for the complex equilibrium adlayer superlattice ordering involving multiple adsorption sites.²

A new effort explored CO-oxidation at high-P on an oxidized surface of Ru, specifically RuO₂(110). This system has been studied extensively by K. Reuter and coworkers, who in particular noted a dramatic failure of MF-rate equation treatment of kinetics due to strong spatial correlations induced by a combination of reaction and limited mobility. We develop a formalism to precisely describe these correlations and also the sluggish dynamics in this system.⁵ 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.⁶

Detailed and precise characterization of chemisorption 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). In another recent and major undertaking, D.-J. Liu performed extensive DFT analysis to elucidate detailed STM studies for a diverse variety of adlayer ordering, reconstruction on terraces and at steps, and metal-S complex formation for S on (111) surfaces of Ag, Cu, Au, and also on (100) and (110) surface of Au. This work resulted in a series of 6 papers in 2014 and 2015. The DFT analyses incorporated comprehensive exploration of low-energy structures, and were sometimes combined with statistical mechanical studies of ordering.

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).² These systems exhibit inhibited passing of reactants and products within pores. Previous analyses, mostly for catalysis in zeolites, had produced only partial understanding of such basic issues such low reactivity due to inhibited transport into pores. We showed that mean-field reaction-diffusion equation (RDE) treatments fail to describe such behavior, instead developing a successful “generalized hydrodynamic” treatment incorporating fluctuation effects near pore openings.² 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. Recent efforts extend modeling to treat concentration-dependent (stereo-) selectivity, and the effect of interactions between reactant and product species.

Reaction yield in these systems increases strongly with the propensity, P , of reactants and products to pass inside narrow pores. A previous TST analysis of P was based on the effective free energy versus separation along the pore. Our detailed Langevin simulations of reactant-product passing showed that TST fails to describe how P vanishes upon reducing the pore diameter to the value where passing is blocked by steric effects.¹⁰ A deeper understanding of behavior was provided by analysis of appropriate (equivalent) Fokker-Planck Equations (FPE).¹⁰

FUTURE PLANS

Future research efforts will include the following: (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. In collaboration with the *Gordon group*, we hope to apply EFP-MD analysis to assess both the solvent-mediated diffusivity and interactions of reactant and product species. This key information will provide input to our coarse-grained modeling. In collaboration with the *Windus group*, we are exploring models for concentration-dependent selectivity in these systems. (ii) Development of realistic and 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. Here, we will collaborate with *Zahariev and Gordon* comparing predictions of high-level

methods including QMC with DFT predictions. **(iii)** Development of appropriate theoretical framework to reliably describe strong correlations due to inhibited mobility in surface reactions at high-pressures. Related more general studies will attempt to provide a fundamental understanding of non-equilibrium poisoning transitions and related phenomena in catalytic reaction systems. **(iv)** Further analysis of the interaction of metal surfaces and nanoclusters with chemisorbed species, particularly S which can act as a promoter or poison. This work involves a collaboration with the *Windus group* to elucidate the nature of the metal-S interaction (comparing plane-wave and localized-orbital based DFT analysis to characterize bonding).

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Excited State Absorption and Dynamics in NWChem

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Project Title: Charge Transfer and Charge Transport in Photoactivated Systems

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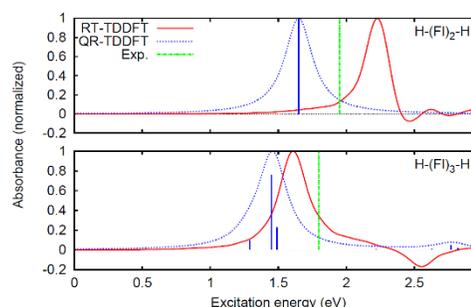
Project Scope: A suite of new theoretical methods is being *developed* and *implemented* in the *NWChem* computational chemistry software suite in order to provide *improved* capabilities for excited-state dynamics in the gas phase and to *add* the capability to perform electronically excited-state dynamics 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)

Here we discuss our recent developments and progress in real-time and linear-response TDDFT within the NWChem program.

Excited State Absorption from Real-Time (RT) Time Dependent Density Functional Theory

The optical response of excited states is a key property used to probe photophysical and photochemical dynamics. Additionally, materials with a large nonlinear absorption cross-section caused by two-photon (TPA) and excited state absorption (ESA) are desirable for optical limiting applications. The ability to predict the optical response of excited states would help in the interpretation of transient absorption experiments and

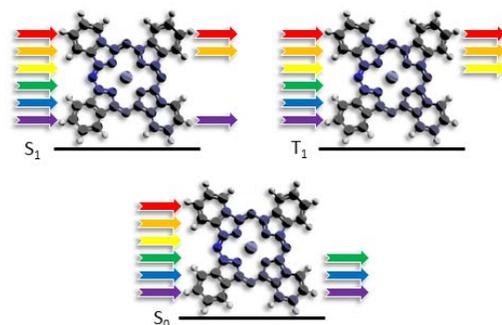


Excited state absorption spectra of oligofluorenes calculated with RT-TDDFT (solid curve) and QR-TDDFT (broken curve/sticks)

aid in the search for and design of optical limiting materials. We have developed an approach to obtain excited state absorption spectra by combining real-time (RT) and linear-response (LR) time-dependent density functional theory (TDDFT). Being based on RT-TDDFT, our method is aimed at tackling larger molecular complexes and materials systems where excited state absorption is predominantly seen and many time-resolved experimental efforts are focused. To demonstrate our method, we have calculated the ground and excited state spectra of H_2^+ and H_2 due to the simplicity in the interpretation of the spectra. We have validated our new approach by comparing our results for butadiene with previously published results based on quadratic response (QR). We have also studied oligofluorenes, where we compare our results with both QR-TDDFT and experimental measurements. Since our method directly measures the response of an excited state, stimulated emission features are also captured; although, these features are underestimated in energy which could be attributed to a change of the reference from the ground to the excited state.

Excited State Absorption from Real-Time (RT) Time Dependent Density Functional Theory: Optical Limiting in Zinc Phthalocyanine

The proliferation of intense light sources has led to a commensurate increase in the need to protect light-sensitive equipment. Optical limiting materials show a strong attenuation of light transmission at high input intensities. Porphyrin and phthalocyanine based materials have attracted a great deal of attention for optical limiting applications due to their large nonlinear optical properties, fast response times, and ability to tune their optical properties through chemical modifications. With excited state absorption (ESA) being the suggested mechanism of optical limiting behavior in phthalocyanines, our method (described earlier) for the calculation of ESA with RT-TDDFT seems well suited to study their optical limiting potential. The optical limiting behavior in these molecules is often interpreted by means of a five state model. An intense light source creates a substantial population of the excited state. Molecules in the excited state can then absorb an additional photon to be excited further. The interplay of the duration of the incident pulse, the excited state lifetime, and the intersystem crossing rate determine whether singlet or triplet ESA is relevant. A necessary, albeit insufficient, condition for effective optical limiting is for the ESA cross-section to be larger than the ground state absorption (GSA) cross section in the relevant region of the spectrum. In this study we have investigated the optical limiting potential of zinc phthalocyanine. We have also investigated the effect of the triplet manifold.



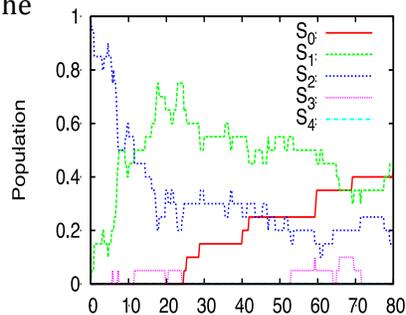
Optical Limiting in Zinc Phthalocyanine

As part of ongoing work, we are performing a benchmark study comparing our excited-state absorption (ESA) approach against quadratic response TDDFT (QR-TDDFT). Ongoing work also includes transient absorption studies.

Non-Adiabatic Molecular Dynamics

As part of developing a non-adiabatic molecular dynamics (NAMD) framework within NWChem, we have implemented Tully's fewest switches surface hopping algorithm¹ for non-adiabatic dynamics. The non-adiabatic couplings are calculated numerically using the pseudo-wavefunction approach via the recent approach of Ryabinkin and co-workers², which is significantly faster than the traditional numerical approach. Both TDDFT and TDDFT/TDA versions have been implemented.

The



Surface Hopping Dynamics in CH₂NH₂⁺
(Protonated Schiff Base 1)

electronic density matrix is propagated via fourth order Runge-Kutta and interpolation and extrapolation are used to obtain values for the elements of the electronic Hamiltonian and non-adiabatic couplings at times between nuclear time steps. We have implemented the decoherence correction due to Truhlar³ and Persico⁴ and co-workers. As part of our prototyping we have performed surface hopping molecular dynamics on the well-studied CH₂NH₂⁺ (Protonated Schiff Base 1) system. Our results are in good agreement with the published results of Tapavicza and co-workers⁵. We are currently studying larger molecular complexes in solvation environments. We will also

be extending this framework to include other NAMD approaches like the Coherent Switches with Decay of Mixing (CSDM)³ developed by the Truhlar group.

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Quantum Dynamics of Elementary Chemical Reactions

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Abstract

We have focused in this grant period on the quantum state resolved dynamics of bimolecular reactions. Two major advances have been made. One is the construction of high-dimensional, permutationally invariant potential energy surfaces (PESs) for reactive scattering, based on high-level ab initio calculations. The other is concerned with the development of novel and more efficient quantum dynamical methods for solving the quantum scattering problems.

With the advances of electronic structure theory, it has become relatively straightforward to compute highly accurate electronic energies for small molecular systems over a large configuration span. However, analytical representations of global PESs remain a challenge. Recently, we proposed a permutation invariant polynomial-neutral network (PIP-NN) method for fitting PESs from ab initio data. This method uses PIPs as symmetry functions in the input layer of NNs, thus enforcing the permutation symmetry rigorously. The NNs, on the other hand, provide an extremely flexible form, thus a highly faithful representation of the ab initio points. This method has been applied to many reactive and non-reactive systems, up to seven atoms with 15 degrees of freedom.¹⁻³ More recently, it has been used to fit inter- as well as intra-molecular PESs for the Ne-C₂H₂ system.⁴ Thanks to this and other methods developed recently, it is probably safe to claim that the previously considered bottleneck of PES fitting is now eliminated, at least for reactions involve a small number of atoms. Our work in this respect has been summarized in a recent Feature Article published on JPCA (Figure 1).⁵

In tandem with the development of multi-dimensional global PESs for reactions, we have also made significant progress in quantum theory on reactive scattering. In addition to quantum dynamical studies of mode specificity and bond selectivity in bimolecular reactions,⁶⁻⁹ much effort has been devoted to the implementation of the so-called transition-state wave packet (TSWP) method, in which the TSWPs are propagated separately in both the reactant and product channels. The S-matrix can then be assembled from the cross-correlation functions from these propagations. The advantages of this method are many fold. Because the scattering calculations are inelastic-like, the grid/basis needed in such calculations is significantly less than typical state-to-state calculations. Perhaps more importantly, it allows insightful analysis of the reaction dynamics in terms of transition state control. More recently, we have also proposed a reactant coordinate based (RCB) method for state-to-state quantum reactive dynamics involving four atoms,¹⁰ which complements the TSWP method.

The TSWP method has been applied to several four-atom reactions on ab initio based PESs. These calculations have revealed interesting features on the transition state control of state-to-state reaction dynamics.¹¹⁻¹³ In particular, we have addressed the so-called “loss of memory” issue in reactive scattering, in which the product state distributions are insensitive to reactant internal state excitations. Based on our quantum state-to-state results, we have proposed the concept of the “state-to-state mode specificity”.¹³ It was

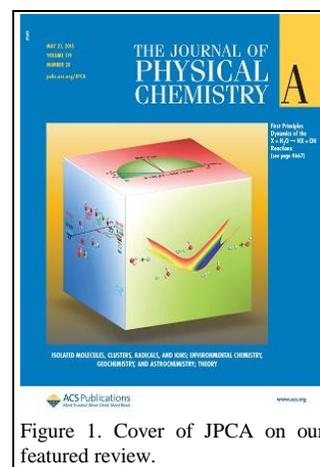


Figure 1. Cover of JPCA on our featured review.

shown that the “loss of memory” effect stems from the energy flow from active reactant modes into the reaction coordinate at the transition state. However, energy is sequestered in spectator modes, gated by the transition state. These new insights help to provide a more in-depth understand the quantum reactive scattering at the state-to-state level.

Other efforts in our group include theoretical studies of photodissociation and photodetachment dynamics,¹⁴⁻¹⁸ ro-vibrational dynamics,¹⁹⁻²¹ and chemical rates of neutral and ion-molecular reactions.²²⁻²⁷ The PI has also been involved in many synergistic activities, including co-organizing a symposium at 2015 Pacificchem and co-editing a JPCA special issue on 50 years of Reaction Dynamics (Figure 2).

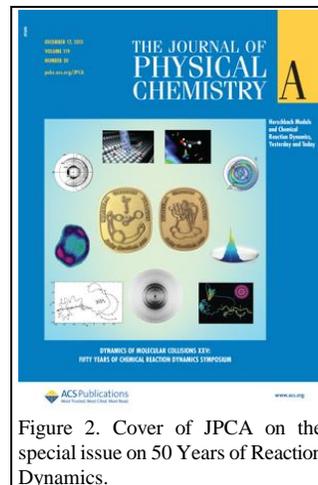


Figure 2. Cover of JPCA on the special issue on 50 Years of Reaction Dynamics.

Grant Numbers and Grant Titles

DE-FG02-05ER15694 **Quantum Dynamics of Elementary Chemical Reactions**

Postdoc(s): Bin Zhao

Student(s): Ben Datko

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Feynman–Goldstone Diagrammatic Theories for Quantum Dynamics

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Abstract

The ultimate goal of this program is to establish systematically converging, efficient, and rigorously (i.e., diagrammatically) size-consistent many-body theories of quantum dynamics in bound potentials (anharmonic vibrational theory), capitalizing on the great successes of such theories in ab initio electronic structure theory, embodied by diagrammatic many-body perturbation and coupled-cluster theories. We aim to apply them to condensed-phase dynamics problems (e.g., thermal expansion, thermal conductivity, infrared, Raman, and inelastic neutron scattering spectra, pressure tuning of Fermi resonance) in which anharmonicity is essential.

In Ref. 4, we have laid out the rules of normal-ordered second quantization for molecular vibrations and derived the vibrational Hamiltonian in a normal-ordered form, which underlies Feynman–Goldstone diagrammatic theories. The zero-, one-, and two-mode amplitudes in the normal-ordered Hamiltonian are identified as the ground-state (zero-point) energy, gradient, and frequency, respectively, of the size-extensive vibrational self-consistent field (XVSCF) method introduced by Keçeli, Hermes, and Hirata [J. Chem. Phys. **135**, 134108 (2011); *ibid* **136**, 234109 (2012)] with support from this DOE grant in the previous funding period.

In Ref. 6, we have formulated and implemented diagrammatic second-order many-body perturbation (XVMP2) and Green’s function theories. We have outlined a set of rules to list all closed (energy) and open (self-energy) diagrams (Fig. 1) and to interpret them into programmable algebraic expressions. The theories yield not only anharmonic corrections to zero-point energies but also those to frequencies directly. Despite being a perturbation theory, they resist divergence when applied to strongly correlated modes such as Fermi resonances. This is achieved by solving the Dyson equation with a frequency-dependent self-energy self-consistently.

In Ref. 1, we have introduced diagrammatic vibrational coupled-cluster (XVCC) theory for ground and excited states, the latter through the equation-of-motion (EOM-XVCC) formalism. It is based on a harmonic or XVSCF reference and utilizes the normal-ordered second quantization in its derivation. Therefore, it differs fundamentally from O. Christiansen’s vibrational coupled-cluster theory, but is a direct extension of M. D. Prasad’s. We have

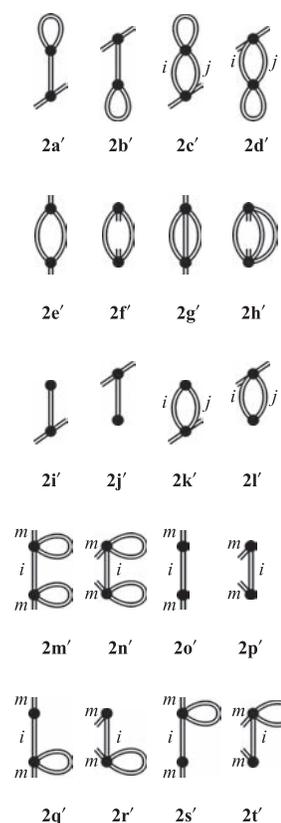


Figure 1. Second-order self-energy diagrams.

established the rules of enumerating diagrams in each theory (Fig. 2) and interpreting them algebraically for numerical evaluation. We have implemented the theories including up to the connected eight-mode excitation operator, using a fully automated scheme for derivation, algorithm optimization, and code synthesis.

A severe computational bottleneck of quantum dynamics tends to be the evaluation and storage of force constants or other similar representations of a potential energy surface (PES). The number of force constants increases exponentially with rank and high-rank polynomially with the number of modes. Their finite-difference evaluation is increasingly unstable with rank and is non-scalable. In Refs. 3 and 5, we have introduced stochastic algorithms of XVSCF and XVMP2 to completely eliminate this bottleneck. We re-express their energy and self-energy expressions into short sums of high-dimensional integrals and evaluate these integrals by the Metropolis Monte Carlo method, which require on-the-fly evaluation of the PES values (but not derivatives or their storage). Our methods constitute one of the first quantum Monte Carlo methods that can calculate energy differences or describe excited states without any noticeable sign errors or a need to assume nodal structures.

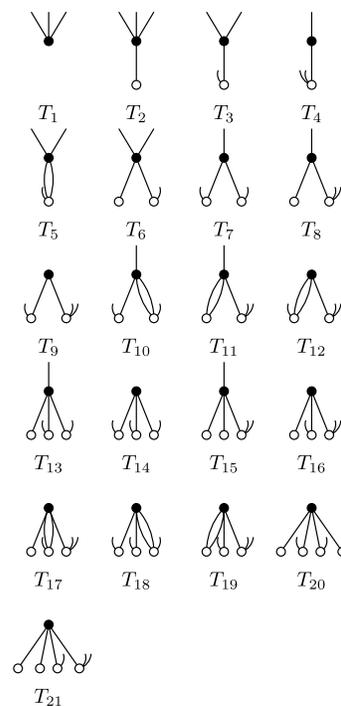


Figure 2. Diagrams of the T_3 amplitude equation of XVCCSDT.

Grant Number and Grant Title

DE-FG02-11ER16211 Breakthrough Design and Implementation of Electronic and Vibrational Many-Body Theories.

Students: Matthew R. Hermes and Jacob A. Faucheaux.

Selected Publications Acknowledging the Grant

1. J. A. Faucheaux and S. Hirata, *The Journal of Chemical Physics* **143**, 134105 (2015), “Higher-order diagrammatic vibrational coupled-cluster theory.”
2. M. R. Hermes and S. Hirata, *International Reviews in Physical Chemistry* **34**, 71-97 (2015), “Diagrammatic theories of anharmonic molecular vibrations.”
3. M. R. Hermes and S. Hirata, *The Journal of Chemical Physics* **141**, 244111 (2014); Erratum **143**, 129904 (2015), “Stochastic algorithm for size-extensive vibrational self-consistent field methods on fully anharmonic potential energy surfaces.”
4. S. Hirata and M. R. Hermes, *The Journal of Chemical Physics* **141**, 184111 (2014), “Normal-ordered second-quantized Hamiltonian for molecular vibrations.”
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Breakthrough Design and Implementation of Electronic and Vibrational Many-Body Theories

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Program Scope

Predictive chemical computing requires hierarchical many-body methods of increasing accuracy for both electrons and vibrations. Such hierarchies are established, at least conceptually, as configuration-interaction (CI), many-body perturbation (MP), and coupled-cluster (CC) methods, which all converge at the exact limit with increasing rank of a hierarchical series. These methods can generate results of which the convergence with respect to various parameters of calculations can be demonstrated and which can thus be predictive in the absence of experimental information.

The wide use of the hierarchical electronic and vibrational many-body methods has, however, been hindered (1) by the immense cost of *executing* the calculations with these methods and, furthermore, the nonphysical rapid increase of the cost with increasing system or computer size; in other words, the conventional matrix-algebra-based algorithms of these methods are fundamentally non-scalable, (2) by the complexity and cost of *developing* some of the high-rank members of these methods, and (3) by the slow convergence of electronic energies and wave functions with respect to one-electron basis set sizes, which further drives up the cost of execution. For applications to large molecules and solids, the additional difficulties arise by the lack of (4) size consistency in some methods (whose energies and other observables scale non-physically with size) and of (5) efficient methods that work for metallic and superconducting states as well as for electronic and/or vibrational strong correlation.

In this funding period, we focus on establishing systematically converging, efficient, and rigorously (i.e., diagrammatically) size-consistent many-body theories of quantum dynamics in bound potentials (anharmonic vibrational theory), capitalizing on the great successes of such theories in ab initio electronic structure theory, embodied by diagrammatic MP and CC theories.

Recent Progress

Normal-ordered vibrational Hamiltonian. In Ref. 4, we have laid out the rules of normal-ordered second quantization for molecular vibrations and derived the vibrational Hamiltonian in a normal-ordered form, which underlies Feynman–Goldstone diagrammatic theories. The zero-, one-, and two-mode amplitudes in the normal-ordered Hamiltonian are identified as the ground-state (zero-point) energy, gradient, and frequency, respectively, of the size-extensive vibrational self-consistent field (XVSCF) method introduced by Keçeli, Hermes, and Hirata [*J. Chem. Phys.* **135**, 134108 (2011); *ibid* **136**, 234109 (2012)] with support from this DOE grant in the previous funding period.

XVMP2. In Ref. 9, we have formulated and implemented diagrammatic second-order many-body perturbation (XVMP2) and Green’s function theories. We have outlined a set of rules to list all closed (energy) and open (self-energy) diagrams (Fig. 1) and to interpret them into programmable algebraic expressions. The theories yield not only anharmonic corrections to zero-point energies but also those to frequencies directly.

Despite being a perturbation theory, they resist divergence when applied to strongly correlated modes such as Fermi resonances. This is achieved by solving the Dyson equation with a frequency-dependent self-energy self-consistently:

$$\nu_m = \{\omega_m^2 + 2\omega_m \Sigma_m(\nu_m)\}^{1/2} \equiv \{F(\nu_m)\}^{1/2}$$

It can be seen that the roots of this equation occur at the intersections of $y = x$ (the left-hand side) and $y = \{F(x)\}^{1/2}$ (the right-hand side). As can be seen in Fig. 2, such intersections can never be divergent for the simple reason that they have to be on $y = x$, even though the self-energy and hence $F(x)$ are indeed frequently divergent.

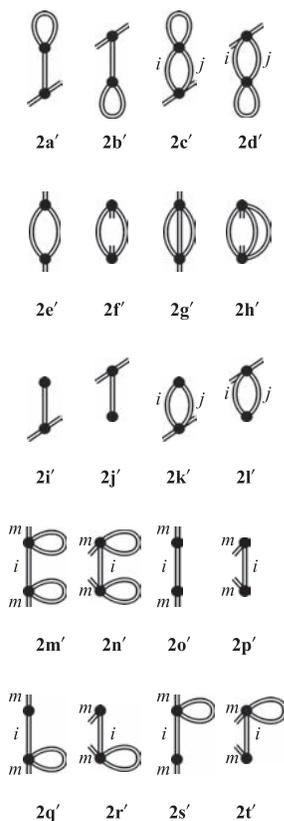


Figure 1. Second-order self-energy diagrams.

completely eliminate this bottleneck. We re-express their energy and self-energy expressions into short sums of high-dimensional integrals and evaluate these integrals by the Metropolis Monte Carlo method, which require on-

Vibrational coupled-cluster theory. In Ref. 1, we have introduced diagrammatic vibrational coupled-cluster (XVCC) theory for ground and excited states, the latter through the equation-of-motion (EOM-XVCC) formalism. It is based on a harmonic or XVSCF reference and utilizes the normal-ordered second quantization in its derivation. Therefore, it differs fundamentally from O. Christiansen’s vibrational coupled-cluster theory, but is a direct extension of M. D. Prasad’s. We have established the rules of enumerating diagrams in each theory (Fig. 3) and interpreting them algebraically for numerical evaluation. We have implemented the theories including up to the connected eight-mode excitation operator, using a fully automated scheme for derivation, algorithm optimization, and code synthesis.

Stochastic vibrational methods. A severe computational bottleneck of quantum dynamics tends to be the evaluation and storage of force constants or other similar representations of a potential energy surface (PES). The number of force constants increases exponentially with rank and high-rank polynomially with the number of modes. Their finite-difference evaluation is increasingly unstable with rank and is non-scalable. In Refs. 3 and 5, we have introduced stochastic algorithms of XVSCF and XVMP2 to

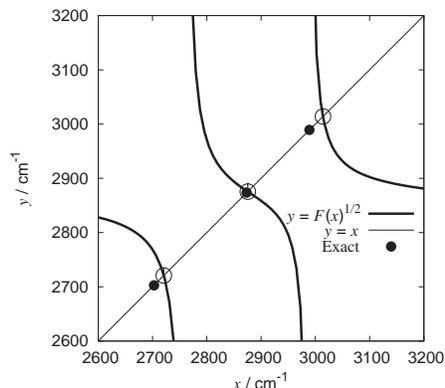


Figure 2. A plot of the left- and right-hand sides of Eq. (1) as a function of $x = \nu_m$ in XVMP2 for formaldehyde near ν_5 .

the-fly evaluation of the PES values (but not derivatives or their storage). Our methods constitute one of the first quantum Monte Carlo methods that can calculate energy differences or describe excited states without any noticeable sign errors or a need to assume nodal structures.

Review. Much of the aforementioned research has been summarized in an invited review published in *Int. Rev. Phys. Chem.* (Ref. 2).

Future Plans

We aim at applying these size-consistent methods to condensed-phase dynamics problems (e.g., anharmonic phonon dispersion curves, infrared, Raman, and inelastic neutron scattering spectra, thermal expansion, thermal conductivity, and pressure tuning of Fermi resonance) in which a proper consideration of anharmonicity is essential.

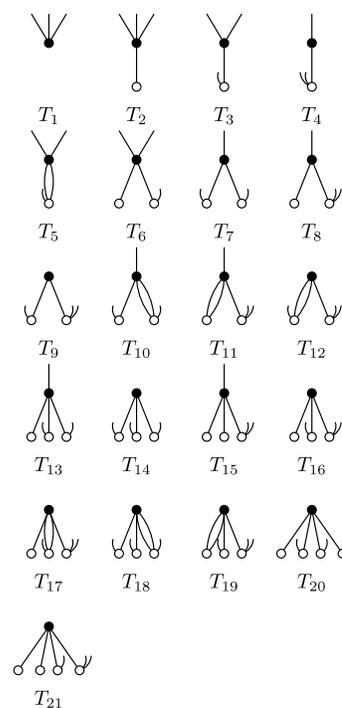


Figure 3. Diagrams of the T_3 amplitude equation of XVCCSDT.

Selected Publications of This DOE Grant Sponsored Research (2013–Present)

1. J. A. Faucheaux and S. Hirata, *The Journal of Chemical Physics* **143**, 134105 (2015), “Higher-order diagrammatic vibrational coupled-cluster theory.”
2. M. R. Hermes and S. Hirata, *International Reviews in Physical Chemistry* **34**, 71-97 (2015), “Diagrammatic theories of anharmonic molecular vibrations.”
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Learning Molecular Level Design Principles from Light Harvesting Complexes

PI: Seogjoo Jang

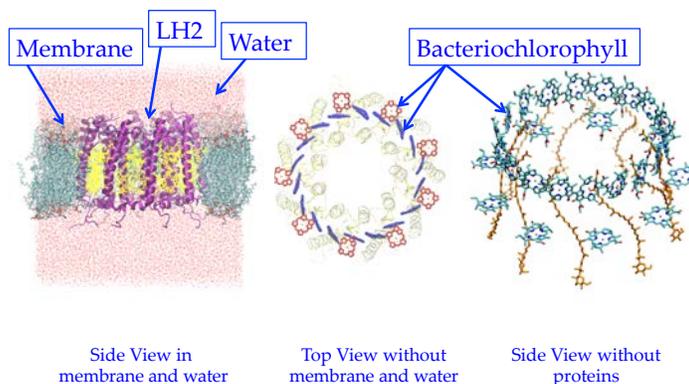
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Abstract

The main objective of this research project is to understand genuine molecular level design principles for robust and efficient exciton migration in photosynthetic light harvesting complexes and to establish general and practical rules that can be utilized by experimentalists for developing biomimetic and plastic photovoltaic devices. To this end, we have been making multifaceted computational and theoretical efforts to understand and model the exciton dynamics involving light harvesting 2 (LH2) complexes, which serve as the major initiator and carrier of the excitation energy in purple bacteria.

Natural LH2s have highly symmetric structures, formed by 8-10 fold circular arrangement of the same protein-pigment complex units, as illustrated in the figure on the right hand side, and are known to allow migration of excitons over 100 nm length scales with almost perfect efficiency. During the last funding period, we made significant progress in atomistic level computational study of the dynamics and the energetics of LH2s and their effects on the spectroscopy and the exciton dynamics.

Light Harvesting 2 (LH2) Complex



Through combination of classical Molecular Dynamics (MD) simulation, *ab initio* calculations, and application of a coarse-grained exciton dynamics calculation method, we have simulated inter-LH2 exciton dynamics including realistic effects of disorder. The calculation results are in reasonable agreement with available experimental data, and offer insights into intriguing competition among quantum delocalization of excitons, structural constraints, and disorder. In particular, our study elucidated new theoretical evidence that the interplay between quantum delocalization of excitons and the disorder dictates the optimal size of LH2 and that hydrogen bonding between pigment molecules and protein residues play a unique role in regulating the disorder.

At present, similar efforts are being pursued to understand molecular level origins of the spectroscopy of light harvesting 3 (LH3) complex, a natural mutant of LH2 formed under low light condition. Longer time MD simulations ranging up to microsecond time scales are also in progress for both LH2 and LH3 complexes. Future research efforts include analyses of these computational results and simulation of long-range exciton dynamics in aggregates of LH2s, LH3s, and other synthetic light harvesting complexes with

similar structural motifs. Outcomes of these studies will provide new insights into how to control molecular level structural details in order to design systems exhibiting efficient and robust exciton migration at larger length scales even in the presence of significant disorder and fluctuations. At the same time, we will continue computational study of the excited states of conjugated organic molecules such as oligothiophenes, oligophenylene-vinylenes, and oligofluorene-fullerene dyads and theoretical modeling of their spectroscopic data. Outcomes of these research projects will be incorporated into the future modeling of exciton dynamics in conjugated organic molecular systems being used for plastic photovoltaic devices.

Grant Numbers and Grant Titles

DE-SC0001393: Molecular Level Characterization of Quantum Design Principles for Efficient and Robust Exciton and Charge Migration

Postdoc(s): Daniel Montemayor and Eva Rivera

Publications Acknowledging this Grant in the last 3-4 years

1. S. Jang and Y.-C. Cheng, "Resonance energy flow dynamics of coherently delocalized excitons in biological and macromolecular systems: Recent theoretical advances and open issues," *WIREs Comput. Mol. Sci.* **3**, 84 (2013).
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Theoretical/Computational Studies of Structural, Electronic, and Chemical Reactivity Properties of Pure and Alloy Metal Clusters for Their Uses as Nanocatalysts

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Abstract

This program focuses on theoretical/computational explorations of structural, electronic, and chemical reactivity properties of pure and alloy metal clusters with an eye on their uses as nanocatalysts. We explore these properties as a function of cluster size, composition (both elemental and percentile), and environment (e.g., functionalization by capping ligands). The work is performed in close contact with experimental studies. Examples of recent work are listed as Refs. 1-9.

The source of novelty and immense added potential - as well as added complexity - of nanocatalysts, as compared to their extended counterparts, is the large number and variety of their morphological forms and the reactive sites on them. These possess different catalytic characteristics, and the task/goal is to identify the structures/sites that exhibit the best catalytic functionalities for the reactions of interest.

In a recent study [9], we considered as a paradigmatic case 5 structural forms of Pt₁₃ as a nanocatalyst for the oxygen reduction reaction (ORR). Four of these are low-energy conformations with low symmetry, and the fifth has a highly symmetric icosahedral form, which for Pt₁₃ turns out to be a high-energy conformation. ORR plays a central role in a number of technologically important processes, including those in proton exchange membrane fuel cells, where a Pt-based cathode serves as the electro(nano)catalyst.

Using extensive state-of-the-art density functional theory (DFT) calculations, we characterized all the topologically non-equivalent reaction sites on each of the 5 structures of Pt₁₃ in terms of H₂, O₂, CO, OH and O adsorption energies and the barrier height for O₂ dissociation (all these play a role in the overall ORR). We also mapped out the complete minimum energy paths for CO oxidation into CO₂ (part of the ORR cycle) via the Langmuir-Hinshelwood mechanisms on each of these structures considering two alternative reaction pathways (cf. Fig. 1). Using the OH and O adsorption energies as gauges of activity and the barrier for O₂ dissociation (which is the rate-limiting step in CO oxidation) as a gauge of CO tolerance, we identified two structures of Pt₁₃, of the five considered, as having the best, overall comparable, catalytic characteristics for the ORR. Our analysis revealed that this best performance is a consequence of the dual role of CO on these two structures: In addition to being a reactant, it also serves as a promoter by lowering the barrier for dissociation of the co-adsorbed O₂.

With further advances in and control over synthesis techniques, computational studies of this type will become indispensable as a guiding tool in the design and manufacture of catalysts with superior, reaction-optimized performance. Future studies will incorporate the effects of the support and alloying with other metals.

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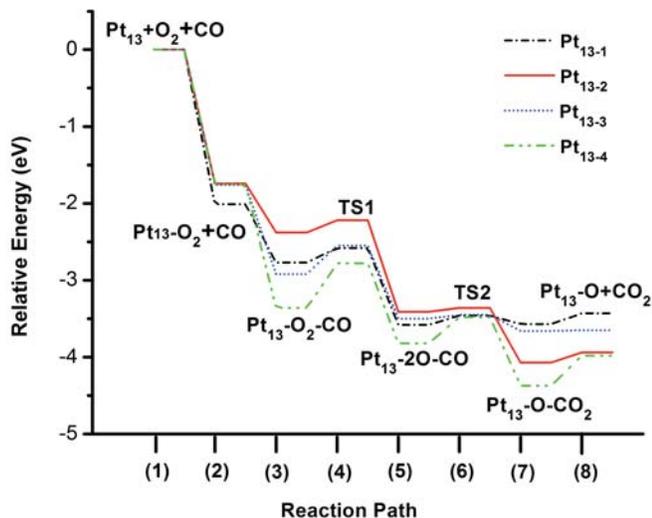


Fig. 1. Minimum energy paths for CO oxidation on 4 forms of Pt_{13} via O_2 dissociation in the presence of the co-adsorbed CO as an intermediate step (the reaction does not occur on Pt_{13-5}).

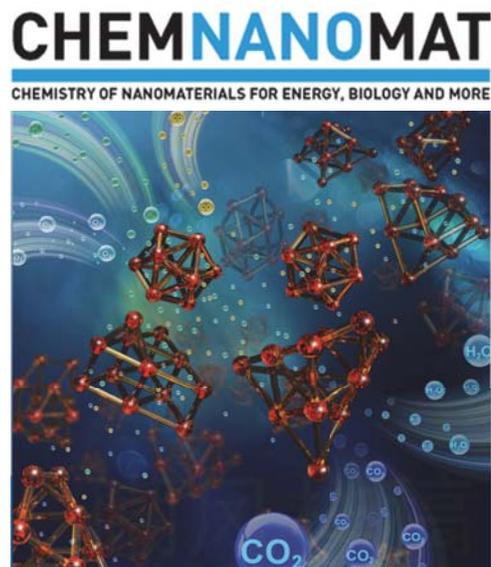


Fig. 2. Our study featured on the front cover of the journal [9].

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Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

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PROGRAM SCOPE

The project aims to advance molecular level understanding, prediction and control of nanoscale hydration in salt solutions by electric stimuli or ionic patterning. It relies on development of state-of-the-art simulation algorithms in statistical mechanics to capture complex processes in open systems under electric control. Parallel studies of wetting and dispersibility of ionizing particles aim to uncover predictive relations between electrowetting, chemical functionalization, and geometry of nanomaterial particles. Permeation of nanoporous electrodes at preset voltage underlies the function of ultracapacitors. Transitory regulation of wetting in nanoporous media by electric field spans an array of applications in materials, energy storage, and separation sciences. The physically related modulation of nanoparticle solubility by surface charges can significantly extend the range of the nanomaterial applications, improve processing techniques, and potentially alleviate environmental concerns.

RECENT PROGRESS

Electrolytes in nanoporous media: Insights from Expanded Ensemble GCMC simulations

Salt absorption in a nanopore. Optimized surface porosity plays a central role in materials design for energy technologies; however, modeling pore absorption of electrolytes remains a challenge. We study pore/bulk equilibria by open ensemble Monte Carlo (GCMC) simulations. To overcome extremely low acceptance of ion exchanges, we use new Expanded Ensemble technique, in which we split ion pair *and* water insertions and deletions to multiple ‘charging’ steps with viable acceptances. We also use fractional exchanges for water molecules. This computationally intense method avoids simulating the external bath and overcomes the inability of pseudo grand canonical Molecular Dynamics approaches (with *NPT* bath fixing chemical potentials) to deal with *laterally extended* confinements. Anisotropic pore conditions also prompted the development of a new and efficient iterative algorithm for self-consistent tail correction of cut-off effects.

According to the Gibbs adsorption isotherm, depletion of salt inside the pore reduces its wettability and vice versa. Our newly developed method shows exclusion of solvated ions from the hydration layers at low-permittivity walls, and unexpected enrichment in the core of the pores relative to the bath. Distribution of ions attracted to the core is correlated with charge-layering due to the orientational order of confined water. The combined result is depletion of ions in the pores of widths below ~2nm, and excess at bigger widths. A striking consequence of the varying sign of excess salt concentration at different pore widths is that the wetting free energy of the confinement walls can either increase or decrease due to the presence of the salt. We confirm this prediction by explicit pressure tensor calculations of the wetting free energy.

Field-assisted electrolyte uptake. Field-induced nanopore wetting by electrolytes underlies diverse applications from surface energy storage to hydrophobic valves and the control of membrane permeability. We use an extension of the Expanded Ensemble GCMC methodology discussed in 1.1 to study thermodynamic effects of electric field spanning semi-infinite pores in implicit equilibrium with an electrolyte bath. Under these circumstances, electrowetting is especially effective as it involves migration of solution from the unperturbed reservoir *into* the region exposed to the field. Under applied voltage, coupling/decoupling processes of fractional particles in Expanded Ensemble include additional interactions of exchanged salt and water molecules with electric field. At up to 0.7 V potential differences across the pores, U_f (Fig. 1), the field consistently enhances the packing of absorbed solution. It also leads to a moderate increase in confined salt molality relative to bulk solution. The presence of up to 6 molal salt solution shows moderate effects on the field induced increase in

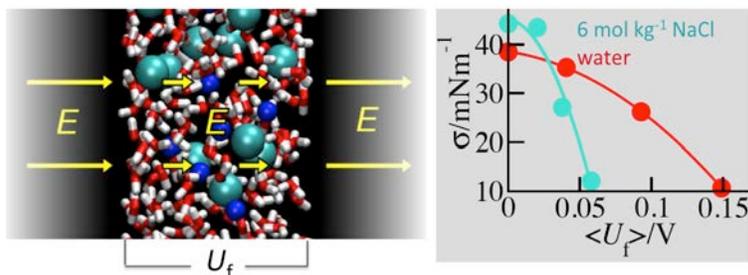


Fig. 1 *Left:* electrolyte film in 1.64 nm wide pore under applied electric field (E). The pore is in equilibrium with bulk 6 mol kg⁻¹ NaCl solution. *Right:* wetting free energy of pore walls as function of voltage across electrolyte film (turquoise) in comparison to deionized system in equilibrium with an aqueous bath. (red).

confinement pressure and reduction in surface free energy. At all conditions, including extreme salt concentrations, the field effect on electrostriction, internal pressure, and reduction in the wetting free energy retains the characteristic quadratic Lippmann-like dependence on the strength of applied field (Fig. 1) in analogy to pure dielectrics. In wide pores and strong electric fields, the concentration of confined salt can exceed the solubility limit of the bulk phase, however, in view of partial demixing of confined ions, no precipitation is indicated during accessible simulation times in these cases. Our newly developed method provides estimates of the material's electric capacitance (per unit volume), confirming a rapid increase with the porosity, and establishes its dependence on the concentration in the electrolyte bath while confined concentration *varies* with the field.

FUTURE PLANS

Our explorations of electrolyte absorption in external field envisage new and demanding methodological developments. A key step forward is to explore the effect of non-additive interactions, in particular the inclusion of molecular polarizabilities (using the Gaussian charge on a spring force fields for water and ions) in our fractional-exchange GCMC setting. Investigation of multi-body interactions is essential in high-concentration regime of interest in surface energy absorption. In another development, we plan to enable a generalization of the Expanded Ensemble GCMC for solutions permeating porous electrodes at *fixed inter-electrode voltage*, a demanding computational task not yet accomplished in *open* systems with molecular solvent electrolyte. In parallel with studies of transient wetting and permeation assisted by electric field, we initiated a study of permanent control using ionic surface functionalization. This approach will provide guidance for robust control of nanoparticle interactions and dispersibility. A central goal is to determine the effectiveness of charge patterning at varied particle geometries and electrolyte content in the dispersion.

Publications Acknowledging DOE Award DE-SC-0004406 from 2012 – 2015:

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Theoretical studies of chemical reactions related to the formation and growth of polycyclic aromatic hydrocarbons and molecular properties of their key intermediates

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Program Scope

In this project, we investigate complex chemical mechanisms of PAH formation, growth, and oxidation via theoretical studies of their critical elementary reactions. Our primary objectives include (i) to unravel reaction mechanisms through detailed, accurate, and reliable calculations of pertinent potential energy surfaces (PESs); (ii) to compute rate constants for individual reaction steps and total absolute reaction rate constants and product branching ratios depending on reaction conditions, such as collision energy or temperature and pressure; (iii) to characterize molecular, energetic, and spectroscopic parameters of various possible reaction intermediates and products including their enthalpies of formation, geometric structure, vibrational frequencies and rotational constants, as well as photoionization and photoexcitation spectra. To achieve these goals, we employ chemically accurate density functional and ab initio calculations (using CCSD(T)/CBS, G3, and explicitly correlated methods) of the PESs of these reactions which are then utilized for statistical (TST and RRKM/Master Equation) computations of absolute reaction rate constants and product branching ratios.

Recent Progress

Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene. In collaboration with S. Klippenstein and Y. Georgievskii (ANL) and A. Jasper (Sandia), we performed RRKM-Master Equation calculations to evaluate temperature- and pressure-dependent rate coefficients for acetylene addition reactions to the C_6H_5 , $C_6H_4C_2H$, $C_6H_5C_2H_2$, and $C_6H_4C_2H_3$ radicals. These calculations indicate a strong pressure dependence for the role of various Hydrogen-Abstraction- C_2H_2 -Addition (HACA) sequences for the formation of naphthalene from benzene. At atmospheric and lower pressures the C_8H_7 radicals, $C_6H_4C_2H_3$ and $C_6H_5C_2H_2$, cannot be stabilized above 1300 K. As a result, both the Bittner-Howard HACA route, in which a second acetylene molecule adds to $C_6H_5C_2H_2$, and the modified Frenklach route, where a second C_2H_2 adds to the aromatic ring of $C_6H_4C_2H_3$ obtained by internal hydrogen abstraction, are unrealistic under low pressure flame conditions. At the higher pressures of some practical combustion devices (e.g., 100 atm) these routes may be operative. Naphthalene is predicted to be the main product of the $C_6H_5C_2H_2 + C_2H_2$ and $C_6H_4C_2H_3 + C_2H_2$ reactions in the entire 500-2500 K temperature range independent of pressure (ignoring the issues related to the instability of C_8H_7 species). Frenklach's original HACA route, where the second C_2H_2 molecule adds to the aromatic ring activated by intermolecular H abstraction from C_8H_6 , involves the $C_6H_4C_2H + C_2H_2$ reaction, which is shown to predominantly form dehydrogenated species with a naphthalene core (naphthyl radicals or naphthynes) at $T < 2000$ K and diethynylbenzene at higher temperatures (see Figure 1). The temperature and pressure dependence of rate coefficients for the various reaction channels has been analyzed and the results clearly demonstrate the importance of pressure for the reaction outcome. Thus, one must use caution when using low-pressure flame studies to validate PAH mechanisms for use in broader ranges of pressure.

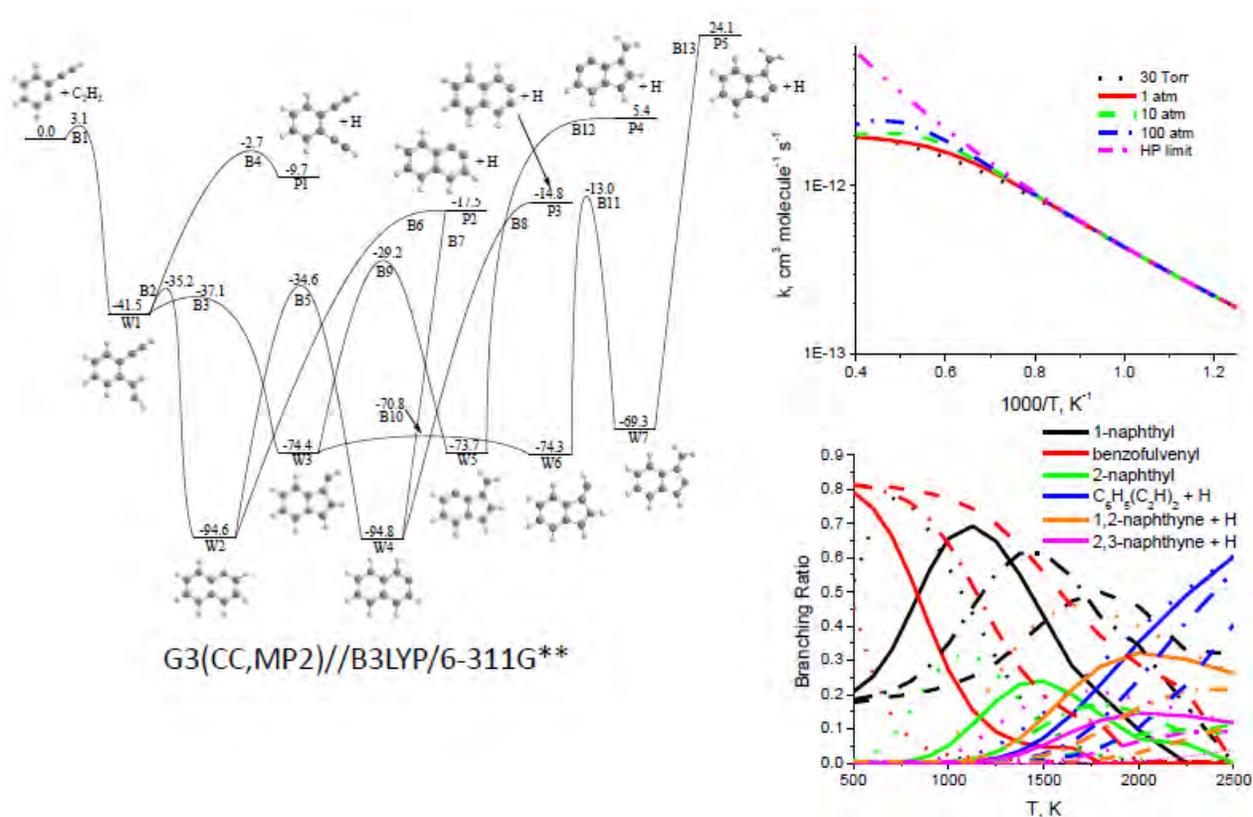


Figure 1. Potential energy diagram, total reaction rate coefficients, and product branching ratios in the $C_6H_4C_2H + C_2H_2$ reaction. Calculated branching ratios are shown at pressures of 30 Torr (dotted), 1 (solid), 10 (dashed-dotted), and 100 atm (dashed).

Formation of resonantly stabilized free radicals via the reactions of atomic carbon, dicarbon, and tricarbon with unsaturated hydrocarbons. Together with R. Kaiser from the University of Hawaii, we completed a comprehensive review of our and literature results on the formation of resonantly stabilized free hydrocarbon radicals (RSFRs), which play an important role in the growth of polycyclic aromatic hydrocarbons and ultimately in the production of soot and carbonaceous particles in combustion flames. We overviewed extensive theoretical ab initio/RRKM and experimental crossed molecular beams studies in the last two decades of the reactions of atomic carbon, $C(^3P)$, dicarbon, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, and tricarbon, $C_3(X^1\Sigma_g^+)$, with unsaturated hydrocarbons, from acetylene to benzene, showing that the reactions form various types of RSFR via $C_n(n = 1-3)$ -for-H, C_n -for- CH_3 , and C_n -for- C_xH_y exchange mechanisms. The RSFRs produced in these reactions include C_xH ($x = 1-8$), propargyl (C_3H_3) and its substituted analogs, 2,4-pentadiynyl-1 (*i*- C_5H_3) and 1,4-pentadiynyl-3 (*n*- C_5H_3) together with their methyl substituted counterparts, iii) butatrienyl (*i*- C_4H_3) and its substituted analogs, and hexenediynyl, *i*- C_6H_3 , as well as cyclic five-, six-, and seven-member ring radicals including aromatic phenyl, benzyl, and tolyls (see Table 1). The reactions of atomic carbon and dicarbon proceed by barrierless additions to double, triple, or „aromatic“ bonds of the unsaturated hydrocarbons, form highly exothermic products, and are fast even at very low temperatures, whereas the reactions of singlet tricarbon require high barriers to be overcome, often leading to endothermic products, and can occur only at high temperatures. We summarized typical reaction mechanisms for small carbon species with unsaturated hydrocarbons and described implications of the considered reactions in combustion chemistry and astrochemistry.

Table 1. Summary of the products of the C/C₂/C₃ reactions with unsaturated hydrocarbons.

	C	C ₂	C ₃
C ₂ H ₂	C ₃ H	C ₄ H	C ₅ H
C ₂ H ₄	C ₃ H ₃	C ₄ H ₃	C ₅ H ₃
C ₃ H ₄ (CH ₃ CCH)	C ₄ H ₃	C ₅ H ₃	C ₆ H ₃
C ₃ H ₄ (H ₂ CCCH ₂)	C ₄ H ₃	C ₅ H ₃	C ₆ H ₃
C ₃ H ₆	C ₄ H ₅	C ₅ H ₅	
C ₄ H ₂	C ₅ H	C ₆ H	C ₇ H
C ₄ H ₄	C ₅ H ₃	C ₆ H ₃	
C ₄ H ₆ (C ₂ H ₃ C ₂ H ₃)	C ₅ H ₅	C ₆ H ₅	
C ₄ H ₆ (CH ₃ CCCH ₃)	C ₅ H ₅	C ₆ H ₅	
C ₄ H ₆ (H ₂ CCCH(CH ₃))	C ₅ H ₅	C ₆ H ₅	
C ₄ H ₆ (HCCC ₂ H ₅)	C ₅ H ₅	C ₆ H ₅	
C ₅ H ₈ (C ₂ H ₃ C(CH ₃)CH ₂)	C ₆ H ₇	C ₇ H ₇	
C ₆ H ₆	C ₇ H ₅	C ₈ H ₅	C ₉ H ₅

Theoretical studies of the mechanism and product branching ratios of the reactions of CH with C₃H₈ and C₃H₆. The C₄H₉ and C₄H₇ potential energy surfaces accessed by the reactions of methylidyne radical with propane and propene have been studied at the CCSD(T)/CBS//B3LYP/6-311G(d,p) level of theory. The computed relative energies and molecular parameters were utilized to calculate collision-energy-dependent unimolecular rate constants at the zero-pressure limit and to evaluate the product branching ratios in the CH + C₃H₈/C₃H₆ reactions under single-collision conditions. The CH + C₃H₈ reaction was shown to mostly produce C₂H₄ + C₂H₅ and C₃H₆ + CH₃, and up to 14% of various C₄H₈ isomers + H. The product branching ratios are sensitive to the initial reaction C₄H₉ adduct formed in the entrance channels via barrierless insertion of the CH radical into the terminal and middle C-H bonds of propane or, possibly, into the single C-C bonds. The CH + C₃H₈ reaction is not likely to lead to the direct growth of the carbon skeleton to C₄ because C-C bond cleavages in C₄H₉ radicals are generally more preferable than C-H bond cleavages. Product branching ratios in the CH + C₃H₆ reaction were found to strongly depend on the initial chemically activated C₄H₇ complex formed in a barrierless entrance channel. If the reaction is initiated via either CH addition to the double bond in propene (which is the most likely scenario according to the literature experimental data) or CH insertions into the terminal sp² C-H or single C-C bonds, then 1,3-butadiene + H are predicted to be the dominant products, ethene + C₂H₃ radical are minor but non-negligible products, and a small amount of 1,2-butadiene + H is also produced. If CH inserts into a C-H bond in the CH₃ group, then the major reaction products are predicted to be C₂H₄ + C₂H₃ and 1,3-butadiene + H. CH insertion into the middle sp² C-H bond predominantly results in the formation of allene + CH₃. The theoretical results closely agree with experiment and the observed quantitative deviations were rationalized in terms of dynamical factors. Overall, the calculations confirmed that the CH + C₃H₆ reaction is a major source of 1,3-butadiene at low *T/p* conditions.

Future Plans

The main goal of this project will continue to be unraveling reaction mechanisms and generating reliable temperature- and pressure-dependent rate constants for various processes in PAH formation, growth, and oxidation. To accomplish this goal we will convert PESs of the pertinent reactions, which are either available in the literature from our previous studies or from

other groups or will be computed within the project, into pressure- and temperature-dependent rate constants using the eigenvalue-based RRKM-ME code developed by Klippenstein and co-workers. In the new three-year project period we will focus on the following systems: 1) all possible reactions and pathways leading to the formation of two-ring PAHs, naphthalene, indene, and their radicals; 2) reactions producing three-ring PAHs, such as anthracene, phenanthrene, and acenaphthalene, including HACA routes and the reactions of naphthyl and indenyl radicals with C_3H_4 and C_4H_4 ; 3) oxidation of six- and five-member rings in aromatic and PAH radicals such as phenanthryl, anthracyl, cyclopentadienyl, indenyl, and acenaphthyl. The rate constants will be included in the latest combustion models in collaboration with S. Klippenstein, L. Harding, Y. Georgievskii, R. Sivaramakrishnan, and J. Miller. In the meantime, we will continue our collaborations with R. Kaiser's and M. Ahmed's groups on the studies of combustion-relevant bimolecular reactions in crossed beams and in the pyrolytic reactor at LBNL, and with A. Suits and R. Tranter on the roaming dynamics of Cl reactions with hydrocarbons.

Grant Number and Grant Title

DE-FG02-04ER15570 Theoretical studies of chemical reactions related to the formation and growth of polycyclic aromatic hydrocarbons and molecular properties of their key intermediates

Postdoc: Vadim. V. Kislov

Students: Joao Marcelo Ribeiro, Daniel Belisario-Lara

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Activity Coefficients and Solubilities of Aqueous Electrolytes from Molecular Models

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Presentation Abstract

In this presentation, I plan to review computational methodologies for accurate determination of chemical potentials, activity coefficients, and solubilities for atomistically detailed, 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. Inclusion of polarizability improves the performance of the models, but the temperature dependence still does not match experiments. In addition, there are still-unresolved discrepancies between solubilities obtained from direct interfacial simulations and from thermodynamic integration calculations of the crystal free energies. These results point to the need for improved water and ion models, as well as for a need for development of reliable computational methodologies for ionic crystal solubility calculations.

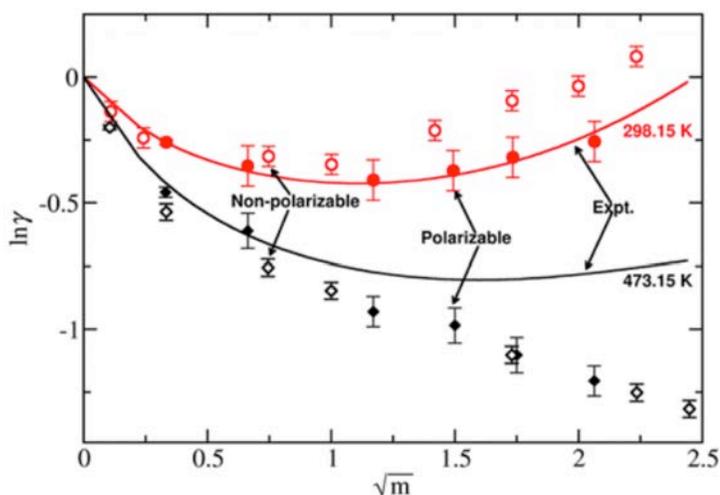


Fig. 1. Natural logarithm of the mean activity coefficient $\ln \gamma$ of NaCl versus salt molality at different temperatures from polarizable and non-polarizable models [12].

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

PI: Athanassios Z. Panagiotopoulos

Postdocs (past 3 years): Dr. Hao Jiang (PhD, U. of Wyoming, partial support from the present award); Dr. Zoltan Mester (PhD, U.C. Santa Barbara, 2014-15).

PhD Students (past 3 years): Kevin Daly (graduated in Nov. 2014, now with ExxonMobil); Andrew Santos (Hispanic-American); Jeffrey Young.

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 CO₂ 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

In the past two years, a major area of work under the project has been the development of efficient methods for obtaining activity and osmotic coefficients in electrolyte solutions [references 4, 7, and 8 in the Publications List on the next page]. We used gradually insertions of an ion pair and water molecule into the solution to obtain the activity and osmotic coefficients, respectively. Several common non-polarizable water and ion models have been examined in the simulations, as well as some recently proposed polarizable models. While the majority of model combinations predict the correct trends in mean ionic activity coefficients, most fail to follow the experimental trend at high salt concentrations, as seen in Fig. 1, with the exception of polarizable models. The solubility predictions also suffer from inaccuracies, with all models underpredicting the experimental values, some by large factors. The temperature dependence of the activity coefficients and solubilities also does not match experiments, even for the polarizable models.

In the broad area of potential model development, the need to obtain accurate polarizable models was identified from our work on electrolyte solutions. Such models would be particularly important for describing phase behavior involving aqueous brines over broad ranges of temperature and pressure. Non-polarizable models for a divalent salt (CaCl₂) were tested in [9] with respect to their ability to model the H₂O-CO₂ system important for geophysical and carbon sequestration applications. A new set of potential models for CO₂ based on Gaussian charge distributions rather than point charges was developed in [11] to provide compatibility with promising recent models for water that were tested in [8].

Finally, in the area of surfactant self-assembly, we completed a detailed study of methods to obtain the critical micelle concentration, and the dependence of free surfactant concentration on total surfactant loading in [10]. We found that correcting for effects of the excluded volume because of existing aggregates leads to a nearly constant free surfactant concentration for non-ionic systems, in sharp contrast to our earlier findings for ionic surfactants [5].

3 FUTURE PLANS

We plan to continue studies of activity coefficients in aqueous electrolyte solutions, following the methodology developed in [4]. There is also a need for resolution of discrepancies between solubilities from direct interfacial simulations on one hand, and from thermodynamic integration calculations of the crystal free energies on the other. These may be due to finite-size or interface electrification effects. In the area of ionic surfactant self-assembly, we plan to investigate force field development that addresses limitations of existing models seen in our earlier work.

4 PUBLICATIONS FROM THIS AWARD (SINCE 2014)

1. K. B. Daly, J. B. Benziger, A. Z. Panagiotopoulos, and P. G. Debenedetti, "Molecular Dynamics Simulations of Water Permeation across Nafion Membrane Interfaces," *J. Phys. Chem. B*, **118**: 8798-8807 (2014).
2. K. B. Daly, A. Z. Panagiotopoulos, P. G. Debenedetti, and J. B. Benziger "Viscosity of Nafion oligomers as a function of hydration and counterion type: a molecular dynamics study," *J. Phys. Chem. B*, **118**:13981–91 (2014).
3. G. A. Orozco, O. A. Moulτος, H. Jiang, I. G. Economou, and A. Z. Panagiotopoulos "Molecular Simulation of Thermodynamic and Transport Properties for the H₂O + NaCl System," *J. Chem. Phys.*, **141**: 234507, 8 pp (2014).
4. Z. Mester and A. Z. Panagiotopoulos, "Mean ionic activity coefficients in aqueous NaCl solutions from molecular dynamics simulations," *J. Chem. Phys.*, **142**: 044507, 10 pp (2015).
5. A. Jusufi and A. Z. Panagiotopoulos, "Explicit- and Implicit-Solvent Simulations of Micellization in Surfactant Solutions," Invited Feature Article, *Langmuir* **31**: 3283-92 (2015).
6. A. Hemmen, A. Z. Panagiotopoulos, J. Gross, "Grand canonical Monte Carlo simulations guided by an analytic equation of state – Transferable anisotropic Mie-potentials for ethers," *J. Phys. Chem. B* **119**: 7087-99 (2015).
7. Z. Mester and A. Z. Panagiotopoulos, "Temperature-Dependent Solubilities and Mean Ionic Activity Coefficients of Alkali Halides in Aqueous Solutions from Molecular Dynamics Simulations," *J. Chem. Phys.* **143**: 044505, 10 pp (2015).
8. H. Jiang, Z. Mester, O. A. Moulτος, I. G. Economou, and A. Z. Panagiotopoulos, "Thermodynamic and Transport Properties of H₂O+NaCl from Polarizable Force Fields," *J. Chem. Theory Comput.* **11**: 3802-3810 (2015).
9. E. Tsai, H. Jiang, and A. Z. Panagiotopoulos, "Monte Carlo Simulations of H₂O-CaCl₂ and H₂O-CaCl₂-CO₂ Mixtures," *Fluid Phase Equil.* **407**: 262-68 (2016).
10. A. P. Santos and A. Z. Panagiotopoulos, "Determination of the critical micelle concentration in simulations of surfactant systems," *J. Chem. Phys.* **144**: 044709, 10 pp (2016).
11. H. Jiang, O. A. Moulτος, I. G. Economou, and A. Z. Panagiotopoulos, "Gaussian-Charge Polarizable and Non-Polarizable Models for CO₂," *J. Phys. Chem. B* **120**: 984-994 (2016).

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

We have significantly expanded [1,2] our development of theory methods that can describe arrays

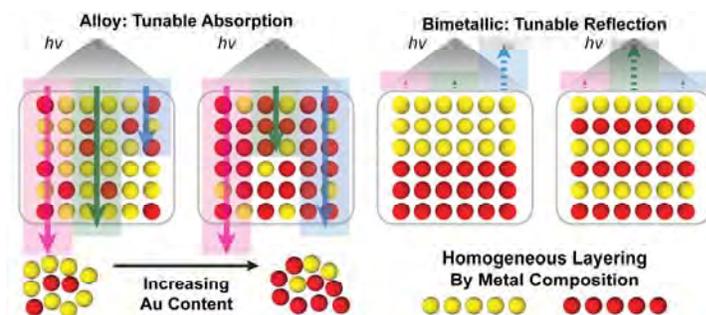


Figure 1: Controlling optical properties using superlattice metal films and compositionally tuned structures with silver and gold nanoparticles. Alloying (random placement) of Ag or Au building blocks (on the atomic or nanoscopic scale) can be used to linearly change absorption (and thus color) in a way that is distinct from atomic-scale alloying [Left]. Bimetallic layered structures, where different metal building blocks are ordered (here by homogeneous layering) can be used to precisely control reflectivity [Right].

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 Chad Mirkin at Northwestern, in collaboration with Schatz, and there is related DOE work on two dimensional superlattices that Schatz is pursuing with Teri Odom. 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.[3] In work completed recently [2] we have developed Fresnel-based theory

methods, as well as methods that involved coupled multipoles and extensions of the discrete dipole approximation (DDA) method to describe the reflection of light from films that are composed of superlattice material with a mixture of silver and gold nanoparticles. Fig. 1 shows a schematic of the structures that are being considered, in which the superlattices can either involve random

mixtures of particles with control of silver/gold ratio, or they can involve layered structures that include the possibility of composition gradients. Fig. 2 shows the emergence of asymmetric reflectivity for the case where the layer is designed with a gradient index.

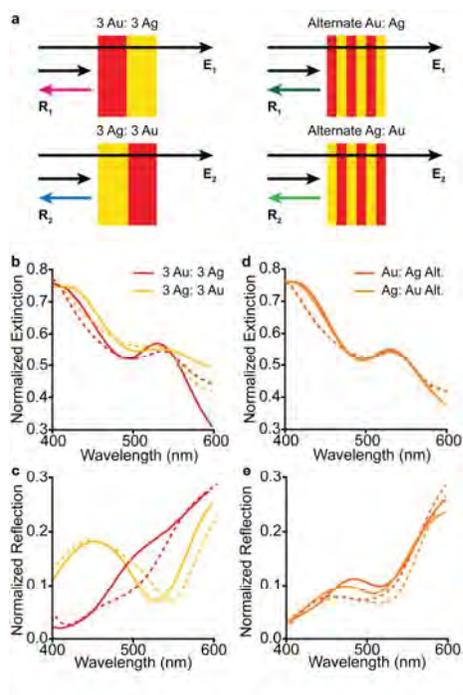


Figure. 2 Asymmetric reflectivity in bimetallic plasmonic assemblies. a). Scheme depicting asymmetric reflectivity (and symmetric extinction) in bimetallic assemblies which depends on the orientation of the assembly to incident light. Extinction (b) and reflection (c) of bimetallic assemblies (showing comparison of Fresnel theory and experiment) where the layers are segregated by composition (*i.e.* 3 layers of Ag nanoparticles on 3 layers of Au nanoparticles, and its inverse). Extinction (d) and reflection (e) of bimetallic assemblies where Ag nanoparticle layers and Au nanoparticles layers alternate.

In other work, we continue to develop electronic structure models of plasmon excitation in silver clusters.[4] Our most recent work has determined the distribution of hot electrons that are produced in plasmon excitation, which is an important property for plasmon-enhanced chemistry. In related work, we have extended our electronic structure methods for describing plasmon enhanced spectroscopic properties [5] to include the effects of averaging over molecule orientations for molecules adsorbed onto surfaces, and to include for the electrodynamics of dimers of nanoparticles.[6] In this approach DFT calculations are used to calculate the chemical contribution to the SERS enhancement factor and the results are combined with a coupled QM/electrodynamics approach for determining electromagnetic enhancements. For nanoparticle dimers involving spherical nanoparticles, we have now implemented a generalized Mie theory approach [7] to calculate the surface-averaged local field enhancements, and we continue to develop real-time TDDFT methods for describing plasmon-driven electron transfer between silver and gold clusters and adsorbed molecules.[8] A number of applications of these approaches have been done in collaboration with the Van Duyne group at Northwestern, including recent work attempting to extend our predictions concerning the exciting plasmonic properties of aluminum nanoparticles [9] to SERS.

In a new project, we have developed a reverse nonequilibrium molecular dynamics method (REMD) in collaboration with Dan Gezelter's group at Notre Dame to describe the evolution of thermal energy following photoexcitation of semiconductor and metal nanoparticles.[8] This method examines the flow of thermal energy starting a few ps after photoexcitation, wherein the nanoparticle can be described by a hot thermal distribution of electrons and phonons, and there is a bottleneck to transport at the nanoparticle interface or in the low conductivity solvent that surrounds the nanoparticles. Our results have provided the first estimates of interfacial thermal conductivity parameters that can be used to interpret recent experimental studies of this effect. The results are important to the thermal stability

of nanoparticles and to the design of ligand/solvent combinations that will reduce the thermal bottlenecks.

Finally, in a new project [11] we discovered that gradient terms in the exchange-correlation functional can be neglected in the TDDFT determination of the excited states of molecular systems. Long range correction to the density functional is important, but a local density treatment of short range effects leads to excited state energies that are in quantitative agreement with theories that include gradient effects.

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 light transmission through gradient films as there is suggestions from unrelated studies that this class of material might be capable of showing asymmetric transmission properties that are of interest in making optical rectifiers. We are also developing theories that can describe dye emission in the superlattice structures, including an exciton Hamiltonian description of the dye, and a Liouville equation description of the time evolution. This will be of relevance for describing both 2D and 3D lattices, including laser-based work that we are doing with the Odom group and plasmon-enhanced fluorescence studies with the Mirkin group.

Our studies of cluster models of plasmon excitation are being extended to the use of semi-empirical (INDO-based) models for the electronic structure of the plasmon excited state. INDO provides an opportunity for describing excited state dynamics that is not impeded by the self-interaction errors associated with the use of TDDFT. A problem in the past has been that there have not been semiempirical parameters that realistically describe the optical properties of metal systems, however very recently we have made progress in this area, and we are now confident that we can use the semiempirical methods to describe plasmon excitation with and without ligands on the nanoclusters. This capability promises to provide a new generation of work related to understanding hot electron effects in charge transfer processes in plasmonic systems.

Grant Numbers and Grant Titles

Theory work in the work described above was supported by: DOE DE-SC0004752 or DE-FG02-10ER16153 (these two numbers refer to the same grant) **Surface Plasmon Enhanced Chemistry**

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

1. Postdocs: Nicolas Large (12), Dhara Trevidi (6)
2. Students: Lindsey Madison (12,p), Adam Ashwell (12), Mike Ross (12,p)

References to DOE supported work (note that experimental collaborators are supported by other grants):

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Donald G. Truhlar

Variational Transition State Theory (-2016)

Nonadiabatic Photochemistry (2016-)

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Program scope. Variational transition state theory

This project involves the development of variational transition state theory (VTST) for gas-phase reactions, including optimized multidimensional tunneling (OMT) contributions and the application of this theory to gas-phase reactions with a special emphasis on developing reaction rate theory in directions that are important for applications to combustion. The development of VTST/OMT as a useful computational tool for combustion kinetics has six objectives: (i) developing and applying new methods of electronic structure calculations for the input potential energy surface, which is an implicit surface defined by an electronic structure model chemistry; (ii) direct dynamics methods to interface reaction-path and reaction-swath dynamics calculations, including multidimensional tunneling, with electronic structure theory; (iii) methods to treat vibrational anharmonicity and vibration-rotation coupling, including multistructural anharmonicity, torsional potential anharmonicity, and different high-frequency anharmonicity at transition states and reactants; (iv) development of the POLYRATE computer program and its various RATE interfaces to electronic structure packages for practical applications of the theory to various classes of reactions and transition states; and (v) applications to specific reactions, with special emphasis on combustion reactions and reactions that provide good test cases for methods needed to study combustion reactions.

Recent accomplishments. Variational transition state theory

Our recent work involves the application of methods developed on this grant to the calculation of reaction rates for processes important in combustion. We calculated rate constants for the several radical reactions with biofuels, in particular abstraction of H from isobutanol and 2-butanol by OH and abstraction of H from 2-butanol and tert-butanol by HO₂. An especially important aspect of these calculations is that we predicted the site dependence of the abstraction, which is very hard to measure experimentally, although it is critical for combustion mechanism modeling. In the process of these applications, we developed new methods for vibrational anharmonicity and path-dependent tunneling, and we elucidated their roles.

Most recently, we extended variational transition state theory to treat pressure-dependent reaction rates. The method combines microcanonical variational transition state theory in the high-pressure limit with a system-specific quantum RRR formalism and a modified strong collision approximation for treating the pressure effect. The method is applicable to both chemical activation and thermally activated unimolecular reactions. The first application, to the chemical activation mechanism for reaction of H with the fuel-constituent toluene, was very successful. The method is also being applied to unimolecular reactions.

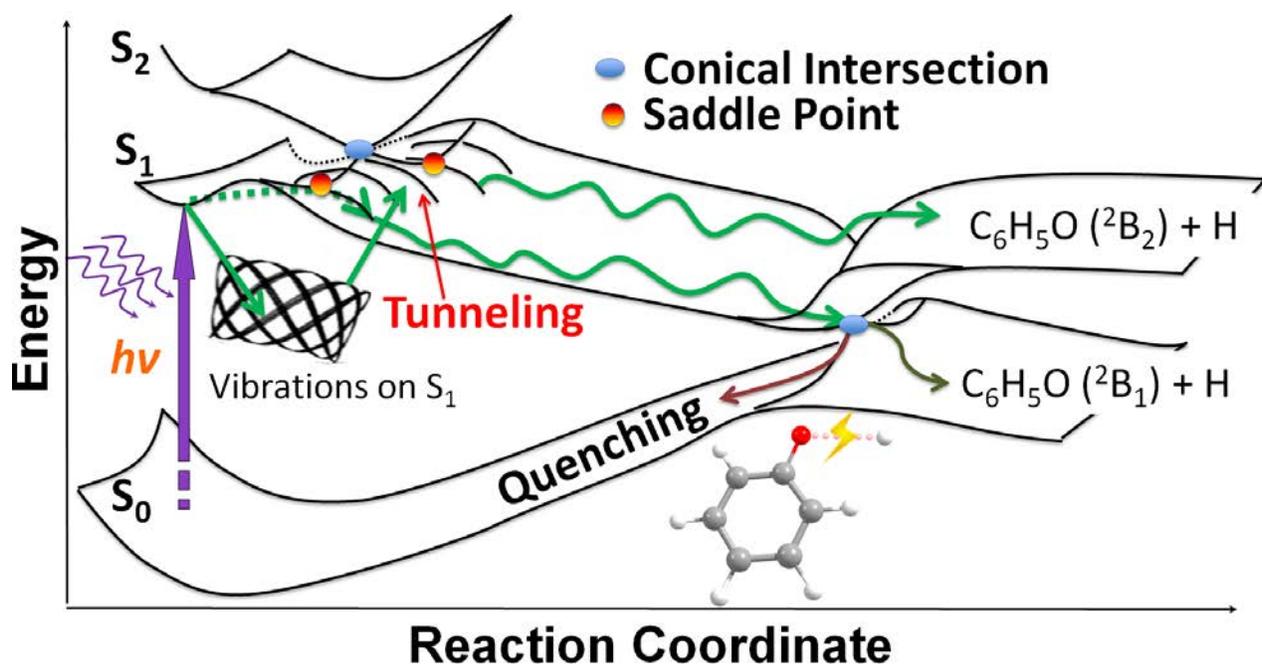


Figure from “Full-Dimensional Potentials and State Couplings and Multidimensional Tunneling Calculations for the Photodissociation of Phenol,” K. R. Yang, X. Xu, J. Zheng, and D. G. Truhlar, *Chemical Science* **5**, 4661-4680 (2014). [dx.doi.org/10.1039/c4sc01967a](https://doi.org/10.1039/c4sc01967a). This work was supported in part by U.S. Department of Energy, Office of Basic Energy Sciences, under SciDAC grant no. DE-SC0008666.

Program scope. Nonadiabatic photochemistry

This project, in collaboration with Hua Guo and David Yarkony, involves the study of electronically nonadiabatic chemical dynamics from first principles. The existing theoretical tools for investigating such phenomena are not sufficient, and this project will develop new and more effective theoretical methods to understand nonadiabatic effects in reaction dynamics. The method development at the University of Minnesota includes electronic structure theory, efficient analytic representation of multi-dimensional coupled diabatic potential energy surfaces, and semiclassical dynamical methods that are capable of handling quantum effects such as coherence, decoherence, and tunneling. The methods developed will be applied to several important prototypes for nonadiabatic dynamics.

Future plans. Nonadiabatic photochemistry

The methods developed will be applied to several important prototypes for nonadiabatic dynamics, including the reaction between H_2 and electronically excited OH, the photodissociation of hydroxymethyl, and the photodissociation of substituted phenols. These systems represent a grand challenge for modeling nonadiabatic systems, and the reactions are of interest not only in their own right but also because they serve as test beds and prototypes for developing the theory of electronically nonadiabatic processes in a way that will be more broadly useful for combustion chemistry, environmental chemistry, and new energy technologies. involving the conversion of solar energy into electrical energy and fuel.

Grant titles and award numbers

Variational Transition State Theory, DE-FG02-86ER13579, ends 2016.

Nonadiabatic Photochemistry, number to be assigned, recommended for funding for start in 2016.

Collaborators

The Nonadiabatic Photochemistry project is a collaboration with Hua Guo (University of New Mexico, PI) and David Yarkony (Johns Hopkins University).

Recent and current postdoctoral associates and research associates

Miho Isegawa, Hannah Leverentz, Steven Mielke, Rubén Meana-Pañeda, Gbenga Oyedepo, Bo Wang, Xuefei Xu, and Jingjing Zheng

Recent and current graduate students

Junwei Lucas Bao, Patrawan Sripa, and Ke R. Yang

Ten most recent publications acknowledging award DE-FG02-86ER13579

"Anchor Points Reactive Potential for Bond-Breaking Reactions," K. R. Yang, X. Xu, and D. G. Truhlar, *Journal of Chemical Theory and Computation* **10**, 924-933 (2014).
[dx.doi.org/10.1021/ct401074s](https://doi.org/10.1021/ct401074s)

"Prediction of Experimentally Unavailable Product Branching Ratios for Biofuel Combustion: The Role of Anharmonicity," J. Zheng, R. Meana-Pañeda, and D. G. Truhlar, *Journal of the American Chemical Society* **136**, 5150-5160 (2014). [dx.doi.org/10.1021/ja5011288](https://doi.org/10.1021/ja5011288).
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"Quantum Mechanical Fragment Methods Based on Partitioning Atoms or Partitioning Coordinates," B. Wang, K. R. Yang, X. Xu, M. Isegawa, H. R. Leverentz, and D. G. Truhlar, *Accounts of Chemical Research* **47**, 2731-2738 (2014). (Special Issue: Beyond QM/MM: Fragment Quantum Mechanical Methods) [dx.doi.org/10.1021/ar500068a](https://doi.org/10.1021/ar500068a)

"Zero-Point Energy, Tunneling, and Vibrational Adiabaticity in the $\text{Mu} + \text{H}_2$ Reaction," S. L. Mielke, B. C. Garrett, D. G. Fleming, and D. G. Truhlar, *Molecular Physics* **113**, 160-175 (2014). [dx.doi.org/10.1080/00268976.2014.951416](https://doi.org/10.1080/00268976.2014.951416)

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- “Multi-Path Variational Transition State Theory for Chiral Molecules: The Site-Dependent Kinetics for Abstraction of Hydrogen from Hydroperoxyl Radical, Analysis of Hydrogen Bonding in the Transition State, and Dramatic Temperature Dependence of the Activation Energy,” J. L. Bao, R. Meana-Pañeda, and D. G. Truhlar, *Chemical Science* **6**, 5866-5881 (2015). [dx.doi.org/10.1039/C5SC01848J](https://doi.org/10.1039/C5SC01848J)
- “Kinetics of the Hydrogen Abstraction Reaction from 2-Butanol by OH Radical,” J. Zheng, G. Odeyepo, and D. G. Truhlar, *Journal of Physical Chemistry A* **117**, 12182-12192 (2015). [dx.doi.org/10.1021/acs.jpca.5b06121](https://doi.org/10.1021/acs.jpca.5b06121)
(in the special issue “Dynamics of Molecular Collisions XXV – Fifty Years of Chemical Reaction Dynamics”: pubs.acs.org/doi/pdfplus/10.1021/acs.jpca.5b08530)
- “Path-Dependent Variational Effects and Multidimensional Tunneling in Multi-Path Variational Transition State Theory: Rate Constants Calculated for the Reactions of HO₂ with *tert*-Butanol by Including all 46 Paths for Abstraction at C and All Six Paths for Abstraction at O,” J. L. Bao, P. Sripa, and D. G. Truhlar, *Physical Chemistry Chemical Physics* **18**, 1032-1041 (2016). [dx.doi.org/10.1039/c5cp05780a](https://doi.org/10.1039/c5cp05780a)
- "A Whole-Path Importance-Sampling Scheme for Feynman Path Integral Calculations of Absolute Partition Functions and Free Energies," S. L. Mielke and D. G. Truhlar, *Journal of Chemical Physics* **144**, 034110/1-9 (2016). [dx.doi.org/10.1063/1.4939869](https://doi.org/10.1063/1.4939869)
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Feb. 29, 2016