Computational and Theoretical Chemistry PI Meeting

Marriott Washingtonian
Gaithersburg Maryland
21-24 May 2019

FORWARD

This book of abstracts provides a record of the fifth 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, U.S. Department of Energy, and includes invited speakers and participants from the core CTC program, Computational Chemical Science projects, Quantum Information Science Projects, 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.

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

We thank Teresa Crockett, Office of Basic Energy Sciences, and Connie Lansdon, Oak Ridge Institute for Science and Education, for their important contributions to the technical and logistical features of this meeting.

Warmest regards and best of luck to all from the Fundamental Interactions Team!

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

22-May 2019

SHORT AGENDA 2019 CTC PI Meeting
Marriott Washingtonian – Gaithersburg

9751 Washingtonian Boulevard Gaithersburg Maryland 20878 USA
For more information and registration: http://www.orau.gov/ctc2019/
Abstracts: http://science.energy.gov/bes/csgb/principal-investigators-meetings/

21 May	**Travel Day to DC**	
6:30	Dinner on your Own	
22 May 7:00AM	**Breakfast**	**Everyone**
7:45AM	**Welcome**	**Mark Pederson**
8:00	**News from CSGB**	**Bruce Garrett**
8:30 AM	**Quantum Information and Quantum Computation (QC) for strongly correlated (SC) systems (Chair: George Schatz)**	
08:30	**QC Algorithms & Applications for coherent SC chemical systems**	**Sabre Kais**
09:00	**ADAPT-VQE: Adaptive variational algorithm for fermionic QC-simulations**	**Nick Mayhall**
09:30	**Embedding QC in many-body frameworks from coupled-cluster ansatz**	**Karol Kowalski**
10:00	**A primer on quantum computing for the many-body theorist**	**Jim Freericks**
10:30AM	**Coffee**	
	Picturing Magnetic and Spin Effects in Chemistry (Chair: Angela WIlson)	
11:00	**Modeling B-Field effects with variational electronic structure methods**	**Xiaosong Li**
11:30	**Ground & excited-states of functional TM-systems in complex environs**	**Hratchian & Strubbe**
12:00PM	**Working Lunch**	**Everyone**
1:15PM	**CCS Ψ Group: Web Page and Plans**	**Ilja Siepmann**
	Machine Learning (ML) in Chemistry (Chair: Marivi Fernandez-Serra)	
1:30PM	**Summary of Efforts – Here and There**	**M. Fernandez-Serra**
1:45	**Boosting *Ab Initio* Molecular Dynamics (MD) with Machine learning**	**Roberto Car**
2:15	***Ab Initio* ML algorithms for kinetics on amorphous catalysts**	**Marco Caricato**
2:45	**Heterogeneous electrocatalysis surfaces with machine learning**	**Andrew Rappe**
3:15PM	**Coffee**	**Everyone**
	Quantum Chemistry (Chair: Henry Schaefer)	
3:45PM	**A Unified Low-Rank Formulation of Coupled-Cluster Theory**	**Ed Hohenstein**
4:15	**The All Configuration Mean Energy (ACME) MCSCF Method**	**Ron Shepard**
4:45	***Ab Initio* Molecular Dynamics beyond Density-Functional Theory (DFT)**	**Tom Miller**
5:30PM	**Dinner at the Marriott**	
7:00PM- 8:30PM	**Poster Session (Moderated by Mark Pederson)** **Wednesday posters should be on the left-hand side of the board.** Additional posters are welcome but please let MRP know. Your poster can be four feet high and should be no more than four feet wide. Please let MRP know if you would like to have your poster upgraded to a talk if there are cancellations.	**Leszczynski, Liu, Wilson, Medford, Baruah, Jackson, Greeley, Steele, Zgid, Isborn, Kara, Neuscamman, Bryantsev, Kulik, Dunietz, Freericks, Aikens, Goldsmith**

23 May 7:30	**Breakfast**	**Everyone**
	Update on CCS Projects (Chair: Koblar Jackson)	
8:30AM	**ECC: Exascale Computational Catalysis**	**Judit Zádor**
9:00	**Exascale software for heterogeneous & interfacial catalysis**	**Mark Gordon**
9:30	**SPEC**	**Zgid and Hirata**
10:15	**Coffee**	
	Machine Learning (Chair: Zachary Ulissi)	
10:45AM	**Bridging time scales in exascale computing of chemical systems**	**Andrew Peterson**
11:15	**Machine learning for excited-state dynamics**	**James Lewis**
11:45	**Genetic algorithms for rapid molecular materials Screening**	**Geoff Hutchison**
12:15	**Lunch**	
	Density Functional Theory: To correct or not to correct? (Chair: Henry Krakauer)	
1:30PM	**PZ SIC: How wrong for uniform densities and large-Z atoms?**	**B. Santra and J. Perdew**
2:00	**Gapping late 3d transition-metal monoxides with SCAN and SIE**	**Jianwei Sun**
2:30	**FLOSIC: Towards practical self-interaction free DFT**	**Juan Peralta**
3:00	**Coffee**	
	Computational Chemical Sciences (Chair: Adam Willard)	
3:30PM	**NMGC vignettes: Amorphous systems and NQEs**	**C. Colina and N. Ananth**
4:15	**Excited-state phenomena in TM-oxide clusters and nanocrystals**	**Serdar Ogut**
4:45	**SPARC-X: Quantum at extreme scale – 1st principles reactive dynamics**	**Phanish Suryanarayana**
23 May Evening	**DINNER ON YOUR OWN**	
8:30PM- 10:30PM	**Poster Session (Moderated by Mark Pederson)** Additional posters are welcome but please let MRP know. Thursday posters should be on the right hand side of the board. Your poster can be four feet high and should be no more than four feet wide. Please let MRP know if you would like to have your poster upgraded to a talk if there are cancellations.	**Siepmann, Yethiraj, Panagiotopoulos, Bylaska, Johnson, Wong, Gunina, Khanna, Markland, Barnes, Xantheas, Pavanello, Gavini, Hanwell, Herbert, Bross, Papaconstantopoulos**
24 May 7:00AM	**Breakfast**	
	Quantum Dynamics and Quantum Molecular Dynamics (QMD) (Chair: Kevin Shuford)	
8:00AM	**Toward *ab initio* QMD in dense manifolds of electronic states**	**Benjamin Levine**
8:30	**Light-matter coupling within cavities or plasmonic materials**	**Joe Subotnik**
9:00	**Driven RNG approaches for nearly-degenerate electronic excitations**	**Francesco Evangelista**
9:30	**Realistic simulation of mixed fluids via many-body representation**	**Francesco Paesani**
10:00AM	**Coffee**	
	Non-Adiabatic Processes and Reaction Dynamics (Chair: Richard Dawes)	
11:00AM	**Enhancing rare event sampling in simulations of complex systems**	**Sapna Sarupria**
11:30	**Design principles for efficient & robust exciton & charge migration**	**Seogjoo Jang**
12:00	**Non-adiabatic photo chemistry**	**Truhlar, Yarkony, Guo**
12:30	**Multicomponent quant. chem. methods electrons, nuclei or positrons**	**Sharon Hammes-Schiffer**
13:00	**Final Remarks**	**Mark Pederson**

Understanding Plasmon Decay and Plasmon-Mediated Processes using Electron and Electron-Nuclear Dynamics

Christine M. Aikens

Department of Chemistry, Kansas State University, Manhattan, KS 66506, cmaikens@ksu.edu

Abstract

Plasmonic nanoparticles have the ability to selectively activate specific chemical bonds during photocatalysis and can act as sensitizers in photocatalysts and photovoltaic devices. However, the role that electron dynamics play in these processes is not fully understood. In this work, both electron dynamics and electron-nuclear dynamics are employed to gain a better understanding of electron and energy transfer processes that occur in gold and silver nanoparticles and related systems.

One area of interest is plasmon-mediated photocatalysis, in which excitation of plasmon resonances in nanoparticles leads to specific bond activations. Silver nanoparticles have been shown experimentally to enable photocatalysis of molecules such as O_2, H_2O, and N_2. In our work, we employ a real-time TDDFT approach to examine the electron dynamics in silver nanoparticles both with and without adsorbed molecules. Use of a long-range corrected functional is found to be important for this work, because charge-transfer states are involved in this process. The presence of the silver nanoparticle enhances excitation into the antibonding orbital of N_2 (Figure 1). The symmetry of the nanoparticle-adsorbate system is an important consideration during this process. The energetically preferred end-on bonding of N_2 to the tip of a silver nanowire enables excitation energy transfer between the transverse plasmon resonance of the silver nanowire and the adsorbate. For H_2 adsorbed on a silver nanowire, the transverse plasmon resonance can excite the antibonding orbital of H_2 only if H_2 is adsorbed in a side-on configuration rather than the end-on configuration; in contrast, the longitudinal plasmon resonance can potentially excite the antibonding orbital only if H_2 is adsorbed in the end-on configuration. Recently, we have extended our studies of plasmon-mediated photocatalysis to study N_2 on aluminum clusters. The presence of the adsorbate distinctly affects the time-dependent oscillations of the dipole moment in the direction of the adsorbate, whereas the orthogonal directions are essentially unaffected.

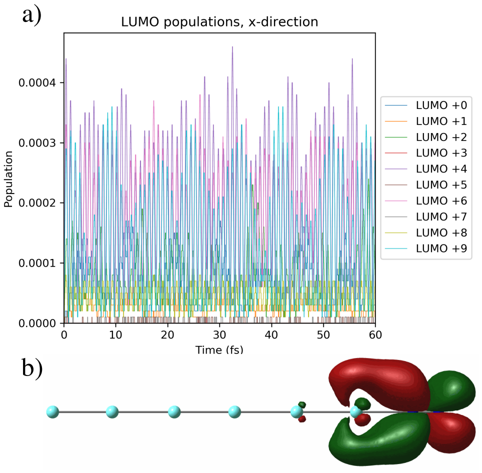


Figure 1. a) Time-dependent RT-TDDFT electron populations of the LUMO+n orbitals of N_2 after excitation of the transverse plasmon resonance of silver wire. b) The antibonding N_2 orbital (LUMO+3). The N_2 molecule is arranged in an end-on fashion along the long axis of the silver wire.

Resonant excitation of the electron dynamics in silver nanoparticles shows that one important mechanism of plasmon decay involves a nonlinear process in which the dipole oscillations corresponding to excitation at a plasmon resonance "decay" into interband transitions. These interband transitions occur at twice the incident frequency, and are greatly affected by the intensity of the incident radiation. The incident field strengths at which this occurs are comparable to similar non-resonant calculations; however, the non-resonant calculations do not lead to the appearance of this nonlinear process. This process most likely originates due to the strong near-fields created by plasmonic excitation.

Acenes (i.e. a class of polycyclic aromatic hydrocarbons composed of linearly-fused benzene rings) are of interest for their applications in organic solar cells and other optoelectronic applications. Our group has previously demonstrated (*J. Phys. Chem. C,* **2013***, 117,* 21466) that these systems exhibit a collective excitation analogous to the plasmon resonances in silver and gold nanoparticles. Thus, understanding the dynamics of this collective excitation can inform investigations into both organic optoelectronics and metal nanoparticle plasmonics. Time-dependent electron-nuclear dynamics have been studied for naphthalene using an Ehrenfest approach. Although most vibrational modes do not lead to significant effects on the "plasmon", two specific vibrational modes have dramatic effects. One vibrational mode leads to plasmon decay on a time scale of approximately 600 fs; the amplitude of the dipolar oscillations decreases drastically over this time period and the corresponding Fourier transform of the dipole moment also decreases to essentially zero (Figure 2). After 600 fs, a slow plasmon revival occurs. A second vibrational mode also leads to plasmon decay (albeit more slowly and less regularly). This vibrational mode has B_{2g} symmetry, which allows the longitudinal "plasmon" mode (B_{1u} symmetry) to couple with a transverse excitation (B_{3u} symmetry). Indeed, the dipole moment of the molecule in the x direction increases, with a corresponding excitation shown in its Fourier transform. In consequence, this vibronic coupling provides a mechanism for plasmon decay.

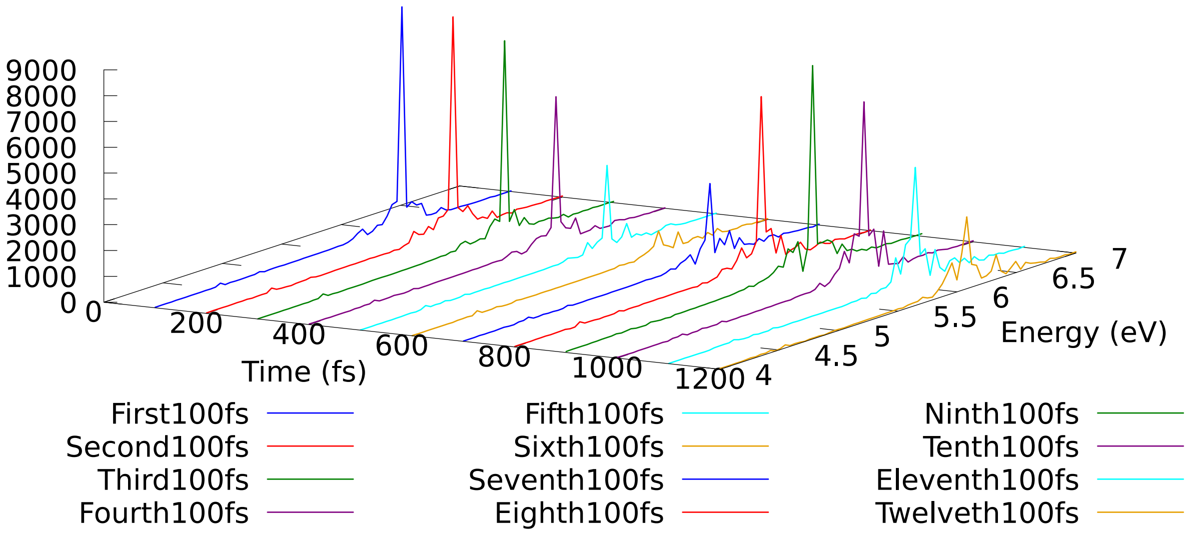


Figure 2. Short-time Fourier transforms of the z dipole moment after electronic excitation of naphthalene in the z direction and vibrational excitation of mode 32 (B_{1u} symmetry), showing the decay and revival of the collective excitation.

Grant Numbers and Grant Titles

DE-SC0012273 Elucidating the Mechanism of Plasmon-Mediated Photocatalysis using Electron Dynamics Calculations

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

Postdoc(s): K. L. Dimuthu M. Weerawardene, Fahri Alkan

Student(s): K. L. Dimuthu M. Weerawardene, Ravithree D. Senanayake, Natalia V. Karimova, Gowri Udayangani, Olivia Hull, Pratima Pandeya

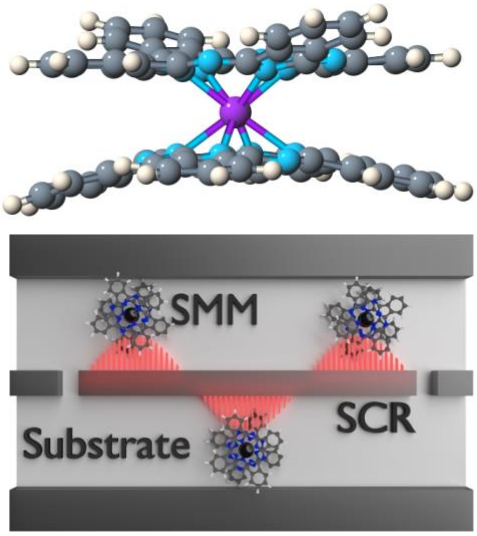
Publications

- Real-time TDDFT Investigation of Optical Absorption in Gold Nanowires. R. D. Senanayake, D. B. Lingerfelt, G. U. Kuda-Singappulige, X. Li, C. M. Aikens, under revision in *Journal of Physical Chemistry C*.
- Electronic and Geometric Structure, Optical Properties, and Excited State Behavior in Atomically-Precise Thiolate-Stabilized Noble Metal Nanoparticles. C. M. Aikens, *Acc. Chem. Res.*, **2018**, *51*, 3065-3073. (Invited article for Special Issue on "Toward Atomic Precision in Nanoscience")
- Theoretical Investigation of Relaxation Dynamics in $Au_{38}(SH)_{24}$ Thiolate-Protected Gold Nanocluster. R. D. Senanayake, E. B. Guidez, A. J. Neukirch, O. V. Prezhdo, C. M. Aikens, *J. Phys. Chem. C*, **2018**, *122*, 16380-16388.
- Anisotropic Polarizability Induced Plasmon Transfer. G. Donati, D. B. Lingerfelt, C. M. Aikens, X. Li, *J. Phys. Chem. C,* **2018**, 122, 10621-10626.
- Molecular Vibration Induced Plasmon Decay. G. Donati, D. B. Lingerfelt, C. M. Aikens, X. Li, *J. Phys. Chem. C*, **2017**, *121*, 15368-15374.
- Photoluminescence Origin of $Au_{38}(SR)_{24}$ and $Au_{22}(SR)_{18}$ Nanoparticles: A Theoretical Perspective. K. L. D. M. Weerawardene, E. B. Guidez, C. M. Aikens, *J. Phys. Chem. C*, **2017**, *121*, 15416-15423.
- Theoretical Investigation of Electron and Nuclear Dynamics in the $[Au_{25}(SH)_{18}]^{-1}$ Thiolate-Protected Gold Nanocluster. R. Senanayake, A. V. Akimov, C. M. Aikens, *J. Phys. Chem. C*, **2017**, *121*, 10653-10662. (Special Issue for ISSPIC XVIII: International Symposium on Small Particles and Inorganic Clusters 2016). http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.6b09731
- Theoretical Insights into the Origin of Photoluminescence of $Au_{25}(SR)_{18}^{-}$ Nanoparticles. K. L. D. M. Weerawardene, C. M. Aikens, *J. Am. Chem. Soc.*, **2016**, *138*, 11202-11210. http://pubs.acs.org/doi/abs/10.1021/jacs.6b05293
- Real-time TDDFT Studies of Exciton Transfer and Decay in Silver Nanowire Arrays. B. Peng, D. Lingerfelt, F. Ding, C. M. Aikens, X. Li, *J. Phys. Chem. C*, **2015**, *119*, 6421-6427. http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.5b00263

Edwin Barnes
850 West Campus Drive
Department of Physics
Virginia Tech
efbarnes@vt.edu

Ab initio design of quantum molecular magnets for information applications

Edwin Barnes, Sophia Economou, Nicholas Mayhall, Kyungwha Park
Virginia Tech



Overview: The demand for greater computing power to solve challenging problems in science, medicine, and economics continues to rise at a rapid pace. This need has fueled large investments from both government and industry in an approach to enhance computational power that exploits the principles of quantum mechanics. Quantum information processing (QIP) is based on storing information in quantum two-level systems (qubits) and takes full advantage of key features of quantum mechanics, such as quantum interference and entanglement, in order to exponentially speed up certain types of problems. Over the past two decades, several quantum systems have been explored as candidate qubits for QIP. An obvious choice is spin (either electronic or nuclear), as it is a true two-level system and tends to be well isolated, leading to relatively long coherence times. Using the spin of a single-molecule magnet (SMM) is a promising approach, however a majority of proposals are based on magnetically controlled SMM electron spin qubits, which have not yet achieved sufficiently long spin coherence times to be feasible for quantum computing. Magnetic interactions between spins also tend to be too weak to create the entanglement necessary for QIP.

Recently, a qubit candidate with remarkable properties was experimentally demonstrated by Wolfgang Wernsdorfer: the SMM $TbPc_2$ (see figure), featuring a nuclear spin as the qubit, with the attractive and unusual property of being electrically controllable. This combines the best of both worlds: long-lived qubit coherence with fast controllability. This recent exciting discovery opens up the opportunity for the development of scalable SMM-based QIP devices. We propose that entanglement generation in such devices can be achieved by coupling multiple SMM spins to the electric field of a superconducting resonator (see figure). Despite the promise offered by these SMMs, critical challenges remain. Integrating SMMs into devices requires a thorough understanding of the chemistry and physics of these large structures (>100 atoms per molecule), both in terms of their properties in isolation, and how these become modified when they are integrated into more complex structures. Exploiting the recent advances in this field, therefore, requires pushing the boundaries of theoretical quantum chemistry and multiscale modeling.

One of the main goals of the project is to develop a multiscale modeling approach for $TbPc_2$-based SMMs for QIP functionality. The $TbPc_2$ molecule is described as a highly open shell Tb(III) ion with many nearly degenerate electronic states, surrounded by a much larger organic ligand with either zero or one unpaired electron, depending on the oxidation state. The goal is to model the Tb ion with a wavefunction-based description which can describe multiple electronic states, while using a more efficient density functional theory (DFT) approach for describing the extended ligand system and environmental effects. Our recent work has been focused in four areas: (i) Density functional theory simulations based on first-principles relativistic multireference methods are used to investigate how different chemical environments influence the magnetic properties of $TbPc_2$-type SMMs; (ii) Quantum embedding theories allow a high-level treatment of the entangled region of the molecule (Tb) with a low-level treatment of the un-entangled region of the molecule (Pc ligands); (iii) The development and implementation of 1SF-EA wavefunction approximations enable efficient multistate ab initio simulations of the embedded (entangled region); (iv) Effective models with parameters extracted from ab initio simulations are used to design time-dependent control schemes for multiple SMMs coupled together. Our work is predominantly focused on $TbPc_2$ due to its extremely attractive features, but the techniques we are developing will be general and transferable to other molecules and other qubits. The quantum chemistry methodologies and simulation codes we are developing will be tested, run, and adapted on one of the NERSC supercomputers for more efficient implementations for other large-scale correlated quantum systems.

Recent progress and future plans: *DFT simulations*: We performed restricted active space self-consistent field (CASSCF) calculations for representative Tb-based SMMs such as $TbPc_2$ and TbPcNc (where Pc=phthalocyanine and Nc=naphthalocyanine) in three charge states, including relativistic spin-orbit interactions. In all the cases considered, we find that the Tb ground J=6 multiplet is well separated from other states. This result allows us to compute crystal-field parameters and construct pseudospin Hamiltonians for the J=6 multiplet. Interestingly, our calculations show that the zero-field splitting varies with oxidation number, while it has a weak dependence on ligand type and molecular geometry. Higher-energy levels are, however, sensitive to all these characteristics. For neutral SMMs TbPc2 and TbPcNc, the Tb magnetic moment and the ligand spin are parallel to each other, and the coupling strength between them does not depend much on ligand type or details of atomic structure. However, ligand distortion and molecular symmetry play a crucial role in transverse crystal-field parameters which lead to tunnel splitting. This work is under review in the Journal of Physical Chemistry A. The calculated crystal-field parameters are being used in our model Hamiltonian.

In addition, we are implementing a general method to compute hyperfine tensors for molecules within the multireference methods. Once this implementation is done, we plan to apply it to $TbPc_2$-like SMMs and investigate the electric-field dependence of the hyperfine tensors. The calculated hyperfine tensor parameters will be included in our model Hamiltonian in order to explore the optimal conditions for QIP applications.

Quantum Embedding: We have recently developed and published[1] a new technique for partitioning a molecular system into high-level and low-level systems. The main idea is inspired by the DMET approach, in which we first obtain a DFT solution and then project the occupied orbitals onto the atomic orbitals of some user-selected set of atoms which constitutes the active site. An SVD of the projected occupied orbitals reveals the extent of entanglement between the active orbitals and the environment orbitals. This provides a new orbital representation which is relatively robust for partitionings. The algorithm produces a bipartition of the occupied space at the point of the largest gap in the singular value spectrum. We provided numerical evidence in the paper to demonstrate that this can yield significantly more accurate embedding calculations in difficult cases, and fewer instances of discontinuous potential energy curves, issues that can be significant when projection-based embedding procedures are used instead.

The projection-based embedding described in our recent publication provides a clear approach for combining wavefunction and DFT methods. However, for very large systems, this can still be computationally expensive due to the large number of atomic orbitals which need to be transformed in a calculation. We are working on two strategies for compressing the virtual space. The first strategy applies a similar SVD projection on the virtual space and provides a path to recovering the untruncated results via sequential transformations. Preliminary results suggest the first approach works quite well. We have also developed a second strategy which should be even more black box and reliable. Our next steps will be to finish the implementations and benchmark the methods and then start applying these methods to $TbPc_2$-based compounds.

1SF-EA method development: Due to the large number of partially occupied orbitals on Tb(III) and the coupling to an open shell ligand, the $TbPc_2$ molecule experiences simultaneous spatial and spin near-degeneracies. The spatial near degeneracies arise from the need to distribute 8 electrons among 7 f-orbitals. The spin near-degeneracies arise from the small energy differences between ferro- and antiferro-magnetic alignment between the Tb ion and the ligand. This quasi-degeneracy means that conventional single reference methods will not be adequate as there is no single electronic configuration which can serve as a meaningful reference wavefunction. To address this, we have implemented and tested two new wavefunction ansatze termed RAS(h,p)-nSF-EA and RAS(h,p)-nSF-IP which are designed to simultaneously treat spin and spatial degeneracies by using a wavefunction generating excitation operator which changes both particle number and spin projection. A general pilot code has been implemented in Psi4, and tested on smaller systems which exhibit spin and spatial degeneracies. The results demonstrate that this new method is highly effective at constructing a qualitatively correct ansatz for the systems studied[2]. More recently, we have nearly finished a completely new implementation for the RAS(h,p)-1SF-EA/IP methods using an excitation-driven algorithm, which is significantly faster than the original string based implementation. Testing and benchmarking are currently underway.

Our next step here will be to finish the efficient implementation and compare the performance to the original model. Once this is finished, our strategy will then be to implement spin-orbit coupling within the state interaction formalism between RAS-1SF-EA eigenstates.

Model Hamiltonians and quantum gate simulations: We constructed a model Hamiltonian describing two SMM spins coupled to a superconducting resonator. In the absence of the SMM-resonator couplings, our model reproduces the energy spectrum reported in recent experiments on single SMMs. We determined the minimal hyperfine tensor and degree of magnetic anisotropy needed to reproduce the electrically driven Rabi oscillations demonstrated in these experiments. In addition, we investigated the suitability of different types of resonators and estimated the effective coupling strength in each case. We then used this information to design a two-SMM-qubit entangling gate using shaped electrical voltage pulses that perform the desired operation with fidelity exceeding 99% and at speeds approaching the theoretical limit. Performing fast quantum logic gates is important for increasing the complexity of algorithms that can be run on the quantum processor.

We are continuing our model Hamiltonian work in several directions. First, we are exploring the possible advantages afforded by the fact that the SMM nuclear spin provides a four-level system rather than just the two levels normally associated with a qubit. The additional levels may allow for novel control schemes in which the stronger coupling that occurs between higher levels is exploited to further enhance entangling-gate fidelities and speeds without diminishing the performance of single-qubit gates. This additional flexibility is not available in most of the leading qubit platforms. Second, we will study systems in which more than two SMMs are coupled together and identify optimal parameter regimes that maximize logic gate and algorithm performance. Third, we will develop schemes for efficiently implementing quantum algorithms in a multi-SMM system.

Grant number and title: DE-SC0018326, Ab initio design of quantum molecular magnets for information applications

Postdocs: Daniel Claudino, Oinam Meitei, Khadijeh Najafi, Aleksander Wysocki

Students: Shannon Houck, Fei Zhuang

List of publications:

1. Claudino, D., & Mayhall, N. J. (2019). Automatic Partition of Orbital Spaces Based on Singular Value Decomposition in the Context of Embedding Theories. Journal of Chemical Theory and Computation, 15(2), 1053–1064. https://doi.org/10.1021/acs.jctc.8b01112
2. Houck, S. E., & Mayhall, N. J. (2019). A Combined Spin-Flip and IP/EA Approach for Handling Spin and Spatial Degeneracies: Application to Double Exchange Systems. *Journal of Chemical Theory and Computation*, *15*(4), 2278–2290. https://doi.org/10.1021/acs.jctc.8b01268

Tunna Baruah

FLOSIC on water cluster and polyacene polarizabilities, transition metal systems, and single SIC Hamiltonian

Tunna Baruah, Rajendra Zope, Yoh Yamamoto, Sharmin Akter, Prakash Mishra, Carlos Diaz

University of Texas at El Paso

Abstract

The Fermi-Lowdin orbital based self-interaction correction (FLOSIC) scheme is applied to study the self-interaction correction effects on molecular properties. The presence of self-interaction errors in density functional approximations leads to excessive electron delocalization. We examine the effect of electron delocalization error on the dipole polarizability of molecules. The polarizability is a measure of the response of the system to an external electric field. To study the static dipole polarizabilities, we have chosen two systems – polyacenes with conjugated carbon-carbon bonds and water clusters. We also present other calculated properties with the FLOSIC methodology on small magnetic molecules with transition metal centers. Finally, we will discuss the incorporation of a single Hamiltonian for variational calculations within the FLOSIC formalism.

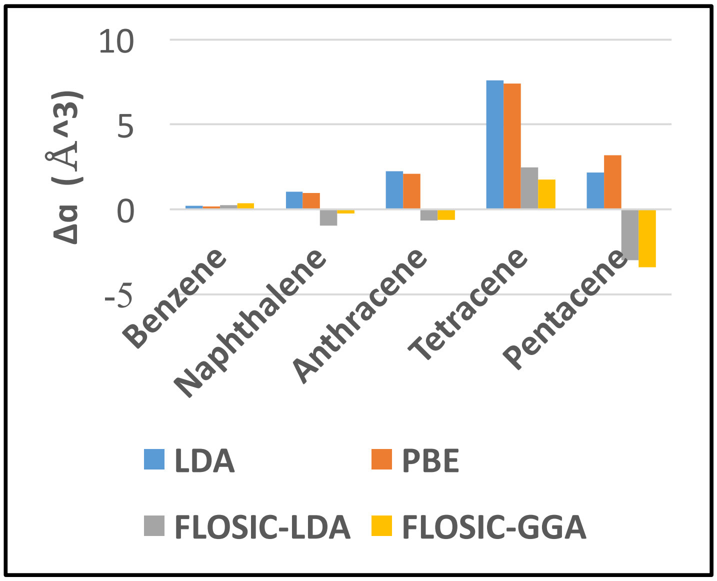


Fig.1: The errors in calculated dipole polarizabilities of polyacenes.

For a systematic study, we have carried out the FLOSIC calculations onpolarizabilities of polyacenes starting from benzene to pentacene. The density functional and FLOSIC calculations include both the LDA with Ceperley-Alder parametrization and generalized gradient approximation parametrized by Perdew, Burke, Ernzerhof. , The calculated polarizability for benzene, within the LDA and PBE-GGA agrees very well with experimental values but as the system size increases the polarizabilities also tend to be overestimates. This trend is, in general, systematic in that the overestimate is larger for the longer polyacenes. The exception is tetracene for which the error is largest (Fig.1). We find that inclusion of self-interaction correction reduces the polarizability but the correction is greater than required, this being particularly so for pentacene. Similar study was carried out on water clusters of size n=1-6. The water clusters reported by Xantheas et al. [J. Chem. Phys. 131, 214103 (2009)] were used for this study. The water clusters below size n=6 are more or less planar. Several isomers of the hexamer are included in the test set. The results indicate that the FLOSIC polarizabilities are smaller than the reported CCSD polarizabilities. The FLOSIC-DFA thus overcorrects the DFA polarizabilities (Fig.2). The polarizability per water molecule follows the same trend as seen in CCSD values for clusters within same size range. The corrections to the density is also evident from the ionization potentials of the water clusters which show that the SI corrected ionization energies are larger than those with DFA. We also note that the prism structure of water is found to be unbound at the PBE level but is stable at the FLOSIC level. This result is consistent with CCSD results.

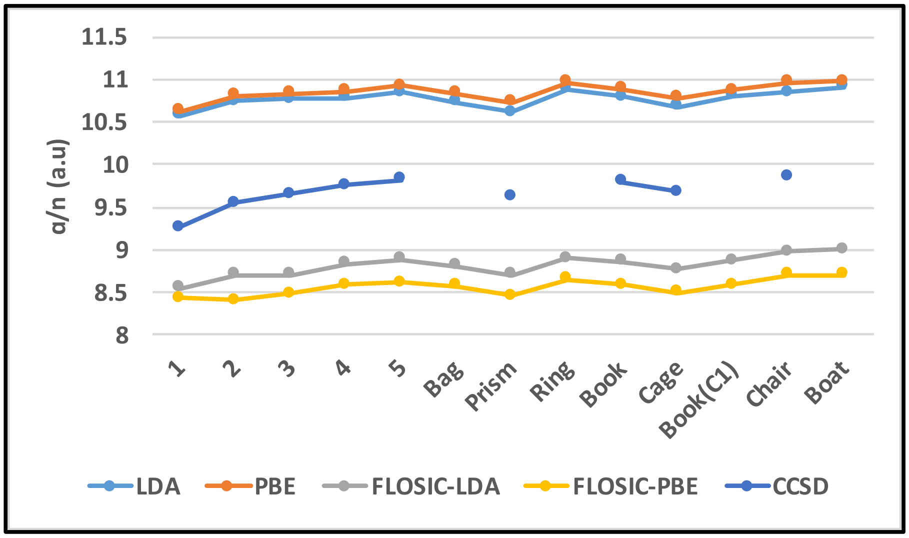


Fig. 2: Calculated polarizabilities per molecule of water clusters.

The performance of the FLOSIC with three different level exchange-correlation functions are tested on the dissociation energies of small transition metal oxide dimers. These are small molecules where the transition metal is under coordinated. Often DFA considered here in are found to be deficient in describing the spin states, dissociation energies, bond lengths, bond angles etc. of such molecules. Application of the DFT+U approach is often found to be necessary for a correct description in such systems. The FLOSIC on the transition metal oxide molecules shows improvement over DFA particularly for the lower rung functionals. We also find that the SCAN meta-GGA functional describes the properties of the small transition metal systems well without any correction.

The self-interaction correction is an orbital by orbital correction which results in an orbital based single particle potential. One way is to overcome this problem is to use the unified Hamiltonian. Another approach that is currently being used is to use an approximation in conjunction with Jacobi method to orthogonalize the orbitals. Both the methods are computationally intensive. We have implemented a new approach to derive a single Hamiltonian which makes the variational minimization of energy simpler and faster. The results of this approach will be presented in the meeting.

DE-SC00018331: FLOSIC - FLO-SIC: efficient density functional theory calculations without self-interaction

DE-SC0002168: Density functional based tools for simulation of photo-induced charge transfer

Postdoc(s): Yoh Yamamoto, Jorge Vargas, Luis Basurto (until Januaruy 2019).

Student(s): Sharmin Akter, Carlos Diaz

Publications:

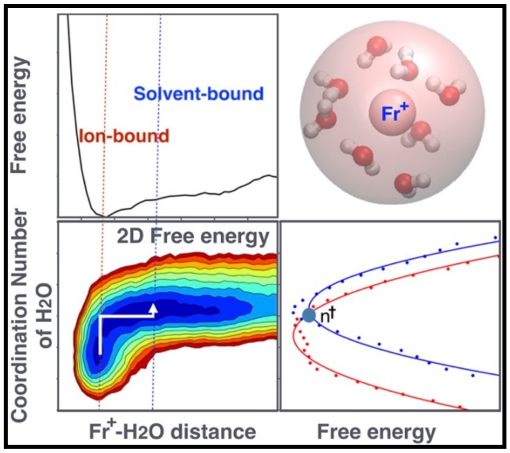
1. ***A DFT analysis of the ground and charge-transfer excited states of Sc3N@Ih–C80 fullerene coupled with metal-free and zinc-phthalocyanine***, Fatemeh Amerikheirabadi, Carlos Diaz, Neetha Mohan, Rajendra R. Zope and Tunna Baruah, Phys. Chem. Chem. Phys., 2018, 20, 25841-25848, DOI: 10.1039/C8CP03849J.
2. ***Electronic structure calculation of vanadium-and scandium-based endohedral fullerenes VSc$_2$N@C$_{2n}$ (2n = 70, 76, 78, 80),*** Shusil Bhusal, Tunna Baruah, Yoh Yamamoto, Rajendra R Zope, International Journal of Quantum Chemistry **118**, 24, e25785 (2018).
3. ***On the Question of the Total Energy in the Fermi–Löwdin Orbital Self-Interaction Correction Method,*** Kushantha P. K. Withanage, Kai Trepte, Juan E. Peralta, Tunna Baruah, Rajendra Zope, and Koblar A. Jackson, *J. Chem. Theory Comput. 14* (8), pp 4122–4128 (2018).DOI: 10.1021/acs.jctc.8b00344
4. ***Fermi-Löwdin orbital self-interaction correction to magnetic exchange couplings,*** Rajendra P. Joshi, Kai Trepte, Kushantha P. K. Withanage, Kamal Sharkas, Yoh Yamamoto, Luis Basurto, Rajendra R. Zope, Tunna Baruah, Koblar A. Jackson, and Juan E. Peralta, J. Chem. Phys. 149, 164101 (2018); https://doi.org/10.1063/1.5050809.
5. ***Donor-Fullerene Dyads for Energy Cascade Organic Solar Cells,*** John S. Cowart Jr., Christopher Liman, Amanda Garnica, Zachariah A. Page, Eunhee Lim, Rajendra R. Zope, Tunna Baruah, Craig J. Hawker, Michael L. Chabinyc, Inorganic Chimica Acta, In press, https://doi.org/10.1016/j.ica.2017.07.008 (2017).
6. ***Electronic and Structural Study of Zn$_x$S$_x$ [x = 12, 16, 24, 28, 36, 48, 96, and 108] Cage Structures,*** S. Bhusal, J.A. Rodriguez Lopez, J. Ulises Reveles, Tunna Baruah, and Rajendra R. Zope, J. Phys. Chem. A 121, 3486 (2017).
7. ***Excited States of Light-Harvesting Systems Based on Fullerene/Graphene Oxide and Porphyrin/Smaragdyrin,*** Gloria Cárdenas-Jirón, Merlys Borges-Martínez, Ember Sikorski, and Tunna Baruah, J. Phys. Chem. C 121, 4859 (2017).
8. ***Electronic and Optical Properties of VSc2N@C68 Fullerene,*** Shusil Bhusal, Rajendra R. Zope, Surendra Bhatt, Tunna Baruah, J. Phys. Chem. C (2016).
9. ***Electronic and Structural Properties of C60 and Sc3N@C80 Supported on Graphene Nanoflakes***, J. U. Reveles-Ramirez, Nakul N. Karle, Tunna Baruah, and Rajendra R. Zope, J. Phys. Chem. C 120, 26083 (2016).
10. ***Density functional investigation of the electronic structure and charge transfer excited states of a multichromophoric antenna***, L. Basurto, Rajendra R. Zope, Tunna Baruah, Chem. Phys. 469, 1 (2016).

Vyacheslav S. Bryantsev

Finding Order in the Disordered Hydration Shells of the heaviest akali ions, Cs^+ and Fr^+

Santanu Roy, Vyacheslav S. Bryantsev
Oak Ridge National Laboratory, Chemical Sciences Division

Abstract



The knowledge of complexation properties of Fr^+ is very limited and mostly based on extrapolations from the smaller alkali metal ions. Here we report the results of molecular dynamics simulations to characterize the structure and dynamics of intrinsically disordered hydration shells of the heaviest alkali Cs^+ and Fr^+ ions. Fr^+ ion shows an extreme example of a disordered solvation structure with no distinction between ion-bound and solvent-bound states based on the ion-water distance alone. However, solvent rearrangement can be monitored using a two-dimensional representation, in which either coordination number or electric field is employed as a collective variable. Utilizing Marcus theory of solvent exchange, the timescales of water exchange for Fr^+ (2.1-2.3 ps) is unexpectedly slower than for Cs^+ (0.5-1.2 ps), because barrier recrossing is more frequent for Fr^+. This work provides a new perspective to investigate weakly hydrated ions and hydrophobic systems that introduce structural disorder in the surrounding solvent.

Principles of Chemical Recognition and Transport in Extractive Separations

Field Work Proposal ERKCC08

PI: Bruce A. Moyer

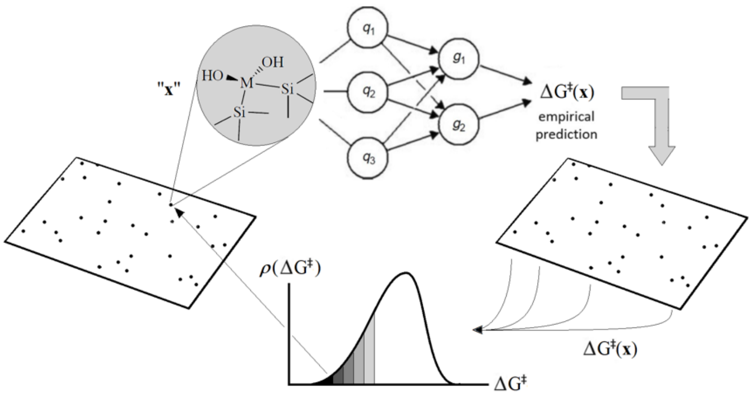
Co-PIs: Vyacheslav Bryantsev, Radu Custelcean, Santa Jansone-Popova

Postdoc(s): Santanu Roy, Neil J. Williams

Ab Initio Machine Learning Algorithms for Modeling Kinetics on Amorphous Catalysts

Marco Caricato[1], Brian B. Laird[1], Baron G. Peters[2], Ward H. Thompson[1]
[1]Department of Chemistry, University of Kansas
[2]Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign

Abstract



We are developing a computational framework that combines machine learning, statistical importance sampling, molecular dynamics (MD) and *ab initio* calculations, and population balance modelling techniques to predict the effective kinetics on heterogeneous, metal-doped amorphous silicate catalysts. These components form the interconnected parts of our importance learning algorithm. Electronic structure calculations on randomly sampled sites built from classical MD simulations will be used to train a model to predict activation barriers from structure. The model will iteratively sample the most active sites, and automatically refine its accuracy in the low activation energy tail of the site distribution.

First, we are exploring amorphous silica models, generated in classical MD simulations, that form the basis for descriptions of the supported catalysts (Thompson group). The initial focus is on roughly planar slabs. Briefly, the procedure is to melt a crystalline silica structure by heating to a high temperature. Then the periodic boundary along one direction is substantially expanded to create a silica-vapor interface in a slab geometry. The slab is equilibrated and then quenched to an amorphous solid by lowering the temperature to room temperature. The slab is then functionalized (OH-terminated) by adding H_2O across selected Si–O bonds (an OH group is bound to Si and an H to the O atom). We have automated the process so that hundreds of slab models can be generated at one time.

These slabs are serving as input for DFT-based models of both grafted (Peters group) and embedded (Caricato group) single-site metal catalysts. We are currently working to determine the optimal conditions for the geometry optimization at DFT level of the MD-generated amorphous silica clusters. We choose the center of mass (COM) of two SiOH groups at the center of the simulation cell to carve out a large cluster of 12 Å radius. The atoms on the edge of the cluster are capped with -H and -OH groups to maintain valency. Beginning at the COM, we conduct separate geometry optimizations where atoms within a radius $N = 3, 4,\ldots,9$ Å are allowed to relax while the rest are kept fixed. We analyze the differences in structure at each incremental radius increase by the RMSD of all atom positions within the relaxation sphere, the RMSD of the internal coordinates of atoms included in the hydrogen bonding network on the surface of the cluster, the change in total energy, and the deprotonation energy of the two central silanol groups. We conducted this analysis over several different clusters. Our current results indicate that the atoms that move the most from their original positions are the OH groups on the surface, while the silica frame does not evolve considerably from the MD structure, and that the same (local) minimum is reached in most cases. Additionally, properties such as the silanol deprotonation energy are not strongly affected by the size of the relaxation sphere. Since another important goal is to represent the heterogeneity of amorphous silica catalyst supports, we are also characterizing the features of the bulk and surface silica structure (*e.g.*, bond and angle distributions, ring statistics, surface roughness) and functionalization patterns (*e.g.*, density, spatial distribution) as a function of the liquid equilibration temperature, quench rate, selection criteria for the Si–O bonds, and force field description. The results show small ring structures (those involving 2 or 3 Si atoms) are preferentially found at the slab surface and that the silica structural features are not strongly affected by the quench rate over a range of 5-50 K/ps.

Simultaneously, we are using classical reactive potential models for the simulation and characterization of metal-doped amorphous silica surfaces (Laird group). These reactive potentials allow for dynamical bond breaking and electron transfer with the goal being to bridge the gap between the classical simulations, which exclude bond breaking, and the far more computationally expensive quantum electronic structure calculations. In our initial work, we are using a Charge-Optimized Many-Body (COMB3) reactive potential, which has shown to give good results for networked oxide materials such as alumina and silica. Starting with amorphous SiO_2 slab configurations equilibrated using classical non-reactive potentials, we are working to produce COMB3-equilibrated configurations and then expose the surface to water. Because COMB3 is a reactive potential, this will allow for reactions that will autofunctionalize the surface with -OH groups. It is hoped that this will produce an improved approach for developing an OH-terminated silica surface. By repeating this functionalization method for small amorphous silica clusters, we will benchmark our results against similar DFT calculations. The next step will be to incorporate catalytic metal atoms into the silica structure allowing us to easily provide large numbers of candidate configurations to the Peters group for the machine-learning dataset.

While the computational protocol to create realistic metal-doped amorphous silicate sites is being generated and tested, we are developing the importance learning algorithm (Peters group). We consider a simple model where each site has the same rate-limiting step, the same most abundant surface intermediate (MASI), and does not deactivate. Each site has a different local geometry and a rate law with simple power-law dependence on concentration. The power law emerges (as they do for many real catalysts) *via* a Langmuir-Hinshelwood mechanism. We assume that (1) reactant adsorption depends on the local environment of the site, (2) conversion of surface species is rate-determining and irreversible, (3) the product quickly and irreversibly desorbs from the surface, and (4) all other steps are quasi-equilibrated. We have developed a simple distorted lattice model of the amorphous silica support including hydroxyls, silanes, and sites for catalyst grafting. Grafting reactions and bonds are described by Morse potentials so that the calculations for each site involve optimizations much like those in an *ab initio* calculation. The specific Morse potential parameters are set to match DFT calculations for Cr sites on amorphous SiO_2. The advantages of this simple model are that (1) we decide the chemistry to investigate whereas the real Cr/SiO_2 catalyst steps remain a mystery, and (2) we can afford to optimize transition states and intermediates at thousands of sites to precisely to converge all averages. The adsorption constant for reactant A at each grafted site is computed by optimizing the surrounding (model) M-O and A-M bonds. The overall activation energy becomes a function of the local environment, represented by a list of four simple coordinates. The collection of computed activation energies is used to develop a kernel regression model for the activation energy – local structure relationship. Because the model is simple, we can compute the activation energy distribution explicitly for all ~20,000 sites. To illustrate the importance learning algorithm, an initial pool of fifty sites were randomly sampled to train an initial model. We then ran thirty iterations of importance learning which appears sufficient to converge the site average for this model system.

The main goals for the near future are: 1) to produce an initial number of realistic doped structures from the combined MD/DFT simulations to test the importance learning algorithm beyond the simple model utilized thus far, 2) to test and possibly reparametrize the reactive classical potential to emulate geometry optimizations of DFT quality, 3) to automate the construction of the optimized metal doped silica structures to allow the machine learning algorithm to update the training set on the fly with minimal human intervention. Once this development and testing phase will be completed, we will be ready to predict the effective kinetics of surface reactions catalysed by these materials and compare with experimental data.

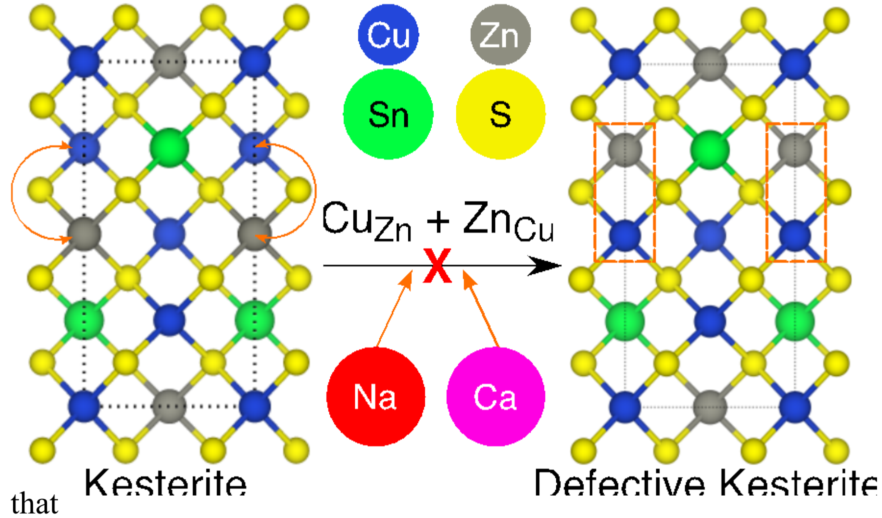
Student(s): Amy M. Jystad (Caricato), Joyce Nguyen (Laird), Craig Vandervelden and Salman Kahn (Peters), Pubudu N. Wimalasiri and Hasini Senanayake (Thompson).

Quantum Mechanical Evaluation of Alternative Photovoltaic Materials

Gopalakrishnan Sai Gautam,[1] Lesheng Li,[1] and Emily A. Carter[2]

Department of Mechanical and Aerospace Engineering,[1] School of Engineering and Applied Science,[2]
Princeton University, 41 Olden Street, Princeton, NJ 08544-5263, eac@princeton.edu

Abstract



This abstract reports our continued exploration of how to stabilize the optimal kesterite phase of Cu_2ZnSnS_4 (CZTS), an inexpensive solar cell material, via first principles thermodynamics calculations but also presents new quantum-dynamics simulations on another promising optoelectronic material, WSe_2. We begin with the former and end with the latter. Due to page limitations, we omit summaries of other publications – including a Feature Article in the *Journal of Physical Chemistry C* that reviews our photovoltaics materials discovery research carried out over the past decade – but we cite them at the end, for the interested reader.

Although Ag and Cd doping can produce significant performance improvements in CZTS solar cells by suppressing disorder-inducing Cu_{Zn}+Zn_{Cu} antisite defects under select synthesis and doping conditions (*Chem. Mater.* 2018, **30**, 4543), the rarity (Ag) and toxicity (Cd) make Ag or Cd unsustainable dopants for practical cells. Hence, we explored whether doping nontoxic, abundant alkali (Na) and alkaline earth (Ca) metals as isovalent dopants for Cu and Zn, respectively, could also suppress disorder within CZTS. Specifically, we calculated the bulk and defect energetics and the electronic structure of Cu_2ZnSnS_4, under various doping concentrations and synthesis conditions, using density-functional-theory-(DFT)-based calculations. In evaluating bulk and defect energies, we use the strongly constrained and appropriately normed (SCAN) functional for describing the electronic exchange-correlation (XC) functional, since SCAN satisfies all 17 known constraints for the behavior of an XC functional (*Phys. Rev. Lett.* 2015, **115**, 36402), unlike the generalized gradient approximation (GGA). For band gap estimates, we use the GGA functional corrected by a Hubbard U (i.e., GGA+U) with values of 3.6, 4.5, and 4.8 eV for Cu, Zn, and Sn, respectively (*J. Chem. Phys.* 2014, **140**, 121105), since our previous benchmarking (*Chem. Mater.* 2018, **30**, 4543) revealed that SCAN does not predict band gaps of semiconductors accurately. Similar to our previous work on Cd- and Ag-doped CZTS (*Chem. Mater.* 2018, **30**, 4543), we considered three chemical scenarios that are relevant during synthesis or operation for evaluating defect formation energies, namely, Cu-rich, constrained Cu-poor, and Cu-poor. In all chemical scenarios, we consider Na- and Ca-containing phases that exhibit the highest possible Na and Ca chemical potentials, respectively, while in equilibrium with CZTS.

The site preference of Na, under low doping concentrations (~0.75 at%), is sensitive to the chemical potential of Cu within CZTS, with Na preferentially occupying Cu sites from Cu-rich to constrained Cu-poor conditions while also occupying Zn sites under Cu-poor conditions. Importantly, both low (~0.75 at.%) and high (6.25 at.%) levels of Na doping could suppress disorder across Cu chemical potentials, as indicated by higher formation energies for disorder-inducing antisites (>0.31 eV) with Na doping than in pure CZTS (0.22-0.25 eV). However, high levels of Na doping will promote phase separation between Cu-rich CZTS and Na-rich Na_2ZnSnS_4 (NZTS) domains, where both CZTS and NZTS adopt the kesterite structure. Additionally, high levels of Na doping will also increase the band gap of CZTS, likely beyond the ideal photovoltaic range, as qualitatively indicated by the increase in the GGA+U band gap of NZTS (2.14 eV) vs. pure CZTS (0.96 eV). Thus, low levels of Na doping may be an effective strategy to improve the performance of CZTS cells by: i) efficiently suppressing disorder within the kesterite structure and ii) avoiding large increases in band gap or phase separation. Indeed, a handful of experimental studies have reported improved efficiencies in low-Na-doped CZTS cells (*J. Am. Chem. Soc.* 2013, **135**, 15998; *ACS Appl. Mater. Interfaces* 2016, **8**, 5017; *Prog. Photovoltaics* 2015, **23**, 862).

At low (0.75 at.%) Ca doping, Ca clearly prefers occupation of Zn over Cu sites in the kesterite structure, as indicated by the lower formation energy for Ca_{Zn} antisites (~1.13 eV) than for Ca_{Cu} antisites (~2.26 – 2.45 eV). Ca inhibits disorder at both low and high (6.25 at.%) doping concentrations, as indicated by the higher energy to form disordering antisites (> 1.3 eV) compared to undoped CZTS (0.22 – 0.25 eV). Ca doping is not expected to modify the band gap of pure CZTS significantly, as indicated by the similarity between the GGA+U band gap of kesterite-Cu_2CaSnS_4 (~1.0 eV) and kesterite-CZTS (0.96 eV). However, high levels of Ca doping destabilize the kesterite structure and promote formation of secondary phases such as CaS and Cu_2SnS_3, signifying that high levels of Ca doping will not be feasible within CZTS. Hence, low levels of Ca doping, if reachable experimentally, should suppress disorder-inducing antisites and improve the performance of CZTS solar cells. All of these findings regarding Na and Ca doping of CZTS appeared in *ACS Sustain. Chem. Eng.* **7**, 5792 (2019). We now turn to our work on WSe_2 (manuscript in preparation).

Nonradiative charge-carrier recombination in transition-metal dichalcogenide (TMD) monolayers severely limits their use in solar energy conversion technologies. Because defects serve as recombination sites, developing a quantitative description of charge-carrier dynamics in defective TMD monolayers can shed light on recombination mechanisms, which then can suggest strategies for performance improvement. We conducted a first-principles investigation of charge-carrier dynamics in pristine and defective WSe_2 monolayers with three of the most probable defects, namely, Se vacancies, W vacancies, and Se_W antisites. Briefly, we predict that Se vacancies slow down recombination by nearly an order of magnitude relative to defect-free samples by breaking the monolayer's symmetry and thereby reducing the spectral intensity of the A_{1g} mode that promotes recombination in the pristine monolayer. By contrast, we find W vacancies accelerate recombination by more than an order of magnitude, with half of the recombination events bypassing charge traps. Although Se_W antisites also slightly accelerate recombination, the predicted mechanism is different from the W vacancy case. First, a shallow energy level traps a photoexcited electron. Then, both shallow- and deep-trap-assisted recombination can occur simultaneously. Accelerated recombination arises for W vacancies and Se_W antisites because they introduce new phonon modes that strongly couple to electron and hole dynamics. Thus, materials engineering, particularly to avoid W vacancies, could advance this technology. The insights derived are important for future design of high-performance photoactive devices based on WSe_2 monolayers. In what follows, we present a more detailed description of the calculations and insights gleaned from the results.

As alluded to above, defects frequently introduce charge-trap energy levels in the band gap that can accelerate nonradiative electron-hole recombination, leading to low photoluminescence quantum yield. However, the mechanisms of these processes in defective WSe_2 monolayers are unclear, as charge-carrier dynamics in this material have not yet been investigated. It therefore is not known whether all defects are equally detrimental to or whether certain defects are particularly consequential for the performance of WSe_2 monolayers. We thus applied first-principles quantum dynamics (DFT-MD-derived surface-hopping) techniques to elucidate how different point defects affect charge trapping and electron-hole recombination in WSe_2 monolayers.

A pristine WSe_2 monolayer was used for direct comparison with defective WSe_2 monolayers containing one Se vacancy (V_{Se}), one W vacancy (V_W), or one antisite defect where a neutral Se atom substitutes for a W atom (Se_W) in a large supercell. These defects were chosen because of their predicted low formation enthalpies. Densities of states analysis indicates that V_{Se} introduces an empty peak in the band gap about 0.5 eV below the conduction band minimum (CBM). By contrast, V_W exhibits one filled peak (0.5 eV above the valence band maximum, VBM) and two empty peaks in the band gap. The two empty peaks are located 0.9 and 1.1 eV below the CBM. Introducing Se_W also produces one filled peak (0.37 eV above the VBM) and two empty peaks at quite different energies in the band gap. The deep empty peak is located 1.05 eV below the CBM, while the shallow empty peak is only 0.16 eV below the CBM. The electronic states introduced by these point defects all localize around the defect sites, while the VBM and CBM maintain their delocalized character within the WSe_2 monolayer for all four cases. The distinct electronic structures associated with pristine and defective WSe_2 monolayers indicate different charge-carrier dynamics. The point defects investigated introduce occupied and unoccupied electronic states in the band gap that can serve as hole and electron traps, respectively. The trap states open up the possibility of several distinct dynamical processes that could occur simultaneously, complicating the entire quantum dynamics of charge-carrier recombination.

In terms of quantitative findings, we predict that the pristine WSe_2 monolayer exhibits direct charge-carrier recombination between the band edges with a characteristic time constant of 405 ps, which is qualitatively consistent with measurements and thus lends credence to our simulation protocol. Phonon spectrum analysis indicates that the out-of-plane A_{1g} mode facilitates electron-hole recombination in the pristine WSe_2 monolayer. The presence of V_{Se} significantly inhibits recombination, with a much longer time constant of 3.1 ns, due to long-lived electrons in trap states. The deceleration occurs because the Se vacancy breaks the symmetry of the monolayer and considerably reduces the spectral intensity of the A_{1g} mode. By contrast, V_W greatly accelerates recombination, with a time constant of 16 ps. Our analysis suggests that roughly half of the recombination events bypass the electron trap and take place directly between the band edges. Competing events include electron-trap-assisted recombination and recombination through simultaneous electron and hole trapping. Although Se_W antisites also accelerate recombination somewhat, with a time constant of 151 ps, the mechanism behind such acceleration is different from the V_W case. First, the photoexcited electrons readily trap in shallow electron levels because of large nonadiabatic couplings. We predict that roughly half of the recombination events bypass the deep electron trap and occur directly between the shallow electron trap and the VBM. Competing events involve deep-electron-trap-assisted recombination and recombination through simultaneous deep electron trapping and hole trapping. Surprisingly, hole-trap-assisted recombination is rare for both W vacancies and Se_W antisites. This is because it is easier for electrons to transfer to electron traps than to recombine with a hole in a hole trap.

Recent theoretical work shows that sulfur (S) vacancies in a MoS_2 monolayer accelerate charge-carrier recombination with a time constant of 225 ps, where the trap states introduced by the S vacancy serve as intermediate states. Not only is the effect of a chalcogen vacancy on charge-carrier dynamics different for different TMDs, but the mechanisms behind these dynamical processes are also different. Chalcogen vacancies in TMDs frequently are regarded to be the most common intrinsic point defect. Normally, the mechanisms found in one material are transferable to other family members. Our work, however, indicates that changes in charge-carrier dynamics induced by chalcogen vacancies in the TMD family and the associated mechanisms found in one TMD material may not be generalizable to other members. Individual investigations of each TMD with chalcogen vacancies therefore will remain important. More importantly, our simulations suggest that W vacancies are the defects most detrimental to the performance of WSe_2 monolayers among the three most probable point defects. Although the Se_W antisite accelerates nonradiative recombination, it does so only by a factor of three. By comparison, the W vacancy accelerates recombination by a factor of 25, with a time constant of 16 ps. The picosecond timescale for nonradiative recombination predicted here is much faster than any recombination time constant ever reported for another technologically important TMD material, MoS_2. The picosecond timescale of the nonradiative electron-hole recombination will produce rapid loss of the charge-carriers to heat and will result in a low photoluminescence quantum yield. Therefore, methods to suppress formation of W vacancies will be critical to manufacturing high-performance optoelectronic devices based on WSe_2 monolayers.

In the near future, we anticipate completing a collaborative effort with experimentalists in Singapore examining the effect of Sn-based defects in CZTS and Cd-substituted CZTS on device performance.

Grant Number, Title, and Personnel Supported

DOE-BES Grant No. DE-SC0002120

Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications

Postdocs: Lesheng Li, Gopalakrishnan Sai Gautam, Xing Zhang, Qi Ou

Publications Since Last Report

S. Berman, G. S. Gautam, and E. A. Carter, "Role of Na and Ca as isovalent dopants in Cu_2ZnSnS_4 solar cells," *ACS Sustain. Chem. Eng.*, **7**, 5792 (2019). doi: 10.1021/acssuschemeng.8b05348

X. Zhang and E. A. Carter, "Subspace density matrix functional embedding theory: Theory, implementation, and applications to molecular systems," *J. Chem. Theor. Comp.*, **15**, 949 (2019). doi: 10.1021/acs.jctc.8b00990

G. S. Gautam, T. P. Senftle, N. Alidoust, and E. A. Carter, "Novel solar cell materials: Insights from first principles," *J. Phys. Chem. C*, **122**, 27107 (2018). doi: 10.1021/acs.jpcc.8b08185

G. S. Gautam, T. P. Senftle, and E. A. Carter, "Understanding the effects of Cd- and Ag-doping in Cu_2ZnSnS_4 solar cells," *Chem. Mater.*, **30**, 4543 (2018). doi: 10.1021/acs.chemmater.8b00677

Richard Dawes

Electronic structure methods and protocols with application to dynamics, kinetics and thermochemistry

Richard Dawes, dawesr@mst.edu

Missouri University of Science and Technology
400 W. 11th street, Rolla, MO 65409

I. Program Scope:

(NOTE – this project is supported jointly through the CTC and GPCP programs and this report will be submitted to both programs)

Hydrocarbon combustion involves the reaction dynamics of a tremendous number of species beginning with many-component fuel mixtures and proceeding via a complex system of intermediates to form primary and secondary products. Combustion conditions corresponding to new advanced engines and/or alternative fuels rely increasingly on autoignition and low-temperature-combustion chemistry. In these regimes various transient radical species such as HO_2, ROO·, ·QOOH, HCO, NO_2, HOCO, and Criegee intermediates play important roles in determining the detailed as well as more general dynamics. A clear understanding and accurate representation of these processes is needed for effective modeling. Given the difficulties associated with making reliable experimental measurements of these systems, computation can play an important role in developing these energy technologies.

Accurate calculations have their own challenges since even within the simplest dynamical approximations such as transition state theory, the rates depend exponentially on critical barrier heights and these may be sensitive to the level of quantum chemistry. Moreover, it is well-known that in many cases it is necessary to go beyond statistical theories and consider the dynamics. Quantum tunneling, resonances, radiative transitions, and non-adiabatic effects governed by spin-orbit or derivative coupling can be determining factors in those dynamics.

Building upon progress made during a period of prior support through the *DOE Early Career Program*, this project combines developments in the areas of potential energy surface (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. Figure 1 illustrates the predictive level of insight that is achievable via these approaches.[1]

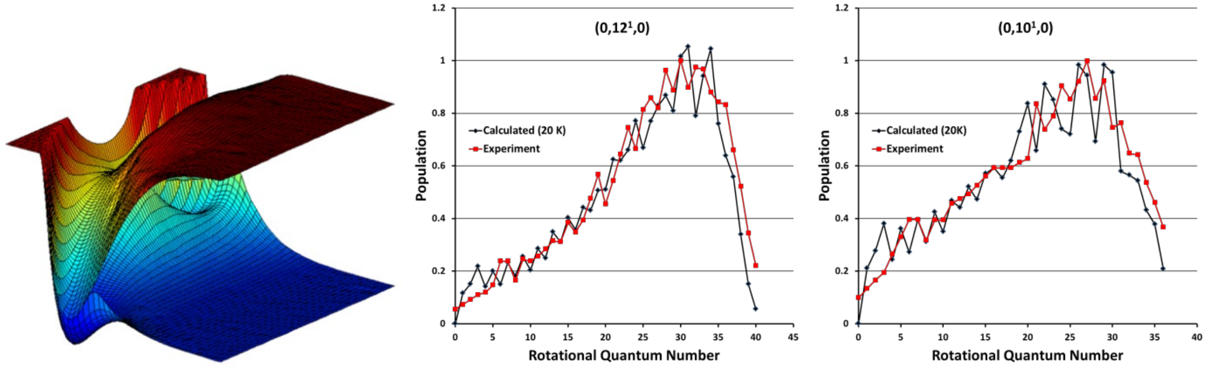


Figure 1: (left) Surface plot of the fitted adiabatic X and A state PESs for HCO in Jacobi coordinates as a function of $R_{\mathrm{H—CO}}$ and theta. (middle) Calculated and recorded rotational distributions of CO product, with thermal averaging over initial rotational states based on the estimated 20 K beam temperature. (right) same as middle panel, but with different excitation.

An ongoing area of investigation is to develop general strategies for robustly convergent electronic structure theory for global multichannel reactive surfaces including diabatization of energy and other relevant surfaces such as dipole transition. 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.

In addition, new methods and approaches to electronic structure theory will be developed and tested through applications. This project will explore limitations in traditional multireference calculations (*e.g.*, MRCI) such as those imposed by internal contraction, lack of high-order correlation treatment and poor scaling. Methods such as DMRG-based extended active-space CASSCF and various Quantum Monte Carlo (QMC) methods will be applied (including VMC/DMC and FCIQMC). Insight into the relative significance of different orbital spaces and the robustness of application of these approaches on leadership class computing architectures will be gained. A computational thermochemistry project recently conducted through support by the DOE SCGSR student fellowship program and collaboration with Branko Ruscic (Argonne National Labs) will be extended. A workflow framework that allows community driven expansion of the ATcT thermochemical database will be further developed. Synergy with other components of this research program such as automated PES fitting and multireference quantum chemistry will be used to address challenges encountered by the standard approaches to computational thermochemistry (those being single-reference quantum chemistry and perturbative treatments of the anharmonic vibrational energy, which break down for some cases of electronic structure or floppy strongly coupled vibrational modes).

II. Recent Progress (NOTE – the start date for this project was March 1, 2019, so only preliminary results have been obtained at the time of writing this report (April 2019)).

Perhaps the most significant progress in the first 6 weeks of this project has been the implementation of automated thermochemical scripts whose development began last summer in collaboration with Branko Ruscic (ANL) and David Bross (ANL).

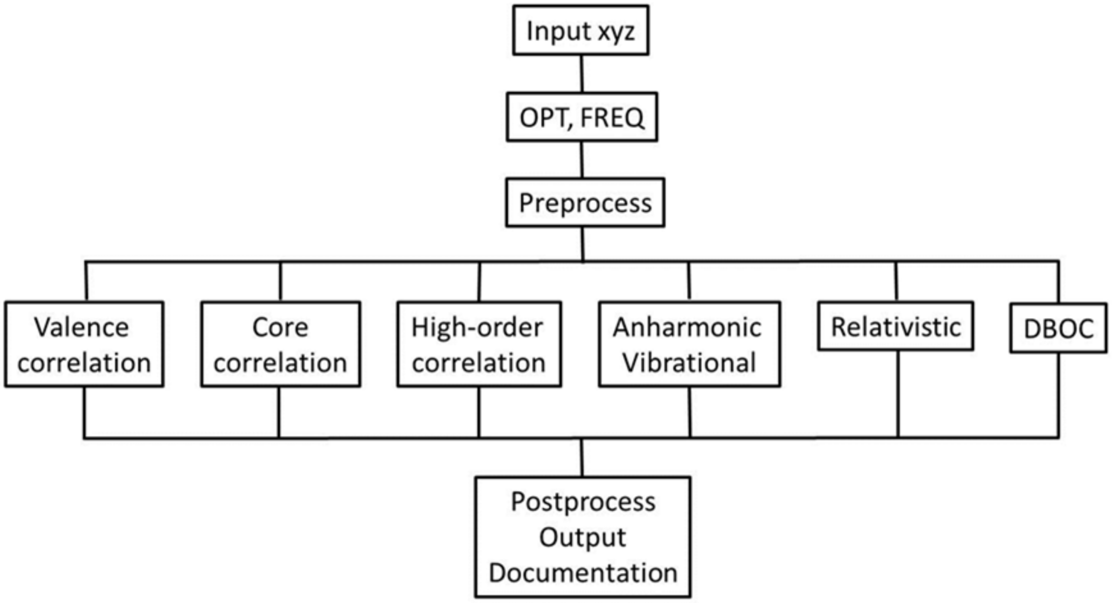


Figure 2: Flowchart of the automated thermochemical protocol.

The Python scripting to distribute and execute a series of high-level quantum chemistry calculations across multiple resources has now been extensively tested on roughly two hundred small to medium sized molecular systems by multiple users (including undergraduate students) and is proving to be very robust, reliable and efficient. Two related publications in preparation are already close to submission. Graduate student Bradley Welch supported on this project will defend his thesis in May 2019. Bradley will continue related work as a postdoc with Angela Wilson (MSU).

Grant Numbers and Grant Titles

Grant No. DE-SC0019740; Electronic structure methods and protocols with application to dynamics, kinetics and thermochemistry

Grant No. DE-SC0010616; Multiple coupled potential energy surfaces with application to combustion

Postdoc(s): Steve A. Ndengué; Ernesto Quintas Sánchez

Student(s): Bradley K. Welch; Sangeeta Sur

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

---

[1] Shanyu Han, Xianfeng Zheng, Steve Ndengué, Yu Song, Richard Dawes, Daiqian Xie, Jingsong Zhang, and Hua Guo. "Dynamical interference in the vibronic bond breaking reaction of HCO." *Science advances* **5**, no. 1 (2019): eaau0582.

[2] R. Dawes and E. Quintas-Sánchez, The Construction Of Ab Initio-Based Potential Energy Surfaces, *Rev. Comput. Chem* **31**, 199-264 (2018).

[3] S. Ndengué, R. Dawes, F. Gatti, H. Guo, The influence of Renner-Teller coupling between electronic states on inelastic scattering, *J. Phys. Chem. A*, **122**, 6381 (2018).

[4] Silver Nyambo, Brandon Uhler, Lloyd Muzangwa, Maxim Ivanov, Bradley K. Welch, Richard Dawes, Scott A Reid, Reactive Pathways in the bromobenzene-ammonia dimer cation radical: evidence for a roaming halogen radical, J. *Mol. Struct*., 1172, **113** (2018).

[5] Andrew Powell, N.S. Dattani, RFK Spada, FBC Machado, H. Lischka, R. Dawes, Investigation of the ozone formation pathway: Comparisons of FCIQMC and fixed node DMC with icMRCI and ucMRCI. *J. Chem. Phys.* **147**, 094306 (2017).

[6] Moumita Majumder, Steve Ndengue, Richard Dawes, new view (with author profile): automated construction of potential energy surfaces, *Molecular Physics* **114**, 1 (2016).

[7] Richard Dawes and Steve Ndengué, Single- and multireference electronic structure calculations for constructing potential energy surfaces, *Int. Rev. Phys. Chem.* **35**, 441, (2016).

[8] Phalgun Lolur, Richard Dawes, Michael Heaven, Theoretical study of vibronic perturbations in Magnesium Carbide, *Molecular Physics* **114**, 162 (2016).

[9] Andrew D. Powell and Richard Dawes, Calculating potential energy curves with fixed-node diffusion Monte Carlo: CO and N_2, *J. Chem. Phys.* **145**, 224308 (2016).

[10] Steve Ndengué, Richard Dawes and Hua Guo, A new set of potential energy surfaces for HCO: Influence of Renner-Teller coupling on the bound and resonance vibrational states. *J. Chem. Phys.* **144**, 244301 (2016).

Presenter: Barry D. Dunietz

Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials

Margaret S. Cheung[1], Barry D. Dunietz[2], Eitan Geva[3]
1. University of Houston, TX; 2. Kent State University, OH; 3. University of Michigan, MI

Abstract

The goal of the research program is to characterize charge transfer (CT) processes in structurally malleable materials, which is key to improve alternative energy applications. In particular we are concerned with CT across interfaces related to organic photovoltaics (OPV) systems. We have established a transformative computational scheme, beyond widely used simplifications, to achieve realistic descriptions of CT processes. This process properly addresses the contribution of molecular environment at ambient conditions to the CT processes. We have provided a unique insight of CT that is most relevant to experimental efforts.

Since the underlying scheme encompasses multiple scales in space and time, we have overcome such substantial challenges by developing an integrative approach that combines analytical theories, quantum mechanical calculations, and computer simulations. Our closely collaborative team comprised of three principal investigators with complementary expertise in molecular dynamics simulations (Cheung), electronic structure calculations (Dunietz), and quantum dynamics theories of the condensed phase (Geva), is uniquely positioned to solve this challenging problem (see introduced in Figure 1).

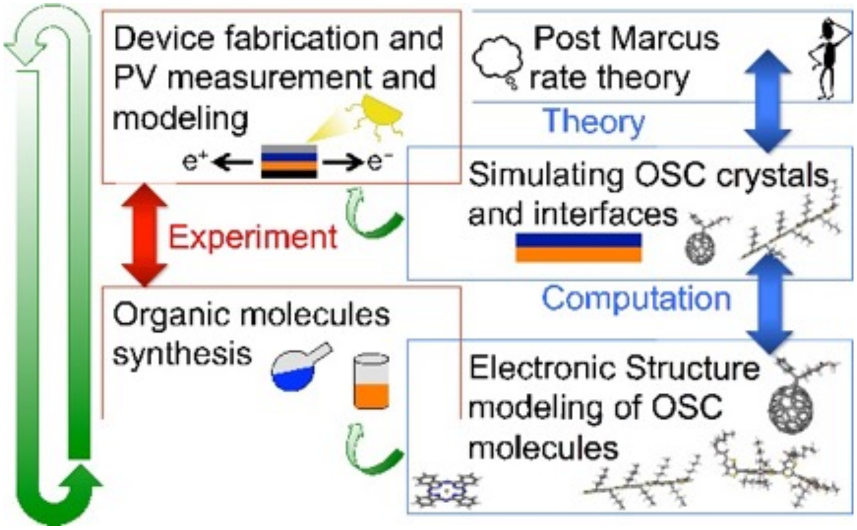


Figure 1: A multiscale and multi PI computational program to investigate charge transfer and transport in experimentally relevant molecular interfaces. Our program combines state-of-the-art electronic structure calculations, molecular dynamics simulations in the framework of quantum dynamical hierarchy of approaches.

We present three advances achieved by our computational research program:

In the first part, we introduce our polarization consistent electronic structure framework, where we combine range-separated hybrid (RSH) functionals with polarized continuum model (PCM). Our approach is shown to achieve physically relevant frontier orbitals with electron removal and addition energies that

reproduce well measured energies in the crystal phase for a benchmark set of organic semiconducting materials. The success stems from invoking the same dielectric screening in the long-range part of the functional as invoked in the PCM treatment. In Figure 2 we demonstrate the success of our approach by following averaged energies, where our screened RSH-PCM values are in excellent agreement with the benchmark values.

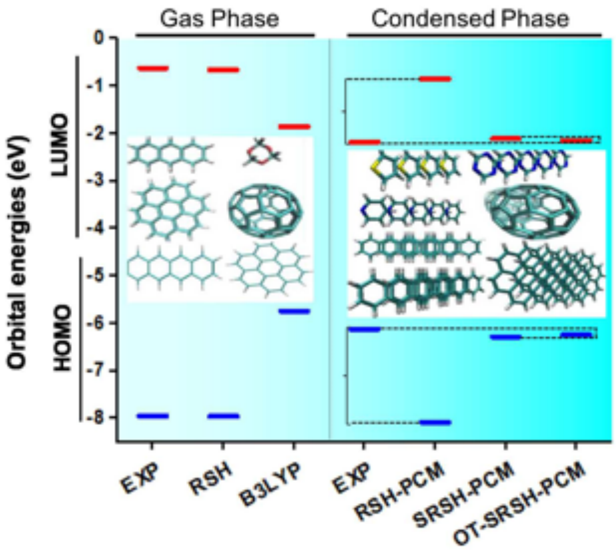


Figure 2: Average frontier orbital (HOMO and LUMO) energies, in eV, calculated in the gas phase and in various combinations with a PCM compared to the averaged benchmark IP and EA energies in gas and thin-film forms (Exp.). The SRSH-PCM and OT-SRSH-PCM present excellent agreement with the measured value in the crystal phase. (*J. Chem. Theory Comput.* **14** (2018) 6287)

In the second part, we study photo induced CT in a complex molecular system of a solvated triad to understand the relationship of the CT to conformational flexibility. See illustrated in Figure 3. In this study we report for the first time the application of the hierarchy of approximations based on the linearized semiclassical (LSC) method for the CT rate constant to a complex molecular system. In particular the triad system is used to test our linearized semi-classical based hierarchy of methodologies that range from a semi-classical (Marcus approach) to a Fermi-Golden rule level where a molecular environment is probed by molecular dynamics simulations. Our approach combines all-atom molecular dynamics simulations with explicit solvent and electronic-state-specific force fields. The validity of the second-order cumulant approximation, which leads to a Marcus-like expression for the rate constant is established by comparing the rate constants calculated with and without resorting to this approximation.

In the third part, we describe our ongoing effort to study CT processes through an interface of SubPC and C_{60}, donor and acceptor materials that are widely used in OPV research. We resolve the various molecular donor-acceptor interfaces and describe their effect on CT rates. In Figure 4 we provide orbital diagrams illustrating the key frontier orbitals involved in the relevant excited states of the different interfaces.

In addition, we are also in the process of implementing new tools for modeling the quantum dynamics that go beyond the perturbative equilibrium Fermi's golden rule level. One such tool is the generalized quantum master equation (GQME), which would allow one to simulate the CT dynamics for electronic coupling of arbitrary strength. Another such tool is based on representing the electronic degrees of freedom in terms of mapping variables with a well defined classical limit and simulating the dynamics of the overall (electronic + nuclear) system within the framework of LSC.

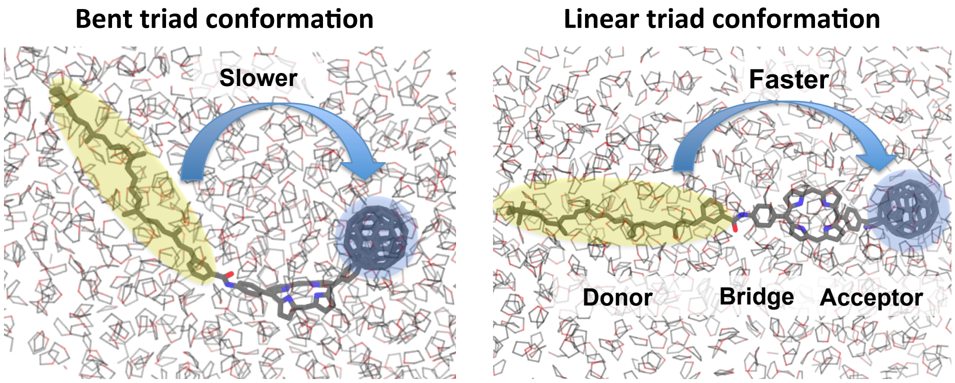


Figure 3: A Marcus-like expression, based on the second order cumulant approximation, is validated for an experimentally-relevant triad system. The strong dependence of CT dynamics on the triad's conformation is demonstrated. We find that the bent→linear conformational change is the rate-determining step for CT in this system. The CT in the solvated molecular triad was found to be driven by the solvent, which highlights the important role that interactions with the host can have on CT kinetics. (*J. Phys. Chem. C.* **122** (2018) 11288-11299)

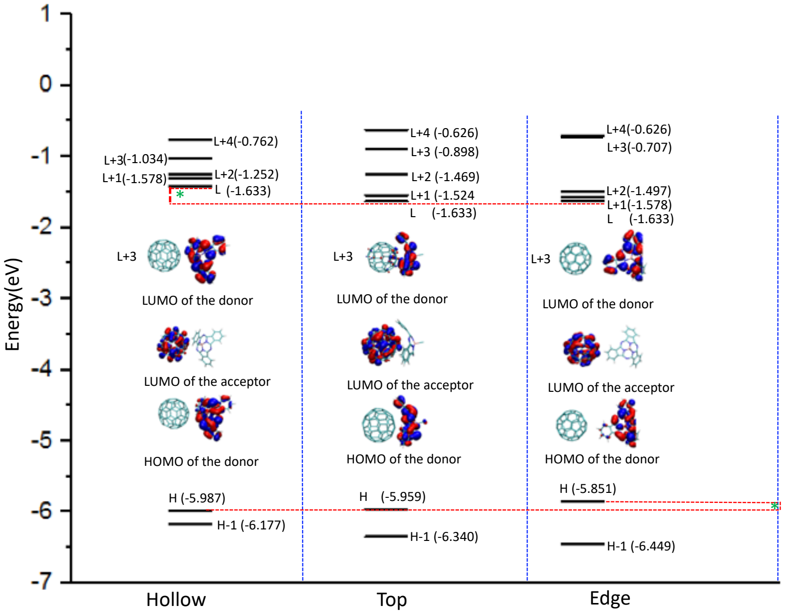


Figure 4: Frontier orbital diagram of the various SubPC-C_{60} interfaces.

Grants: DE-SC0004924, DE- FG02-10ER16174, and DE-SC0016501 Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials

Postdoc(s): Alexander Schubert, Atsushi Yamada, Qinguo Feng, Arun Manna, Huseyin Aksu, Buddhadev Maiti, Jaebeom Han, Pengzhi Zhang, Xing Gao

Student(s): Srijana Bhandari, Jacob Tinnin, Ellen Mulvihill, Yudan Liu

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

- A modified generalized quantum master equation for simulating electronically nonadiabtic dynamics
  Ellen Mulvihill, Alexander Schubert, Xiang Sun, Barry D. Dunietz, and Eitan Geva, *J. Chem. Phys.* **160** (2019) 034101.

- Fundamental gaps of condensed-phase organic semiconductors from single-molecule calculations using polarization-consistent optimally tuned screened range-separated hybrid functionals
  Srijana Bhandari, Margeret Cheung, Eitan. Geva, Leeor Kronik, and Barry D. Dunietz *J. Chem. Theory Comput.* **14** (2018) 6287.

- Computational study of charge transfer dynamics in the carotenoid-porphyrin-C_{60} molecular triad solvated in explicit tetrahydrofuran and its spectroscopic signature
  Xiang Sun, Pengzhi Zhang, Yifan Lai, Kai Williams, Margaret Cheung, Barry D. Dunietz, Eitan Geva, *J. Phys. Chem. C.* **122** (2018) 11288-11299.

- A Comparative Study of Different Methods for Calculating Electronic Transition Rates
  Alexei A. Kananenka, Xiang Sun, Alexander Schubert, Barry D. Dunietz, and Eitan Geva, *J. Chem. Phys.* , **148** (2018) 102304.

- Enhancing charge mobilities in organic semiconductors by selective fluorination: a design approach based on a quantum mechanical perspective
  Buddhadev Maiti, Alexander Schubert, Sunandan Sarkar, Srijana Bhandari, Kunlun Wang, Zhe Li, Eitan Geva, Robert J. Twieg, and Barry D. Dunietz *Chem. Sci.* , **8** (2017) 6947-6953.

- Conductance of Junctions with Acetyl-Functionalized Thiols: A First-Principles-Based Analysis
  Atsushi Yamada, Qingguo Feng, Qi Zhou, Austin Hoskins, Kim M. Lewis, and Barry D. Dunietz *J. Phys. Chem. C.* , **121** (2017) 10298-10304

- Achieving Predictive Description of Molecular Conductance by using a Range-Separated Hybrid Functional
  Atsushi Yamada, Qingguo Feng, Austin Hoskins,Kevin D. Fenk, and Barry D. Dunietz, *Nano Lett.* , **16** (2016) 6092-6098

- Deleterious Effects of Exact Exchange Functionals on Predictions of Molecular Conductance
  Qingguo Feng, Atsushi Yamada, Roi Baer, and Barry D. Dunietz *J. Chem. Theory Comput.* , **12** (2016) 3431-3435

- Unraveling the Mechanism of Photoinduced Charge Transfer in Carotenoid–Porphyrin–C60 Molecular Triad Arun K. Manna, B. Balamurugan, Margaret S. Cheung, and Barry D. Dunietz *J. Phys. Chem. Lett.* , **6** (2015) 1231-1237

- Ultrafast Charge-Transfer Dynamics at the Boron Subphthalocyanine Chloride/C60 Heterojunction: Comparison between Experiment and Theory
  Daniel E. Wilcox, Myeong H. Lee, Matthew E. Sykes, Andrew Niedringhaus, Eitan Geva, Barry D. Dunietz, Max Shtein, and Jennifer P. Ogilvie *J. Phys. Chem. Lett.* , **6** (2015) 569-574

Francesco A. Evangelista

Driven similarity renormalization group approaches for near-degenerate electronically excited states

Chenyang Li, Jeffrey B. Schriber, Tianyuan Zhang, Francesco A. Evangelista

Department of Chemistry and Cherry L. Emerson Center for Scientific Computation, Emory University,
Atlanta, Georgia, 30322, USA

Abstract

Program Scope. This project aims to study and develop of new multireference many-body theories based on the driven similarity renormalization group (DSRG), a new many-body formalism introduced by our group.[1] We have developed state-specific multireference DSRG (MRDSRG) methods to treat dynamical electron correlation effects in molecular systems and shown that it provides a convenient framework to derive numerically-robust multireference theories with electron correlation treated perturbatively (second- and third-order)[2–3] or at a level comparable to that of coupled cluster methods.[4] Another advantage of the DSRG is that it leads to equations that are relatively simple, and therefore, can be implemented in efficient algorithms that are amenable to parallelization. This talk will cover recent developments, focusing on new schemes to treat near-degenerate states and conical intersections.

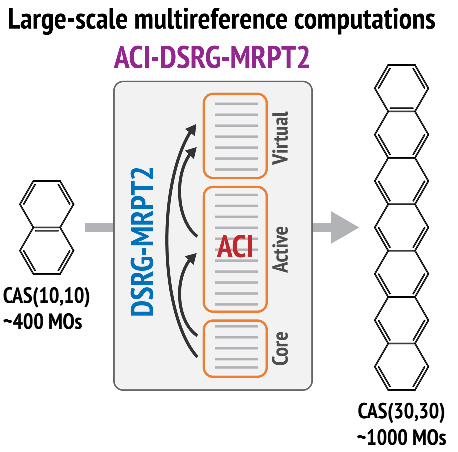


Figure 1. Our recent development of a scheme that combines selected CI with the MR-DSRG opens the door to large-scale multireference computations using large active spaces.

Recent progress

In the past year, we have focused on two main directions. First, we have developed a computational method based on the MR-DSRG to treat active spaces with large active spaces (~30 orbitals). The major bottleneck in applying traditional multireference methods like CASPT2/NEVPT2 to large active spaces arises from high-order density matrices of the reference wave function, limiting them to about twenty orbitals. Multireference methods based on the DSRG have an advantage in this respect because they only require at most the three-body density matrix. We have recently proposed a computational scheme (see Fig. 1) that uses selected CI (sCI) for a zeroth-order description of strong electron correlation and the DSRG to correct for the missing dynamical electron correlation [*J. Chem. Theory Comput.* **14**, 6295 (2018)]. We have used the sCI/DSRG scheme to predict singlet-triplet gaps, metrics of open-shell character, and spin-spin correlation functions for oligoacenes (2−7 benzene rings), reporting computations with active spaces containing up to 30 electrons in 30 orbitals and as many as 1350 basis functions. Our results provide benchmark theoretical gaps for the oligoacenes that are in good agreement with available experimental results. Contrary to the conclusions of previous studies that focused on π orbital correlation, our work showed that large bases and relaxation of the reference under the effect of dynamical correlation lead to a significant reduction in the estimated radical character of the oligoacenes.

Our second area of research has been the formulation of excited state DSRG methods for studying near-degenerate electronic states, including avoided crossings and conical intersections. In the previous period, we developed a state-averaged DSRG formalism (Ref. 5) where we generalize the DSRG to study an ensemble of electronic states. In this approach, we perform a *single* unitary transformation of the Hamiltonian to decouple a chosen ensemble of states from excited configurations. One potential deficiency of the state-average strategy is that states with very different chemical nature (e.g., charge-transfer vs. Rydberg) may be poorly described using a due to the averaging of dynamical correlation effects. This problem may be solved by a multi-state formulation, whereby several electronic states are first independently optimized and used as a basis to diagonalize the Hamiltonian. In a recent paper [*J. Chem. Phys.* **150,** 144107 (2019)], we have studied the deficiency of the state-averaged DSRG, developed and implemented a multi-state DSRG scheme, and introduced a new dynamically-weighted method that combines the advantages of the state-averaged and multi-state schemes (see Fig. 2). The dynamically-weighted approach can accurately describe both situations where electronic states are near-degenerate or energetically well separated.

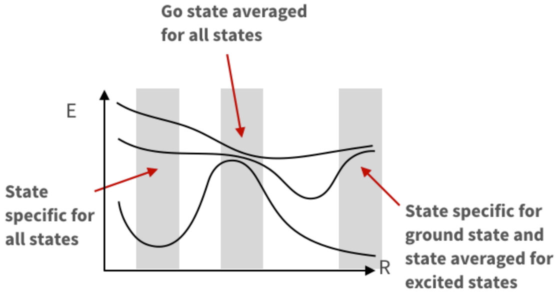


Figure 2. The dynamically-weighted DSRG combines the advantages of multi-state and state-averaged formalisms for treating multiple electronic states.

Lastly, we have submitted a paper in which we reported a density-fitted implementation of the nonperturbative MR-DSRG truncated to one- and two-body excitations with computational and memory scaling equivalent to that of CCSD. Our work on the DSRG was also described in a Perspective [*J. Chem. Phys.* **149,** 030901 (2018)] and a review [*Annu. Rev. Phys. Chem.* **70**, 052416 (2019)].

Future plans

- Formulations of analytic energy gradients for MR-DSRG methods.
- Development and benchmarking of wave function-based embedding for MR-DSRG methods.
- Benchmark sets for quantum computing algorithms
- Hybrid quantum-classical algorithms for quantum computers based on the DSRG.

References

1. Evangelista, F. A., A driven similarity renormalization group approach to quantum many-body problems. *J. Chem. Phys.* **141,** 054109 (2014).
2. Li, C. and Evangelista, F. A. Multireference Driven Similarity Renormalization Group: A Second-Order Perturbative Analysis. *J. Chem. Theory Comput.* **11,** 2097–2108 (2015).
3. Li, C.; Evangelista, F. A., Driven Similarity Renormalization Group: Third-Order Multireference Perturbation Theory. *J. Chem. Phys.* **146**, 124132 (2017).
4. Li, C.; Evangelista, F. A. Towards Numerically Robust Multireference Theories: The Driven Similarity Renormalization Group Truncated to One- and Two-Body Operators. *J. Chem. Phys.* **144**, 164114, (2016).
5. Li, C.; Evangelista, F. A., Driven similarity renormalization group for excited states: A state-averaged perturbation theory. *J. Chem. Phys.***148**, 124106 (2018).

Grant Numbers and Grant Titles

DE-SC0016004—Advanced Electronic Structure Theories for Strongly Correlated Ground and Excited States

Postdoc(s): Chenyang Li

Student(s): Jeffrey B. Schriber (partial), Tianyuan Zhang, Shuhe Wang, Nan He

DE-SC0019374 —Quantum Chemistry for Quantum Computers

Postdoc(s): Chenyang Li

Student(s): Nicholas Stair, Jeffrey B. Schriber

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

a) Li, C.; Evangelista, F. A., Driven Similarity Renormalization Group: Third-Order Multireference Perturbation Theory. *J. Chem. Phys.* **146**, 124132 (2017).

b) Li, C.; Verma, P.; Hannon, K. P.; Evangelista, F. A., A low-cost approach to electronic excitation energies based on the driven similarity renormalization group. *J. Chem. Phys.* **147**, 074107 (2017).

c) Parrish, R. M.; Smith, D.; L. Burns *et al.*, Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. *J. Chem. Theory Comput.* **13**, 3185 (2017).

d) Li, C.; Evangelista, F. A. Driven similarity renormalization group for excited states: A state-averaged perturbation theory, *J. Chem. Phys.* **148**, 124106 (2018).

e) Smith, D.; L. Burns; D. Sirianni *et al.*, Psi4NumPy: An Interactive Quantum Chemistry Programming Environment for Reference Implementations and Rapid Development. *J. Chem. Theory Comput.* **14,** 3504–3511 (2018).

f) Evangelista, F. A., Perspective: Multireference coupled cluster theories of dynamical electron correlation. *J. Chem. Phys.* **149,** 030901 (2018).

g) Huang, Y.; Xu, Z.; Jin, S.; Li, C.; Warncke, K.; Evangelista, F.A.; Lian, T.; Egap, E., Conjugated Oligomers with Stable Radical Substituents: Synthesis, Single Crystal Structures, Electronic Structure, and Excited State Dynamics. *Chem. Mater.* **30**, 7840 (2018).

h) Schriber, J. B.; Hannon, K. P.; Li, C.; Evangelista, F. A., A Combined Selected Configuration Interaction and Many-Body Treatment of Static and Dynamical Correlation in Oligoacenes. *J. Chem. Theory Comput.* **14**, 6295 (2018).

i) Li, C.; Evangelista, F. A., Multireference Theories of Electron Correlation Based on the Driven Similarity Renormalization Group. *Annu. Rev. Phys. Chem.* **70**, 052416 (2019).

j) Li, C.; Lindh, R.; Evangelista, F. A., Dynamically weighted multireference perturbation theory: Combining the advantages of multi-state and state-averaged methods. *J. Chem. Phys.* **150,** 144107 (2019).

Large-scale real-space all-electron Kohn-Sham density functional theory calculations

Bikash Kanungo, Nelson Rufus, Krishnendu Ghosh, Vikram Gavini
University of Michigan, Ann Arbor

Abstract

The pseudopotential approximation has been widely used in the past two decades to predict bulk mechanical, electrical and chemical properties. However, despite their success, pseudopotentials are often sensitive to the choice of core-size used in their construction and tend to oversimplify the treatment of core electrons as chemically inert for various systems and external conditions. Examples include properties of materials systems containing transition metals, phase transitions in systems under high pressure, spectroscopic properties in heavy metals, band-gaps and excited state properties. Further, systematically convergent all-electron calculations are needed for an accurate computation of the spin Hamiltonian parameters that require an accurate description of the electron density at the nuclear positions. Moreover, accurate all-electron calculations in a complete basis are crucial to tackling the inverse DFT problem of computing the exact XC potential from correlated ab-initio ground-state densities. Thus, the objective of this work is to develop systematically convergent, computationally efficient and scalable large-scale real-scale all-electron DFT calculation.

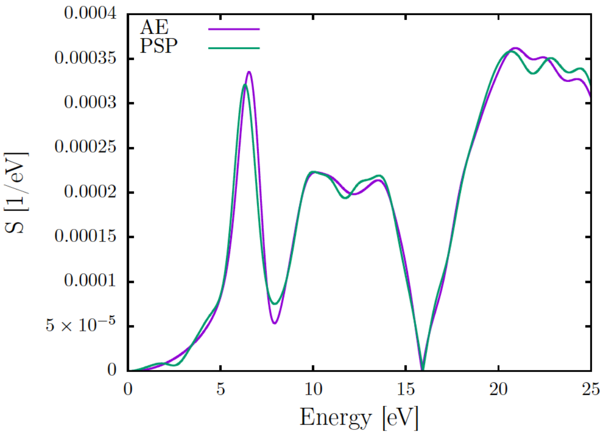


Figure 1: Absorption spectra of benzene; comparison between all-electron and pseudopotential calculations.

The recent progress in our effort over the past year is three-fold. Firstly, we developed and implemented the framework for conducting systematically convergent and scalable all-electron DFT calculations into the recently released *open-source* DFT-FE code (https://github.com/dftfeDevelopers/dftfe) [1], which is based on spatially adaptive higher-order finite-element (FE) basis—a piecewise polynomial basis. Importantly, the framework has been developed such that all-electron and pseudopotential calculations are treated in a unified manner, which enables: (i) transferability studies assessing the accuracy of pseudopotentials; (ii) mixed all-electron pseudopotential calculations, which treats some atoms at the all-electron level and others using a pseudopotential approximation. We have also developed an *a-posteriori* mesh adaption scheme based on error estimates to construct efficient spatially adapted FE basis for all-electron calculations. Benchmark all-electron studies have been conducted on a wide range of non-periodic and periodic systems alongside comparisons with NWChem and Exciting codes. A second aspect of our effort has been focused towards extending our prior work in developing and using enriched FE basis, where the FE basis functions are enriched with compactly supported single atom orbitals. The accuracy, scalability and computational efficiency of the enriched FE basis has recently been demonstrated [2]. In particular, significant outperformance by the enriched basis has been demonstrated when compared to the Gaussian basis even for modest system sizes (~1000 electrons). In the recent effort, we have worked towards improving the enriched FE basis, where the enrichment functions are constructed to be orthogonal to the subspace spanned by the FE basis. This significantly improves the conditioning of the enriched FE basis. Further, we have extended the framework of enriched FE basis to include periodic systems, and benchmarking studies on the accuracy, computational efficiency and scalability for periodic systems are ongoing. A third aspect of our recent work applied these methodological developments in all-electron DFT calculations to two application problems: (i) computing the spin Hamiltonian parameters of various molecules and periodic systems [3]; (ii) leveraging these developments to tackle the inverse DFT problem, where we computed, to unprecedented accuracy, the exact XC potentials for ab-initio correlated densities on molecules.

Future plans include: (i) incorporating enriched FE basis into DFT-FE, which will be a major undertaking that will bring these developments into the public domain; (ii) combining the developed framework for enriched FE basis with localization techniques [2,5] to realize reduced-order computational complexity in the solution of KS equations; (iii) extending the enriched FE basis all-electron framework to TDDFT calculations [6]; (iv) computing spin Hamiltonian parameters for large-scale periodic systems using mixed all-electron pseudopotential capability of DFT-FE code; (v) generating exact XC potentials for a wide range of molecular systems.

References:

1. P. Motamarri, S. Das, S. Rudraraju, K. Ghosh, D. Davydov, V. Gavini, DFT-FE: A massively parallel adaptive finite-element code for large-scale density functional theory calculations, *arXiv*:1903.10959 (2019).

2. B. Kanungo, V. Gavini, Large-scale all-electron density functional theory calculations using an enriched finite element basis, *Phys. Rev. B* **95**, 035112 (2017).

3. K. Ghosh, H. Ma, V. Gavini, G. Galli, All-electron density functional calculations for electron and nuclear spin interactions in molecules and solids, *Phys. Rev. Mater.* **3**, 043801 (2019).

4. P. Motamarri, V. Gavini, A subquadratic-scaling subspace projection method for large-scale Kohn-Sham DFT calculations using spectral finite element discretization, *Phys. Rev. B* **90**, 115127 (2014).

5. P. Motamarri, V. Gavini, K. Bhattacharya, M. Ortiz, Spectrum splitting approach for Fermi-operator expansion in all-electron Kohn-Sham DFT calculations, *Phys. Rev. B* **95**, 035111 (2017).

6. B. Kanungo, V. Gavini, Real-time time-dependent density functional theory using higher-order finite-element methods, *arXiv*:1810.13130 (2018).

Grant Numbers and Grant Titles

DE-SC0017380: Development of large-scale linear scaling all-electron density functional theory calculations.

Postdoc(s): Krishnendu Ghosh

Student(s): Nelson Rufus; Bikash Kanungo

DE-SC0008637: Software center for predictive theory and modelling

Postdoc(s): Phani Motamarri

Student(s): Sambit Das

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

1. P. Motamarri, S. Das, S. Rudraraju, K. Ghosh, D. Davydov, V. Gavini, DFT-FE: A massively parallel adaptive finite-element code for large-scale density functional theory calculations, *arXiv*:1903.10959 (2019).
2. K. Ghosh, H. Ma, V. Gavini, G. Galli, All-electron density functional calculations for electron and nuclear spin interactions in molecules and solids, *Phys. Rev. Mater.* **3**, 043801 (2019).
3. B. Kanungo, V. Gavini, Real-time time-dependent density functional theory using higher-order finite-element methods, *arXiv*:1810.13130 (2018).
4. P. Motamarri, V. Gavini, Configurational forces in electronic structure calculations using Kohn-Sham density functional theory, *Phys. Rev. B* **97**, 165132 (2018).
5. L.K. Aagesen, J.F. Adams, J.E. Allison, B.Andrews, V. Araullo-Peters, T. Berman, Z. Chen, S. Daly, S. Das, S. Dewitt, S. Ganesan, K. Garikipati, V. Gavini, A. Githens, M. Hedstrom, Z. Huang, H.V. Jagadish, J.W. Jones, J. Luce, E.A. Marquis, A. Misra, D. Montiel, P. Motamarri, A.D. Murphy, A.R. Natrajan, S. Panwar, B. Puchala, L. Qi, S. Rudraraju, K. Sagiyama, E.L.S. Soloman, V. Sundararaghavan, G. Tarcea, G.H., Teichert, J.C. Thomas, K. Thornton, A. Van der Ven, Z. Wang, T. Weymouth, C.Yang, PRISMS: An integrated, open-source framework for accelerating predictive structural materials science, *JOM - J. Min. Met. Mat. S.* **70**, 2298-2314 (2018).
6. S. Das, V. Gavini, Electronic structure study of screw dislocation core energetics in Aluminum and core energetics informed forces in a dislocation aggregate, *J. Mech. Phys. Solids* **104**, 115-143 (2017).
7. S. Das, M. Iyer, V. Gavini, Real-space formulation of orbital-free density functional theory using finite-element discretization: The case for Al, Mg, and Al-Mg intermetallics, *Phys. Rev. B* **92**, 014104 (2015).
8. M. Iyer, B. Radhakrishnan, V. Gavini, Electronic structure of an edge dislocation in Aluminum and the role of macroscopic deformations on its energetics, *J. Mech. Phys. Solids* **76**, 260-275 (2015).

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

Principal Investigator: Mark S. Gordon, 201 Spedding Hall, Iowa Sate University and Ames Laboratory, Ames, IA 50011; mark@si.msg.chem.iastate.edu

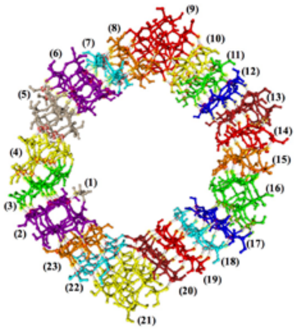
Program Scope. Our research effort combines new theory and highly scalable code developments (aiming at the exascale) with applications to a variety of problems in surface science and heterogeneous catalysis, and the investigation of intermolecular interactions, including solvent effects in ground and excited electronic states and the liquid-surface interface. Many of the surface science and heterogeneous catalysis studies are in collaboration with Drs. James Evans and Igor Slowing.

Recent Progress. A significant effort involves the development of efficient methods that can be applied to large systems, such as surfaces, nanoparticles and liquids. One such method is the effective fragment potential (EFP) method whose accuracy for intermolecular interactions rivals that of second order perturbation theory (MP2). The EFP method, a highly sophisticated model potential, can be combined with essentially any electronic structure method to, for example, provide insights about solvent effects and liquid behavior. The EFP method has been combined with our spin-flip TDDFT method to study solvent effects on the location and energy profile of conical intersections, which have a profound effect on excited states, photochemistry and photobiology.

Another (fully quantum) fragmentation approach is the fragment molecular orbital (FMO) method. The FMO method divides a large species into fragments to facilitate accurate QM calculations on very large systems. The FMO method can be used in concert with any electronic structure method in GAMESS. In order to optimize geometries using the FMO method, or to perform molecular dynamics (MD) simulations, it is necessary to derive and code fully analytic gradients for each method that is combined with the FMO, such as Hartree-Fock (HF) or DFT. Fully analytic FMO/HF, FMO/DFT, and FMO/MP2 gradients have been derived and implemented in GAMESS, to enable geometry optimizations and MD simulations. We have shown previously that one can do FMO/HF MD simulations with periodic boundary conditions and that fully analytic gradients are absolutely essential. The FMO method is also highly scalable, because the calculation for each fragment can be performed on a separate compute node. Advances have also been made in high performance computational chemistry. An INCITE grant enabled us to have access to the BlueGene /Q at Argonne, where we have demonstrated that the FMO method allows essentially perfect scaling to the petascale (more than 262,000 processors). One bottleneck in the FMO method is that FMO3 calculations with explicit three-body interactions, interactions that are important for many types of systems like water, are computationally demanding. This problem has been solved in two ways. The entire FMO code has been made essentially file-less, with virtually no I/O overhead. Also, a new method, the effective fragment molecular orbital (EFMO) method has been developed that replaces the bath potential with the EFP. This incorporates the EFP induction component that includes many body interactions. It has been shown that the EFMO method is both more accurate and faster than the FMO2 method. Fully analytic EFMO gradients have been derived and implemented.

A concern about applying methods like HF and DFT to excited states is that it is difficult to maintain orthogonality between the excited state and the ground state. In a very exciting development we have shown that if one can ensure that the excited state satisfies the correct nodal characteristics (easier than explicitly maintaining orthogonality), one has a valid excited state. A paper on this work has been published.

Mesoporous silica nanoparticles (MSN) have received increasing attention due to their catalytic capabilities. Because the MSN species are very important for their selective heterogeneous catalytic capability, we have an ongoing effort to model these complex species, in collaboration with the Evans and Slowing groups. Electronic structure theory calculations have been combined with the non-equilibrium statistical mechanics methods of the Evans group to provide insights about processes that occur within a MSN. The FMO method has been used to study the formation of carbinolamine, catalyzed by a section of MSN.



Fragmentation scheme for 1700-atom MSN

The GAMESS development group is part of the Department of Energy Exascale Computing Project (ECP) and the Computational Chemical Sciences (CCS) program. The GAMESS ECP is focused on a broad refactorization of the GAMESS code, with the main focus on improving the scaling of key modules that are the most computationally demanding and on developing a seamless interface between GAMESS and the quantum Monte Carlo code QMCPACK. A GAMESS-QMCPACK interface has been established and a paper on QMC-EFMO calculations has been published.

A collaboration with Theresa Windus has led to a study of the use of the EFP method to study atmospheric clustering using the dynamic nucleation theory Monte Carlo (DNTMC) method. It was demonstrated that DNTMC/EFP is an accurate and computationally efficient approach, and that charge transfer plays an important role.

An important component of the EFP method is the treatment of Coulombic (electrostatic) effects using the Stone distributed multipole analysis (DMA). A collaboration with the Stone group considered alternatives to the DMA[9]. The outcome of this study is that no alternative treatment of Coulomb effects is better than the DMA.

A collaboration with the Evans group at the Ames Laboratory on reactions that occur on the Pd surface combines accurate electronic structure theory with kinetic Monte Carlo studies. These studies are complicated by the existence of several spin states of varying multiplicities, even for large Pd clusters. So, we have carried out a systematic analysis of the binding of substrates on metal clusters as a function of the spin state and the size of the cluster. These calculations set the stage for the more extensive calculations of Co on Pd surfaces.

Current and Future Plans. Having completed an FMO study of the heterogeneous catalysis of carbinolamine formation inside an MSN cage, an examination of the full mechanism for this reaction is being investigated, including solvent effects. It was demonstrated that small models of the MSN catalyst do not capture the correct chemistry, so larger cages, with thousands of atoms will be required. These calculations will be made feasible by access to pre exascale computers made possible by the aforementioned ECP grant.

An important component of the MSN catalysis problem is the diffusion of the various molecules through the rather narrow pore. In a collaboration with Jim Evans, we are exploring the potential energy surfaces for intermolecular interactions between molecules that interact in the pore, using the EFP method. All of the potential energy surfaces explored so far reveal that the interactions are dominated by dispersion interactions. The potential energy surfaced developed in this manner will provide input into the Evans kinetic Monte Carlo studies. We are also performing EFP MD simulations to predict diffusion constants inside the pore.

In order to fully analyze surface crossings and conical intersections, one needs the ability to calculate non-adiabatic coupling matrix elements (NACME) that couple multiple surfaces when they are in close proximity. For large systems, TDDFT and SF-TDDFT are the most efficient methods for exploring excited state phenomena, so the derivation and implementation of TDDFT and SF-TDDFT NACME are in progress, now that we have developed a spin-correct SF-TDDFT energy + gradient method.

References to 10 recent publications of DOE sponsored research

1. Ana P. de Lima Batista**,** Federico Zahariev, Igor I. Slowing, Ataualpa A. C. Braga, Fernando R. Ornellas, Mark S. Gordon, "Silanol-Assisted Carbinolamine Formation in an Amine-Functionalized Mesoporous Silica Surface: Theoretical Investigation by Fragmentation Methods", J. Phys. Chem. B, 120, 1660 (2016).
2. S.R. Pruitt, H. Nakata, T. Nagata, M. Mayes, Y. Alexeev, G.D. Fletcher, D.G. Fedorov, K. Kitaura, and M.S. Gordon, "The Importance of Three-Body Interactions in Molecular Dynamics Simulations of Water", J. Chem. Theory Comp., 12, 1423 (2016)
3. C. Bertoni and M.S. Gordon, "Analytic gradients for the Effective Fragment Molecular Orbital method", J. Chem. Theory Comp., 12, 4743 (2016).
4. Y. Zhang, M. W. Schmidt, S. Kumari, M. S. Gordon, and D.-S. Yang, "Threshold Ionization and Spin-Orbit Coupling of Ceracyclopropene Formed by Ethylene Dehydrogenation", J. Phys. Chem. A, 120, 6963 (2016)

5. D.-J. Liu, F. Zahariev, M.S. Gordon and J.W. Evans, “Predictive Beyond Mean-Field Rate Equations for Multisite Lattice-Gas Models of Catalytic Surface Reactions: CO-Oxidation on Pd(100)”, J. Phys. Chem. C, 120, 28639 (2016)
6. C. Bertoni , L.V. Slipchenko, A. Misquitta, and M.S. Gordon, “Multipole moments in the Effective Fragment Potential method”, J. Phys. Chem. A, 121, 2056 (2017)
7. A. Devarajan, A. Gaenko, M.S. Gordon and T.L. Windus, “Nucleation Using the Effective Fragment Potential and Two-Level Parallelism”, in Fragmentation: Toward Accurate Calculations on Complex Molecular Systems, M.S. Gordon Editor, Wiley, 2017.
8. P. Xu, E.B. Guidez, C. Bertoni and M.S. Gordon, “Perspective: Ab Initio Force Field Methods Derived From Quantum Mechanics”, J. Chem. Phys., 148, 090901 (2018).
9. F. Zahariev, M.S. Gordon, and Mel Levy, “Nodal Variational Principle for Excited States”, Phys. Rev. A, 98, 012144 (2018)
10. S. Koseki, N. Matsunaga, T. Asada, M.W. Schmidt and M.S. Gordon, “Spin-Orbit Coupling Constants in Atoms and Ions of Transition Elements: Comparison of Effective Core Potentials, Model Core Potentials, and All-Electron Methods”, J. Phys. Chem. A, in press. DOI: 10.1021/acs.jpca.8b09218

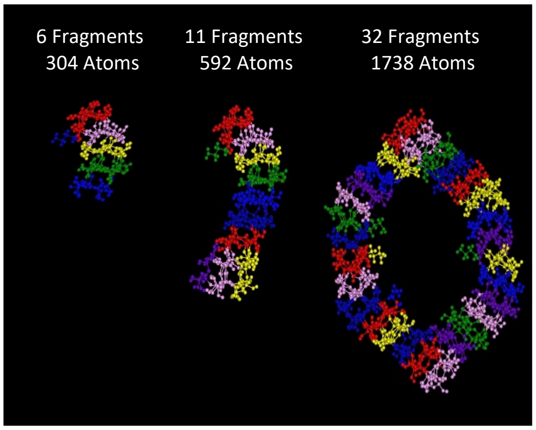
presenter: Anastasia O. Gunina

Development of Massively Parallel Fragmentation Approach for Modeling Selective Heterogeneous Catalysis

Anastasia O. Gunina, Mark S. Gordon
Ames Laboratory of US DOE and Iowa State University
201 Spedding Hall, Ames, IA 50011
mark@si.msg.chem.iastate.edu

Program scope

Computational investigations of heterogeneous catalysis require describing a nanopore, catalytic functional groups, gatekeeper groups, solvent, reactants, and products. It was shown that the catalytic activity is greatly influenced by both nanopore and solvent environment, which implies a need of the explicit incorporation of many thousands of atoms in the simulations at high level of theory. Such a challenge requires both significant computational hardware resources and highly efficient, multi-level parallel code, with minimal disk utilization and RAM footprint.



Recent progress

Fragmentation approaches provide an attractive opportunity to meet these requirements by tackling the full system in significantly independent MPI-ready pieces, with minimal approximations. Among those approaches, the Effective Fragment Molecular Orbital (EFMO) method offers, by its construction, minimal communication and a natural opportunity to accommodate complex CPU-accelerators and memory hierarchies, while being compatible with any *ab initio* method and keeping fragments fully flexible. The EFMO method uses the fragmentation scheme from the Fragment Molecular Orbital (FMO) method, describing short-range interfragment interactions with an *ab initio* method of choice, but utilizing the Effective Fragment Potential (EFP) method for long-range interactions as well as for many-body polarization. The EFP parameters are pre-computed for every system geometry to allow for fragments flexibility. Previously, a pilot code for EFMO energies and analytic gradients was developed in the Gordon group [1]. In order to be ready for modeling the target catalyst – functionalized Mesoporous Silica Nanoparticles (MSN) – or any other realistic system, the implementation should be enabled for large systems and its efficiency needs to be maximized. The main effort in the EFMO development was focused on its bottleneck step, which was shown [2] to be the one generating EFP parameters, called MAKEFP. For every MAKEFP term, pilot OpenMP parallelization was implemented, to allow the program to take advantage of shared memory architecture within fragments, distributed over MPI. In addition, batches of legacy code were rewritten or cleaned up around MAKEFP module. Disk usage was significantly reduced, too, which yielded 50% wall time improvement. The main EFMO driver received upgrades in

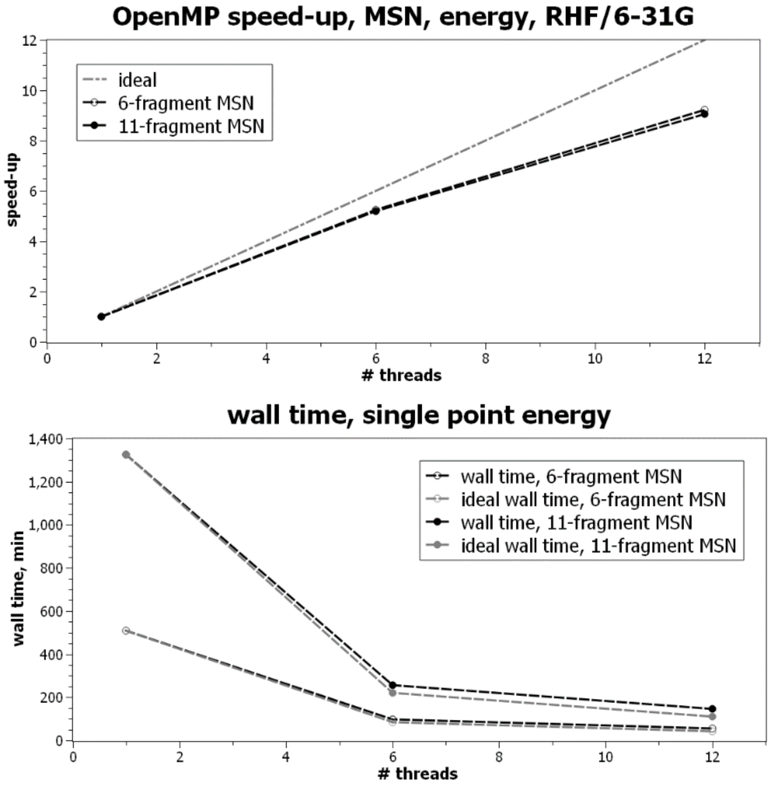


Fig. 1. OpenMP parallel efficiency of the EFMO/RHF code, with dispersion term off. 304-atoms and 592-atoms pieces of MSN. Single node with 12 CPU threads.

accessible system sizes, which allowed one to start calculations on MSN ring and perform scaling studies and debugging on a realistic system. Based on the benchmarks on supercomputers, EFMO printing and punching was cleaned up and optimized. The resulting parallel performance was tested on two sectors of the MSN ring, with 6 fragment/304 atoms/2395 basis functions and 11 fragments/592 atoms/4885 basis functions. Tests were run on a single node with 12 CPU threads, at EFMO/RHF level of theory with all the terms except dispersion (which is currently under development). The results are shown in Figure 1. Wall time and RAM requirements were also tested against number of basis functions and number of fragments, for sectors of MSN up to the full ring. A linear increase was observed for the same job setup and the entire ring was fitting in the node memory, in contrast to cubic scaling of unfragmented RHF, which could not run by half of the ring. The code improvements are available in the recent GAMESS release.

Ongoing development and future work

Current MSN benchmarks are performed on a ring with attached catalytic groups, but in the absence of solvent. In the modeling of the catalyst active site, performed previously [3], presence of water was shown to change the reaction mechanism, which is in excellent agreement with experimentally observed significant difference in reaction rates in aqueous solutions for MSN-catalyzed reactions. This suggests that at least part of the solvent should be described quantum mechanically, which will significantly increase both size of the system and number of fragments. Detailed analysis of performance for such cases is a very important next step. Also, this will allow us to determine a physically optimal way of modeling catalysis in solution.

With current benchmarks showing optimal performance and parallel efficiency of the code with all terms but dispersion, analysis and optimization of the latter is currently in progress. A special challenge is describing dispersion for systems with broken bonds between fragments, which includes MSN. In addition, with optimal single-node performance, various cases of hybrid OpenMP/MPI runs will need to be analyzed. Several orbital localization schemes will be analyzed for robustness for the case of large and challenging system of MSN.

References

1. C. Bertoni, M.S. Gordon. J. Chem. Theory Comput., 12, 4743–4767 (2016)
2. P. Xu, E.B. Guidez, C. Bertoni, M.S. Gordon. J. Chem. Phys., 148, 090901 (2018)
3. A.P. de Lima Batista**,** F. Zahariev, I.I. Slowing, A.A.C. Braga, F.R. Ornellas, M.S. Gordon. J. Phys. Chem. B, 120, 1660 (2016)

Funding

Development of Exascale Software for Heterogeneous and Interfacial Catalysis, *Computational Chemical Sciences, Department of Energy:* lead PI Mark S. Gordon (ISU/Ames lab)

Nonadiabatic Photochemistry

Donald Truhlar,[1] David R. Yarkony,[2] and Hua Guo[3]

[1]Deparatment of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455
[2]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218
[3]Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, 87131

Abstract

Program Scope

This project involves the development and application of methods for treating electronically nonadiabatic processes with the emphasis on photochemical dynamics studied on accurate coupled potential energy surfaces generated by quantum mechanical electronic structure theory.

Recent Progress

Donald G. Truhlar

The electronic spectrum of thiophenol was simulated by a normal-mode sampling approach combined with TDDFT in the Tamm-Dancoff approximation (TDA). The vertical excitation energies were compared with electronic structure calculations by completely renormalized equation-of-motion coupled cluster theory with single and double excitations and noniterative inclusion of connected triples (CR-EOM-CCSD(T)) and by multi-reference perturbation theory. The spectrum was computed both with and without solvation effects, and these spectra are compared to each other and to experiment. Using multireference-perturbation-theory adiabatic wave functions and model-space diabatization by the fourfold way, diabatic potential energy surfaces of the lowest three singlet states ($^1\pi\pi$, $^1\pi\pi^*$, and $^1n_\pi\sigma^*$) were constructed along the S−H stretching coordinate, the C−C−S−H torsion coordinate, and the ν_{16a} and ν_{16b} normal coordinates. The first two of these two are primary coordinates for the photodissociation, and the diabatic crossing seams of the three states were calculated and plotted as functions of the two coordinates. The other two coordinates are out-of-plane ring distortion modes studied to assess the extent of their role in coupling the states near the first conical intersection, and the ν_{16a} mode was shown to be an important coupling mode there. The current study is the first step toward a detailed mechanistic analysis of the photoinduced S-H fission process of thiophenol, a test system to understand 1nπσ*-mediated reactions, at the same time already providing a better understanding of the thiophenol electronic excitations by clarifying the assignment of the experimental results.

It is well known that classical trajectories, even if they are initiated with zero point energy (ZPE) in each mode (trajectories initiated this way are commonly called quasiclassical trajectories) do not maintain ZPE in the final states. The energy of high-frequency modes will typically leak into low-frequency modes or relative translation of subsystems during the time evolution. This can lead to severe problems such as unphysical dissociation of a molecule, production of energetically disallowed reaction products, and unphysical product energy distributions. Here a new molecular dynamics method called extended Hamiltonian molecular dynamics (EHMD) is developed to improve the ZPE problem in classical molecular dynamics. In EHMD, two images of a trajectory are connected by one or more springs. The EHMD method is tested with the Henon-Heiles Hamiltonian in reduced and real units and with a Hamiltonian with quartic anharmonicity in real units, and the method is found to improve zero-point maintenance as intended.

We will soon publish a paper on the calculation and fitting externally correlated coupled potential energy surfaces and surface couplings for the electronically inelastic reaction $OH^* + H_2 \rightarrow H_2O + H$, where * denotes electronic excitation. We used the orbital-based fourfold way for diabatization of adiabatic surfaces computed by XMS-CASPT2.

David R. Yarkony:

Diabatization/Fitting Algorithm

Our algorithm for diabatizing electronic structure developed previously is unique in two respects. It simultaneously fits and diabatizes the *ab initio* adiabatic electronic structure data and uses derivative couplings to define the diabatic representation. This is accomplished by fitting *ab initio* data, energies, energy gradients, and energy difference scaled derivative couplings to construct quasi-diabatic Hamiltonians (H^d). Since the *ab initio* data are obtained from multireference (single and double excitation) configuration interaction (MRCISD) wave functions the local topology of a conical intersections is correctly described. Owing to the importance of CIs in nonadiabatic dynamics our algorithm takes special care to accurately represent the CI seam, using a partially diagonalized representation. The original algorithm, known as SURFGEN, uses a flexible functional form to construct $\mathbf{H}^d$. The use of fit representations, to be distinguished from on the fly methods, enables us to address computational problems that require high accuracy, quantum nuclear dynamics and or long propagation times.

Neural Network based Algorithm

The algorithmic part of our DoE sponsored research has as its goal, in collaboration with Guo, the incorporation Neural Networks (*NN*) into SURFGEN. SURGEN has the advantage that the symmetry-adapted functions used to construct the quasi diabatic representation $\mathbf{H}^d$ can be tailored to the problem at hand. While this is advantageous in controlling the size of the expansion, the choice of additional functions is often not obvious and the construction of an improved expansion can be tedious. In addition, the incorporation of complete nuclear permutation inversion (CNPI) symmetry can be challenging owing to the general product form allowed by SURFGEN.

Neural networks (*NN*s) can ameliorate this situation. The neurons in the m^{th} layer of a feed-forward *NN* have the general form

$$n_{i,q}^{m} = \sum_{j=1}^{S^{m-1}} (w_{i,j}^{m} a_{j,q}^{m-1}) + b_{i}^{m} \quad a_{i,q}^{m} = f^{m}(n_{i,q}^{m}),$$

where **w**, **b** and **f** are the weights and biases (which are fit) and the transfer functions (usually in our work hyperbolic tangents). The $\boldsymbol{a}^0$ are the (flexible) input layer which are user defined, but symmetry adapted

Incorporation of complete nuclear permutation inversion (CNPI) symmetry can significantly reduce the number of parameters which must be fit. The nonlinear character of f^m requires some care. If the inputs $\boldsymbol{a}^0$ are chosen to carry the totally symmetric representation of the CNPI group in question then regardless of the form chosen for f^m the a^m will carry the totally symmetric representation. Then multiplying that result by a function with the appropriate symmetry gives a function of the desired overall symmetry. The matrix elements below illustrate the situation for a two-state problem with electronic states that carry A_1 and $\kappa = A_2$ symmetry of an abelian CNPI group

$$H_{1,1}^{(d)} = NN_1(PIIP) \quad H_{2,2}^{(d)} = NN_2(PIIP)$$
$$H_{1,2}^{(d)} = \sum_i Q_i^k NN_{i+2}(PIIP)$$

Here $NN_i(PIIP)$ is a feed-forward Neural Network based on permutation inversion invariant polynomials.

Applications

We completed the determination of accurate (based exclusively on MRCISD wave functions) coupled diabatic potential energy surfaces for the photodissociation reactions

$C_6H_5OH(X)+hv \rightarrow C_6H_5OH(A) \rightarrow C_6H_5O(X)+H$

$CH_2OH(X)+hv \rightarrow CH_2OH(X,A,B) \rightarrow CH_2O\ (X) + H$, (cis,trans)$HCOH(X) + H$

These accurate surfaces have been used by Guo in full and reduced dimensional quantum nuclear dynamics, described in previous and current reports, to address both practical and conceptual issues, the geometric phase and vector potential, in nonadiabatic quantum chemistry. These combined structure/dynamics studies have appeared as JACS communications and as an Account of Chemical Research.

Hua Guo:

In collaboration with Yarkony, we have devoted much effort to advancing neural network (NN) representations of quasi-diabatic potential energy matrix (PEM). One such approach is to use different NNs for the elements of the PEM, after diabatizaton has already been done. A key issue is the implementation of the permutation symmetry for identical nuclei in the molecular system. The permutation symmetry of individual elements of the PEM is dependent on the system and electronic states involved. For the dissociation of water and ammonia, for example, we have introduced symmetry adaptation based on the permutation invariant polynomial-neural network (PIP-NN) approach. When a PEM element is symmetric under exchange of identical atoms, the PIPs can be directly used as the input of the NN. When a PEM element is antisymmetric, such as those in the off-diagonal position in the NH_3 system, its symmetry adaption can also be based on PIPs, but with an additional multiplicative factor that enforces the antisymmetry. This approach has been demonstrated to be quite accurate. Another approach is based on the simultaneous diabatization-fitting method, which is described above.

We continue to investigate nonadiabatic dynamics in photochemical systems using quantum dynamical methods. One such example is the predissociation of HCO, which has been extensively investigated before. A better resolved experimental study by Zhang (UC Riverside) has recently been carried out, which showed strong oscillations in the CO rotational state distribution. Using the latest diabatic PEM developed by Dawes (Missouri U Sci. and Tech), we have collaborated with Xie (Nanjing U) to provide a quantum mechanical characterization of the predissociation dynamics. Our investigation revealed that the oscillation in the CO product rotational state distribution can be attributed to interference between different dissociation pathways on the ground electronic state potential, facilitated by the isomerization barrier. This system can be likened to Young's double slit experiment, but with a molecular twist. Another example is the photodissociation of hydroxymethyl in the $3p_x$ Rydberg state. Using the diabatic PEM developed by Yarkony, we determined its absorption spectrum with quantum dynamical calculations in all nine degrees of freedom. The agreement with experimental measurement of Riesler (USC) was excellent, which helped to confirm the assignments of the vibronic features and their lifetimes. We have written two reviews on our recent work with Yarkony.

In addition to the nonadiabatic dynamics in photochemical reactions, we have also engaged in theoretical studies of various bimolecular reactions, using quantum mechanical, quasi-classical, and statistical methods. These studies helped us to advance our understanding of kinetics and dynamics of these important prototypical reactions in the gas phase.

Future Plans

We will coordinate our efforts to provide state of the art descriptions of two archetypical nonadiabatic process: (i) methylamine photodissociation

$$CH_3NH_2(\tilde{X})+h\nu \rightarrow CH_3NH_2(2^1A) \rightarrow CH_3NH(\tilde{X})+H, \text{ principal product}$$

$$\rightarrow CH_3 + NH_2(\tilde{X}\ \ \tilde{A}), \text{ minor product}$$

and (ii) $OH(A)+H_2$ collisional quenching.

$$OH(A)+H_2 \rightarrow OH_3 \rightarrow OH(X)+H_2$$

$$\rightarrow H_2O(\tilde{X})+H$$

When excited to its 2^1A state, methylamine undergoes multichannel photodissociation. The N-H bond breaking and C-N bond breaking (thermodynamically favored) channels each have a saddle point and a 1^1A-2^1A conical intersection at lower energy. While the C-N channel minimum energy conical intersection is lower in energy than that in the N-H channel the much higher barrier in the C-N channel precludes access to this efficient quenching channel. Instead it has been suggested that $CH_3 + NH_2(\tilde{X}, \tilde{A})$ is produced indirectly through the N-H breaking conical intersection, via routing.

For the OH_3 system, Truhlar has produced/reported a full 6-dimensional three state coupled PEM based on his 4-fold way diabatization and Yarkony is testing (with help of Guo) his coupled state representation based on his fit and diabatization approach. These disparate approaches will be compared and used in complementary quantum dynamical studies by Guo of this surprisingly challenging archetypical nonadiabatic reaction where for example in the reactive quenching channel the mechanism of H_2O production including the abstraction vs insertion ratio has yet to be explained.

Donald G. Truhlar

We will also finish a set of diabatic potential energy surfaces for electronically nonadiabatic photodissociation of methylamine, for which we are using orbital-free DQ diabatization. The fitting is based on extending the anchor points reactive potential method to include more primary coordinates and reactive molecular mechanics. We will complete the fitting of the surfaces and couplings, and we will perform semiclassical dynamics simulations of the electronically nonadiabatic processes by the CSDM method. These calculations will include electronically adiabatic and electronically nonadiabatic tunneling by our recently developed army ants tunneling approximation. We will also provide these surfaces and couplings to Hua Guo for quantum mechanical wave packet calculations.

We will compare semiclassical dynamics calculations on the OH_3 system to quantum wave packet calculations of Guo.

We are working on new orbital-fee diabatization schemes that use the nonadiabatic coupling vectors as input.

We also propose to further develop the dual-functional Tamm-Dancoff approximation.

David R. Yarkony

In the coming performance period we, working with Guo, will continue to develop our neural network version of SURFGEN, incorporating parallel computing techniques to reduce the time to solution while increasing the size of the systems that are tractable.

We will compare our coupled diabatic PESs for OH_3 and CH_3NH_2 (currently being tested by Guo) with those produced by Truhlar's group. We will work with Guo to study the quantum dynamics of methylamine photodissociation and of OH(A)+H_2 collisional quenching.

Hua Guo

We plan to devote our future effort in the next year to the elucidation of the H_2 + OH(A) reaction, which can lead to the non-reactive H_2 + OH(X) channel (quenching of OH(A)) and the reactive H + H_2O channel, using both the PEMs recently developed by Truhlar and Yarkony.

Another system we plan to work on is the photodissociation of methylami ne (CH_3NH_2), for which PEMs are being developed by Truhlar and Yarkony. This molecule bears some similarity with the more extensively investigated NH3 system. The initial step is to determine the absorption spectrum for CH_3NH_2 and its deuterated isotopomers. This will be followed by quantum dynamics of the dissociation.

Grant Number and Grant Title

“Nonadiabatic Photochemistry,” PI: Hua Guo, Co-PIs: David Yarkony, Donald G. Truhlar; Grant No. DE-SC0015997

Postdoctoral associates, Mar. 2018-Mar 2019: Yinan Shu (UMN), Changjian Xie (UNM) Christopher Malbon (JHU), Yuchen Wang (JHU).

Graduate students, Mar. 2018-Mar 2019: Kelsey A. Parker (UMN), Siriluk Kanchanakungwankul (UMN), Erik Hoy (JHU), Guan, Yafu (JHU)

Selected recent publications acknowledging this grant[1-26]

1. Hu, S.-X.; Li, W.-L.; Lu, J.-B.; Bao, J. L.; Yu, H. S.; Truhlar, D. G.; Gibson, J. K.; Marçalo, J.; Zhou, M.; Riedel, S., et al. On the Upper Limits of Oxidation States in Chemistry, *Angew. Chem. Int. Ed.* **2018,** *57*, 3242-3245.

2. Gao, L. G.; Zheng, J.; Fernández-Ramos, A.; Truhlar, D. G.; Xu, X. Kinetics of the methanol reaction with OH at interstellar, atmospheric, and combustion temperatures, *J. Am. Chem. Soc.* **2018,** *140*, 2906-2918.

3. Shu, Y.; Truhlar, D. G. Improved potential energy surfaces of thioanisole and the effect of upper surface variations on the product distribution upon photodissociation, *Chem. Phys.* **2018,** *in press*.

4. Xing, L.; Bao, J. L.; Wang, Z.; Wang, X.; Truhlar, D. G. Hydrogen shift isomerizations in the kinetics of the second oxidation mechanism of alkane combustion. Reactions of the hydroperoxypentylperoxy OOQOOH radical, *Combus. Flame* **2018,** *197*, 88-101.

5. Zhang, L.; Truhlar, D. G.; Sun, S. Electronic spectrum and characterization of diabatic potential energy surfaces for thiophenol, *Phys. Chem. Chem. Phys.* **2018,** *20*, 28144-28154.

6. Shu, Y.; Dong, S. S.; Parker, K. A.; Bao, J. L.; Zhang, L.; Truhlar, D. G. Extended Hamiltonian molecular dynamics: semiclassical trajectories with improved maintenance of zero point energy, *Phys. Chem. Chem. Phys.* **2018,** *20*, 30209-30218.

7. Xing, L.; Bao, J. L.; Wang, Z.; Wang, X.; Truhlar, D. G. Relative rates of hydrogen shift isomerizations depend strongly on multiple-structure anharmonicity, *J. Am. Chem. Soc.* **2018,** *140*, 17556-17570.

8. Bao, J. L.; Truhlar, D. G. Effect of energy dependence of the density of states on pressure-dependent rate constants, *Phys. Chem. Chem. Phys.* **2018,** *20*, 30475-30479.

9. Long, B.; Bao, J. L.; Truhlar, D. G. Kinetics of the strongly correlated $CH_3O + O_2$ reaction: The importance of quadruple excitations in atmospheric and combustion chemistry, *J. Am. Chem. Soc.* **2019,** *141*, 611-617.

10. Zhang, R. M.; Truhlar, D. G.; Xu, X. Kinetics of the toluene reaction with OH radical, *Research* **in press**.

11. Shu, Y.; Kryven, J.; Oliveira-Filho, A. G. S. d.; Mielke, S. L.; Song, G.-L.; Li, S. L.; Meana-Pañeda, R.; Fu, B.; Bowman, J. M.; Truhlar, D. G. Direct diabatization and analytic representation of coupled potential energy surfaces and couplings for the reactive quenching of the excited $^2\Sigma^+$ state of OH by molecular hydrogen, *J. Chem. Phys.* **submitted**.

12. Caracciolo, A.; Lu, D.; Balucani, N.; Vanuzzo, G.; Stranges, D.; Wang, X.; Li, J.; Guo, H.; Casavecchia, P. Combined experimental–theoretical study of the $OH + CO \rightarrow H + CO_2$ reaction dynamics, *J. Phys. Chem. Lett.* **2018,** *9*, 1229-1236.

13. Li, J.; Guo, H. Thermal rate coefficients and kinetic isotope effects for the reaction $OH + CH_4 \rightarrow$

$H_2O + CH_3$ on an ab initio-based potential energy surface, *J. Phys. Chem. A* **2018,** *122*, 2645-2652.

14. Liu, X.; Xie, C.; Guo, H. A new potential energy surface and state-to-state quantum dynamics of the $\mathrm{Li} + \mathrm{HF} \rightarrow \mathrm{H} + \mathrm{LiF}$ reaction, *Chem. Phys.* **2018,** *509*, 66-71.

15. Zhao, B.; Manthe, U.; Guo, H. Fermi resonance controlled product branching in the H + HOD reaction, *Phys. Chem. Chem. Phys.* **2018,** *20*, 17029-17037.

16. Ndengué, S.; Dawes, R.; Gatti, F.; Guo, H. Influence of Renner–Teller coupling between electronic states on H + CO inelastic scattering, *J. Phys. Chem. A* **2018,** *122*, 6381-6390.

17. Xie, C.; Zhu, X.; Yarkony, D. R.; Guo, H. Permutation invariant polynomial neural network approach to fitting potential energy surfaces. IV. Coupled diabatic potential energy matrices, *J. Chem. Phys.* **2018,** *149*, 144107.

18. Han, S.; Xie, D.; Guo, H. Modified Gaussian wave packet method for calculating initial state wave functions in photodissociation, *J. Chem. Theo. Comput.* **2018,** *14*, 5527-5534.

19. Xie, C.; Liu, X.; Guo, H. State-to-state quantum dynamics of the $\mathrm{H} + \mathrm{LiF} \rightarrow \mathrm{Li} + \mathrm{HF}$ reaction on an accurate ab initio potential energy surface, *Chem. Phys.* **2018,** *515*, 427-433.

20. Han, S.; Zheng, X.; Ndengué, S.; Song, Y.; Dawes, R.; Xie, D.; Zhang, J.; Guo, H. Dynamical interference in the vibronic bond breaking reaction of HCO, *Sci. Adv.* **2019,** *5*, eaau0582.

21. Zuo, J.; Chen, Q.; Hu, X.; Guo, H.; Xie, D. Dissection of the multichannel reaction of acetylene with atomic oxygen: from the global potential energy surface to rate coefficients and branching dynamics, *Phys. Chem. Chem. Phys.* **2019,** *21*, 1408-1416.

22. Xie, C.; Malbon, C. L.; Guo, H.; Yarkony, D. R. Up to a sign. The insidious effects of energetically inaccessible conical intersections on unimolecular reactions, *Acc. Chem. Res.* **2019,** *52*, 501-509.

23. Yarkony, D. R.; Xie, C.; Zhu, X.; Wang, Y.; Malbon, C. L.; Guo, H. Diabatic and adiabatic representations: Electronic structure caveats, *Comput. Theo. Chem.* **2019,** *1152*, 41-52.

24. Lu, D.-d.; Xie, C.-j.; Li, J.; Guo, H. Rate coefficients and branching ratio for multi-channel hydrogen abstractions from CH_3OH by F, *Chin. J. Chem. Phys.* **2019,** *32*, 84-88.

25. Xie, C.; Malbon, C. L.; Xie, D.; Yarkony, D. R.; Guo, H. Nonadiabatic dynamics in photodissociation of hydroxymethyl in the $3^2A(3p_x)$ Rydberg state: A nine-dimensional quantum study, *J. Phys. Chem. A* **2019,** *123*, 1937-1944.

26. Guan, Y.; Zhang, D. H.; Guo, H.; Yarkony, D. R. Representation of coupled adiabatic potential energy surfaces using neural network based quasi-diabatic Hamiltonians: $1,2\ ^2A'$ states of LiFH, *Phys. Chem. Chem. Phys.* **2019,** *in press*.

Accurate wave functions expressed as polynomial product states

Gustavo E. Scuseria

Rice University, Houston, Texas, USA

`guscus@rice.edu`

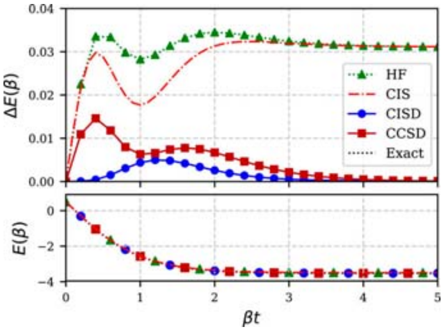
Program Scope

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 near 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.

We are exploring novel routes 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. Major progress was made in our group during the past few years understanding symmetry coherent states as non-exponential polynomials of particle-hole excitations that permeate the entire Hilbert space of the problem. These collective excitations are non-negligible and factorize (non-exponentially) from lower order ones, so their accurate treatment is plausible.

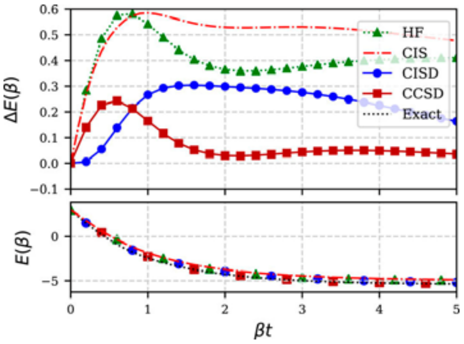
Recent Progress

A recent publication [9] summarizes our progress on the polynomial product state (PPS) front. On a separate topic, we have become interested on extending wave function correlated methods to finite temperature. Thermofield dynamics has proven to be a very useful theory in high-energy physics, particularly since it permits the treatment of both time and temperature-dependence on an equal footing. In recent work [10], we have shown that it also has an excellent potential for studying thermal properties of electronic systems in physics and chemistry. We have described a general framework for constructing finite temperature correlated wave function methods typical of ground state approaches. Our method yields an imaginary time Schrödinger equation, which we solve following a "covariant" approach. Details of the theory and benchmark results for the Hubbard model are presented below and in [10].



Left: Internal energy and error in thermal HF, covariant CIS, CISD, and CCSD for the 2-site Hubbard model with U/t = 1 at half filling on average.

Right: Same for 6-site Hubbard model with U/t = 2 at half filling on average.



Future Plans

We are developing a finite temperature coupled cluster theory based on thermofield dynamics. On the PPS front, we have become interested in geminal theories based on number-projected BCS states, also known as antisymmetrized geminal power (AGP) state in quantum chemistry.

Grant Number and Grant Title

DE-FG02-09ER16053 Computational and Theoretical Chemistry
Accurate Wave Functions Expressed as Polynomial Product States

Personnel

Gaurav Harsha (Graduate Student, 100%), John Gomez (Graduate Student, 100%)

Ten Publications Acknowledging this Grant

1. Composite fermion-boson mapping for fermionic lattice models, J. Zhao, C. A. Jiménez-Hoyos, G. E. Scuseria, D. Huerga, J. Dukelsky, S. M. A. Rombouts, and G. Ortiz, *J. Phys.: Condens. Matt*. **26,** 455601 (2014). http://stacks.iop.org/0953-8984/26/455601

2. 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). http://link.aps.org/doi/10.1103/PhysRevB.92.085101

3. Merging symmetry projection methods with coupled cluster theory: Lessons from the Lipkin model Hamiltonian, J. M. Wahlen-Strothman, T. M. Henderson, M. R. Hermes, M. Degroote, Y. Qiu, J. Zhao, J. Dukelsky, and G. E. Scuseria, J. Chem. Phys. **146**, 054110 (2017). http://scitation.aip.org/content/aip/journal/jcp/146/5/10.1063/1.4974989

4. Semilocal exchange hole with an application to range-separated density functionals, J. Tao, I. W. Bulik, and G. E. Scuseria, *Phys. Rev B* **95**, 125115 (2017). http://link.aps.org/doi/10.1103/PhysRevB.95.125115

5. Projected Hartree-Fock as a polynomial of particle-hole excitations and its combination with variational coupled cluster theory, Y. Qiu, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **146**, 184105 (2017). http://dx.doi.org/10.1063/1.4983065

6. Combining symmetry collective states with coupled cluster theory: Lessons from the Agassi model Hamiltonian, M. R. Hermes, J. Dukelsky, and G. E. Scuseria, *Phys. Rev*. **C 95,** 064306 (2017). http://link.aps.org/doi/10.1103/PhysRevC.95.064306

7. Spin-projected generalized Hartree-Fock as a polynomial of particle-hole excitations, T. M. Henderson and G. E. Scuseria, *Phys. Rev*. **A 96**, 022506 (2017). https://link.aps.org/doi/10.1103/PhysRevA.96.022506

8. On the difference between variational and unitary coupled cluster theories, G. Harsha, T. Shiozaki, and G. E. Scuseria, *J. Chem. Phys*. **148**, 044107 (2018). https://doi.org/10.1063/1.5011033

9. Polynomial-Product States: A Symmetry-Projection-Based Factorization of the Full Coupled Cluster Wavefunction in Terms of Polynomials of Double Excitations, J. A. Gomez, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **150**, 144108 (2019). https://doi.org/10.1063/1.5085314

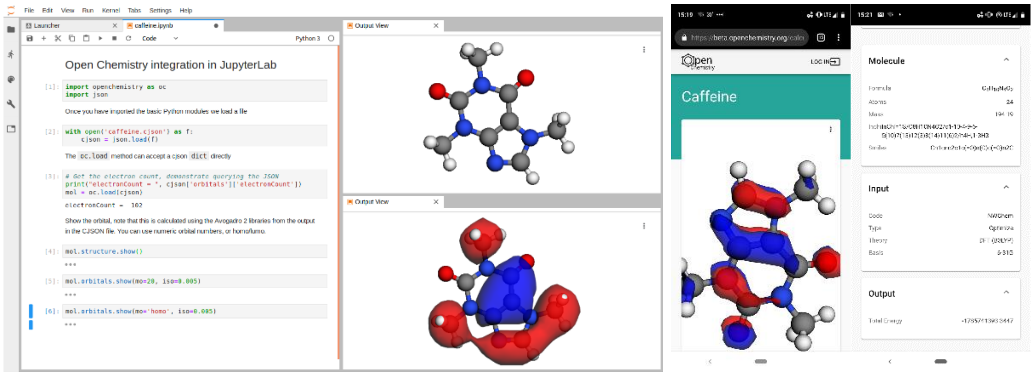
10. Thermofield Theory for Finite-Temperature Quantum Chemistry, G. Harsha, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys*. **150**, 154109 (2019). https://doi.org/10.1063/1.5089560

Open Chemistry, Jupyter and Data: Reproducible Quantum Chemistry

Marcus D. Hanwell[1], Wibe A. de Jong[2], and Johannes Hachmann[3]
1. Kitware, Inc., 2. Lawrence Berkeley National Laboratory, 3. SUNY Buffalo

Abstract

The Open Chemistry project is developing an ambitious platform to facilitate reproducible quantum chemistry workflows. It has integrated best of breed open source projects currently available in a cohesive platform that features extensions specific to the needs of quantum chemistry. The core of the project is a Python-based data server capable of storing metadata, executing quantum codes, and processing the output. The use of RESTful endpoints enable language agnostic interfaces to all capabilities, with Linux container technologies offering a solution to reproducible binary payloads that can be reproducibly executed and versioned.



Open Chemistry integration in JupyterLab

```
[1]: import openchemistry as oc
     import json
```

Once you have imported the basic Python modules we load a file

```
[2]: with open('caffeine.cjson') as f:
         cjson = json.load(f)
```

The `oc.load` method can accept a cjson `dict` directly

```
[3]: # Get the electron count, demonstrate querying the JSON
     print("electronCount = ", cjson['orbitals']['electronCount'])
     mol = oc.load(cjson)

     electronCount =  102
```

Show the orbital, note that this is calculated using the Avogadro 2 libraries from the output in the CJSON file. You can use numeric orbital numbers, or homo/lumo.

```
[4]: mol.structure.show()
     ...
[5]: mol.orbitals.show(mo=20, iso=0.005)
     ...
[6]: mol.orbitals.show(mo='homo', iso=0.005)
     ...
```

Caffeine

Molecule

Formula $C_8H_{10}N_4O_2$
Atoms 24
Mass 194.19

Input

Code NWChem
Type Optimize
Theory DFT (B3LYP)
Basis 6-31G

Output

Total Energy

The Jupyter project has been extended to offer a web-based frontend where reproducible workflows are core to the platform. This has been coupled with a data server capable of executing codes and machine learning models on supercomputers, the cloud, and local hardware. The data server can cache results, search previous data, and offer simple views of data artifacts produced as notebooks are executed. Several libraries including Avogadro, Open Babel, cclib, and RDKit have been used to provide capabilities exposed. The data server has a single-page interface offering a unique web link for a given record/visualization that reuses the same web components displayed in the JupyterLab cells. Exporting data to the Binder platform has been demonstrated, the above images show the Binder export along with responsive pages being rendered on a cell phone showing simulation output produced by a notebook.

NWChem, Psi4, and machine learning models have been demonstrated on the platform, with plans for more. A simple container-based interface has been established, making it easy to add new codes to the platform without editing any server code. The development of JSON data standards, along with simple execution strategies, will enable the wide reuse of the data server. The use of Docker, Singularity, and Shifter offer a wide range of deployment options. Phase II focuses on developing a software platform focusing on five major areas: data/metadata, server platform, Jupyter integration, web application, and extending desktop/command-line tools to interact with the server.

Grant title: Open Interactive Data Analytics Platform for Chemical-Physics Simulations and Experiments

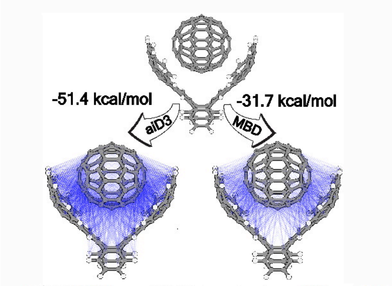
Grant number: DE-SC0017193

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

John M. Herbert (herbert@chemistry.ohio-state.edu)
Dept. of Chemistry & Biochemistry, The Ohio State University, Columbus, OH 43210

Abstract

Project Scope



$$E_{\text{int}}^{\text{XSAPT+MBD}} = E_{\text{int}}^{\text{SAPT}}(\text{disp-free}) + E_{\text{pol}}^{\text{MB}} + E_{\text{disp}}^{\text{MB}}$$

This project aims to develop and implement new fragment-based quantum chemistry algorithms for accurate yet efficient calculation of non-covalent interactions and, separately, energy transport in large systems composed of "soft" materials, *e.g.*, liquids, molecular crystals and aggregates, or organic semiconductors. These methods are tailored towards applications that require quantitative description of intermolecular interaction energies, and to semi-quantitative calculation of excitation energies and energy-transport properties in organic semiconductors. The natural parallelizability provided by the fragment-based approach makes these methods amenable to large systems. We have, for example, demonstrated proof-of-principle calculations of excitation energy transfer in a 150-chromophore model of an organic semiconductor nanotube, a calculation that would involve the equivalent of more than 50,000 Gaussian basis functions if carried out using traditional methods. DFT-quality energetics in proteins with > 1,100 atoms have also been demonstrated, while requiring no single calculation larger than four amino acids.

Recent Progress

A major result of this project has been the development of an "extended" version of symmetry-adapted perturbation theory (SAPT) that we call "XSAPT". This method extends traditional SAPT to many-body systems, *i.e.*, those containing more than two monomers. A self-consistent charge embedding is used to incorporate many-body polarization effects, and the method generalizes the usual SAPT energy decomposition scheme, so that intermolecular (non-covalent) interaction energies can be partitioned into physically-meaningful components. In the past year we have been working on incorporating *many-body* dispersion, going beyond the pairwise atom–atom $-C_6/R^6$ approximation. This is crucially important for large systems, such as the $C_{60}@C_{60}H_{28}$ "buckycatcher" complex that is shown in the figure. For this and other complexes involving similarly large monomer units, we found that our previously-developed XSAPT+*ai*D3 approach, involving *ab initio* dispersion potentials of the $-C_6/R^6$ form, affords much larger errors as compared to the same method in smaller systems. As such, we have developed a version of the Tkatchenko-Scheffler "many-body dispersion" (MBD) method that works with XSAPT. The new XSAPT+MBD method affords ~1 kcal/mol accuracy against the best-available CCSD(T) benchmarks for large supramolecular complexes, or ~4 kcal/mol against solution-phase, experimental binding affinities that are back-corrected to the gas phase. At the same time, we have significantly improved the efficiency and parallelization of our implementation, so that calculations with 5,000–6,000 basis functions can be run in ~6 hours on a single compute node.

Future Plans

In previous work we have developed a well-defined way to separate polarization and charge-transfer energies in energy decomposition analysis. Our approach uses constrained DFT to define a charge-transfer-free reference state, and the result is a definition of charge transfer that is stable with respect to expansion of the one particle basis set, whereas other definitions (going all the way back to Kitaura-Morokuma analysis) manifestly are not. In applying this methodology to understand non-covalent interactions in open-shell complexes such as the $[C_6H_6\cdots C_{10}H_8]^+$ cation dimer, questions arose about whether the interactions were primarily dispersion-driven (which is the XSAPT+*ai*D3 prediction) or charge-transfer-driven (which is the prediction of other competing energy decomposition analyses). Now that we have a new way to compute the dispersion that is closer to a first-principles approach (but which so far is qualitatively consistent with *ai*D3), we are prepared to revisit this issue. We are also starting to work towards definitions of dispersion that are valid in electronically excited states. This will allow us to address the common understanding that excited states ought to exhibit larger dispersion interactions as compared to the ground state (because the excited-state wave function is more polarizable) but also larger Pauli repulsion interactions (because the excited-state wave function is larger). Accurate energy decomposition analysis in the excited state will help with force field parameterization, since we know that van der Waals parameters ought to change upon molecular excitation but it is unclear what data should be used to fit such parameters.

Grant Numbers and Grant Titles

DE-SC0008550 Fragment-Based Quantum Chemistry for Non-Covalent Interactions and Excitation Energy Transfer

Student(s): Adrian F. Morrison, Kuan-Yu Liu, Kevin Carter-Fenk

Publications

1. K. Carter-Fenk, K. U. Lao, K.-Y. Liu, and J. M. Herbert, *Accurate and efficient* ab initio *calculations for supramolecular complexes: Symmetry-adapted perturbation theory with many-body dispersion.* Journal of Physical Chemistry Letters **10**, 2706 (2019).
2. A. F. Morrison, E. Epifanovsky, and J. M. Herbert, *Double-buffered, heterogeneous CPU + GPU integral digestion algorithm for single-excitation calculations involving a large number of excited states.* Journal of Computational Chemistry **39**, 2173 (2018).
3. K. U. Lao and J. M. Herbert, *A simple correction for nonadditive dispersion within extended symmetry-adapted perturbation theory (XSAPT).* Journal of Chemical Theory and Computation **14**, 5128 (2018).
4. K. U. Lao and J. M. Herbert, *Atomic orbital implementation of extended symmetry-adapted perturbation theory (XSAPT) and benchmark calculations for large supramolecular complexes.* Journal of Chemical Theory and Computation **14**, 2955 (2018).
5. K.-Y Liu and J. M. Herbert, *Understanding the many-body expansion for large systems. III. Critical role of four-body terms, counterpoise corrections, and cutoffs.* Journal of Chemical Physics **147**, 161729 (2017).
6. A. F. Morrison and J. M. Herbert, *Analytic derivative couplings and first-principles exciton/phonon coupling constants for an* ab initio *Frenkel-Davydov exciton model: Theory, implementation, and application to compute triplet exciton mobility parameters for crystalline tetracene.* Journal of Chemical Physics **146**, 224110 (2017).
7. A. F. Morrison and J. M. Herbert, *Evidence for singlet fission driven by vibronic coherence in crystalline tetracene.* Journal of Physical Chemistry Letters **8**, 1442 (2017).

8. J. M. Herbert, X. Zhang, A. F. Morrison, and J. Liu, *Beyond time-dependent density functional theory using only single excitations: Methods for computational studies of excited states in complex systems.* Accounts of Chemical Research **49**, 931 (2016).
9. K. U. Lao, K.-Y. Liu, and J. M. Herbert, *Understanding the many-body expansion for large systems. II. Accuracy considerations.* Journal of Chemical Physics **144**, 164105 (2016).
10. 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).

A Unified Low-Rank Formulation of Coupled-Cluster Theory

Yao Zhao, Edward G. Hohenstein

Department of Chemistry and Biochemistry, City College of New York

Ph.D. Program in Chemistry, The Graduate Center of the City University of New York

SLAC National Accelerator Laboratory

Abstract

The overarching goal of this project is the development of reduced-scaling coupled-cluster methods. Our approach is the introduction of low-rank tensor factorizations to the electron repulsion integrals as well as the amplitudes defining the coupled-cluster wavefunction. We have developed a reformulation of coupled-cluster theory in terms of low-rank tensors by starting from the coupled-cluster energy functional that typically appears in the definition of coupled-cluster properties. Recently, we have applied this idea to ground-state coupled-cluster singles and doubles (CCSD) in an approach we refer to as rank-reduced CCSD (RR-CCSD). Here, the usual coupled-cluster amplitudes are projected into a reduced space where the usual CCSD equations are solved. We have shown that this approach can be applied while maintaining accurate correlation energies (see Figure 1), reducing the storage requirements of the doubles amplitudes from $O(N^4)$ to $O(N^2)$, and allowing certain contributions to the CCSD amplitudes equations to be implemented more efficiently (including the term involving contributions from the four-virtual index integrals). Work is currently underway to extend this approach to excited states via equation-of-motion CCSD (EOM-CCSD), to incorporate an approximate treatment of triple excitations, and to develop a high performance implementation.

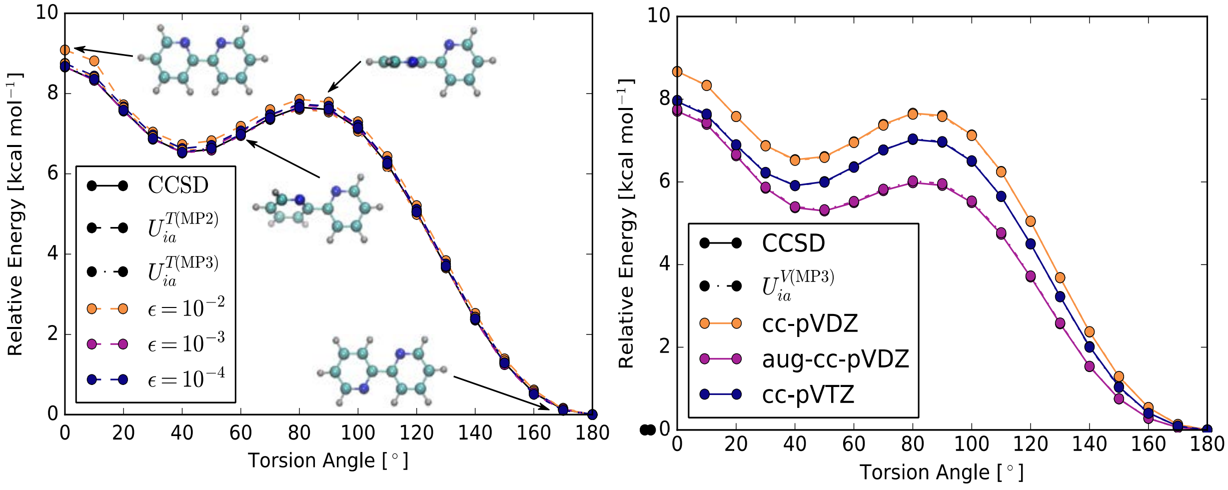


Figure 1. Accuracy of RR-CCSD for the torsional potential of bipyridine using various projectors in a cc-pVDZ basis (left). RR-CCSD using an MP3 derived projector with an eigenvalue cutoff of 10^{-3} evaluated in several basis sets (right).

We have begun to extend the ideas of RR-CCSD to RR-EOM-CCSD. In this case, the starting point is the EOM-CCSD energy functional and low-rank approximations for the left and right linear excitaiton amplitudes are applied. This provides a straightforward approach to the solution of the EOM-CCSD eigenvalue problem in a compressed space. Preliminary results (see Figure 2) suggest that sufficient accuracy (better than 0.01 eV) can be achieved with hundredfold compression of the linear doubles amplitudes. Our formulation rigorously preserves size intensivity of the EOM-CCSD excitation energies. The RR-EOM-CCSD excited states can be determined with O(N^5) effort by optimally exploiting the low-rank factorization of the doubles amplitudes and work is underway to develop a fully optimized implementation of this method.

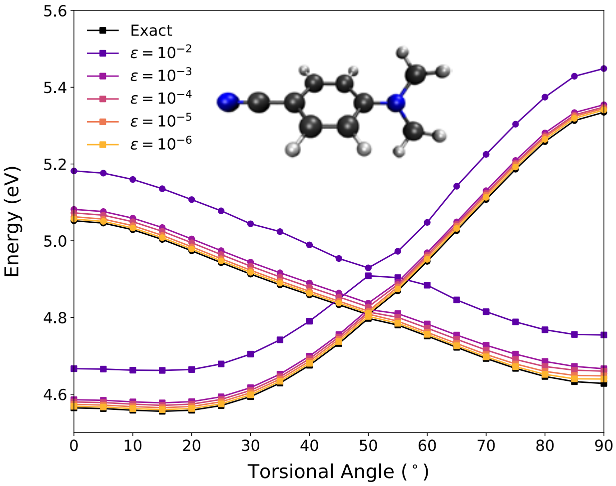


Fig. 2. Torsional potential of the S_1 and S_2 excited electronic states of 4-(dimethylamino) benzonitrile (DMABN) computed at the EOM-CCSD/cc-pVDZ level of theory. Decreasing cutoffs, ε, on the doubles amplitude eigenvalues are applied.

In addition to CCSD and EOM-CCSD, we are also persuing rank-reduced formulations of triples corrections to CCSD. In this context, we are using the Tensor HyperContraction (THC) representation of the electron repulsion integrals and CCSD amplitudes. We have developed pilot implementation of the perturbative triples corrections to CCSD, CCSD(T), that scales with the fifth-power of system size, O(N^5), instead of its usual O(N^7) scaling. Further, we are applying similar ideas to the approximate coupled-cluster singles, doubles and triples method, CC3. In this case, the triples contributions in the CC3 method are evaluated with O(N^5) scaling, while the remaining terms (i.e. the usual CCSD equations) are evaluated as usual in O(N^6) time. These approaches offer the promise to make triples corrected methods as efficient as the underlying CCSD. While considerable effort will be devoted to the optimization of these pilot implementations over the next few years, we have found that our THC-CC3 implementation is already more efficient than the canonical CC3 implementation in the PSI4 program when systems with more than 15 atoms are considered.

Grant Numbers and Grant Titles: FWP#100384: SciDAC: Designing Photocatalysts Through Scalable Quantum Mechanics and Dynamics

Student(s): Yao Zhao

Publications:

"Rank reduced coupled cluster theory. I. Ground state energies and wavefunctions," R.M. Parrish, Y. Zhao, E.G. Hohenstein, and T.J. Martínez, *J. Chem. Phys.* **150**, 164118 (2019).

Improved Methods for Modeling Functional Transition Metal Compounds in Complex Environments: Ground States, Excited States, and Spectroscopies

Hrant P. Hratchian (PI, hhratchian@ucmerced.edu), Christine M. Isborn (cisborn@ucmerced.edu), Aurora Pribram-Jones (apribram-jones@ucmerced.edu), Liang Shi (lshi4@ucmerced.edu), and David A. Strubbe (dstrubbe@ucmerced.edu)

University of California, Merced, 5200 N. Lake Rd., Merced, CA 95343

Abstract

Rapid advances in energy applications require new theory and computational models to provide guidance for interpretation of experimental results and mechanistic understanding. New theory development is necessary to treat systems of increasing complexity, size, and relevance to real applications. Functional transition metal compounds, including molecules, clusters, nanoparticles, surfaces, and solids, provide particular promise for magnetic, optical, and catalytic applications. However, such systems can be exceptionally challenging to model. To make progress in understanding and designing transition metal compounds for energy applications, theory must be able to simulate such systems in complex environments, as well as simulate the spectra of such complex systems to provide direct connections with experiment. Leveraging the independent expertise of the team's members, this project will make inroads to the theoretical and computational challenges associated with studying transition metal compounds, their reaction chemistry, photophysics and photochemistry, and response to spectroscopic interrogation. The team's recent work is focused on developing spin-flip (SF) Bethe-Salpeter Equation method (BSE) and understanding the role of the environment in models of two-dimensional electronic spectroscopy (2DES).

The SF method allows for description of multi-reference states by considering excitations of a single high-spin reference state. It was originally developed for use with wavefunction-based approaches such as equation-of-motion coupled-cluster (EOMSF-CC or SF-CC) and configuration interaction (SF-CI), and later extended for use with the density-functional-based linear-response approach of time-dependent density-functional theory (SF-TDDFT). SF-TDDFT, SF-CI, and SF-CC approaches have been used to describe the energies of various electronic states of open- and closed-shell atoms and molecules. While SF-TDDFT is significantly less computationally expensive than SF-CI and SF-CC, it has difficulty describing Rydberg states and bond-breaking due to the necessary approximations intrinsic to conventional functionals. A method from condensed-matter physics, the GW/BSE approach, is akin to TDDFT but with an ab initio long-ranged and non-local interaction kernel, which allows for an improvement of excited-state energies. We consider a spin-flip BSE (SF-BSE) approach, which has a more moderate expense than SF-CC and can be used also for extended systems. The proper derivation of SF-BSE from many-body perturbation theory necessitates

careful treatment of the spin-coupling between electron-hole excitations and the high-spin reference state. We present the theory of SF-BSE and apply it to simple molecular examples of bond-breaking and unpaired spins. This approach will enable calculations on open-shell transition metal complexes with applications for catalysis and quantum information, and be extensible to condensed phase systems like open-shell defects in nanostructures or solids.

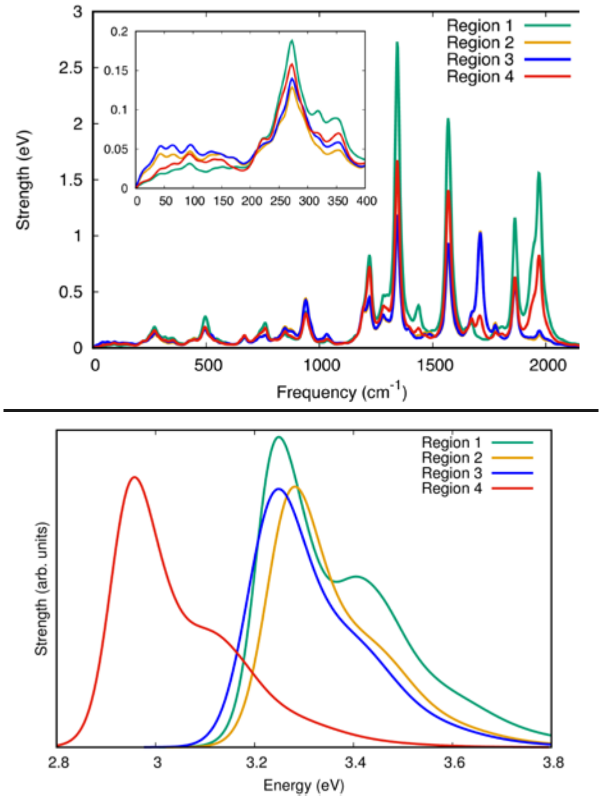


Figure 1. Computed spectral densities (top) and accompanying linear absorption spectra (bottom) show large changes when treating more of the environment quantum mechanically for a chromophore embedded in a protein environment. Work is underway exploring how spectral density changes affect relaxation rate and two-dimensional electronic spectra of various condensed phase

To probe and simulate ultrafast relaxation of electronic excited states, work is underway to develop techniques and best practices for modeling two-dimensional electronic spectroscopy (2DES) based on the cumulant expansion. We are exploring how different condensed phase models affect the spectral density and the resulting linear and 2D electronic spectra. Our preliminary results on a chromophore embedded in a protein show that solvent polarization can strongly affect the couplings between electronic excitation and vibrations as manifested in the computed spectral densities (see the top panel of Fig. 1). When more of the environment is treated quantum mechanically, some peaks in the spectral density may be enhanced or suppressed, leading to significant changes of the vibronic features in the linear absorption spectra (see the bottom panel of Fig. 1). The solvent polarization effects on the spectral density and optical spectra vary with the nature of the chromophore and the solvent. Our initial results (see Figure) suggest that the quantum mechanical treatment of the environment plays a key role in controlling the spectral density and will likely also be key to accurately modeling 2DES.

In the next year, the ccCAT team will continue advances in the development and application of SF-BSE and related models and will pursue improved simulation of two-dimensional electronic spectroscopy. We will also see progress in our design of new ground state models for addressing spin-contamination in TD-DFT and SF-BSE calculations, some of which will build on implementation and formal development of ensemble DFT for ground and excited electronic states.

Grant Number and Title

DE-SC0019053. Improved Methods for Modeling Functional Transition Metal Compounds in Complex Environments: Ground States, Excited States, and Spectroscopies.

Postdocs: Bradford Barker and Hector Corzo

Publications

While initial manuscripts are currently in preparation and under review, none have yet appeared in-press.

Genetic Algorithms for Rapid Molecular Materials Screening

Geoffrey R. Hutchison

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260
geoffh@pitt.edu

Abstract

Program Scope

This project will develop efficient genetic algorithm (GA) methods for rapid computational screening of conjugated polymers and oligomers with optimal photovoltaic, dielectric, piezoelectric, and other properties. We hypothesize that improved genetic algorithm screening techniques, combined with accurate electronic structure calculations can efficiently find optimal and near-optimal molecular targets across over 100 billion possibilities. A key promise of organic materials is that using the incredible tailorability of synthetic organic chemistry enables experimental optimization of performance across multiple relevant properties. The fundamental challenge is inverse design: how one finds the molecular or polymer structures with desired properties in the face of a near-infinite (e.g., $>10^{20}$ - 10^{60}) number of possible structures, combined with time-consuming experiments or electronic structure calculations. We have already performed screening for organic photovoltaic targets across sets of 50 million compounds with efficiencies over 8,000 times faster than brute force.

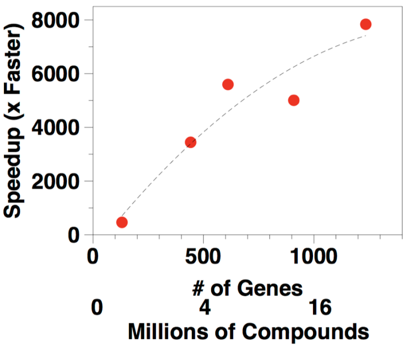


Fig. 1. Speedup from genetic algorithm search for efficient organic photovoltaics.

Recent Progress

Our efforts have focused in two parallel projects: (1) to leverage improvements in machine learning (ML) in chemistry, as fast surrogate methods for computationally-intensive electronic structure methods, for classification to improve GA scaling in massive parallel searches, as well as to accelerate convergence of searches across many generations, and (2) to apply the GA techniques to find interesting molecular species with new properties, including large polarizabilities, high predicted dielectric constants, large electromechanical coupling, and low energy triplet states. Beyond potential technological applications, such targets benefit fundamental science as interesting test cases for electronic structure methods and by providing balanced training and test sets for machine learning beyond typical "drug-like" molecules in current databases.

One current focus is to find molecular targets with large polarizabilities. Molecular polarizabilities are relevant to applications in high dielectric constants for improved charge separation in organic photovoltaics, high capacitance energy storage, and refractive index and nonlinear optics. We have now completed extensive benchmarking of static isotropic molecular polarizabilities, including over 1,100 experimental data points and multiple density functional and *ab initio* methods. By including molecules up to $C_{18}H_{12}$, we find systematic errors in many current electronic structure methods.

Using efficient electronic structure methods, we have generated large (~3.4 million compounds) diverse data sets of molecular static polarizabilities for atomistic machine learning methods. In turn, these ML methods feed the genetic algorithm search, which have uncovered new targets with high polarizability per unit volume and thus high predicted dielectric constants.

Future Plans

We are currently working on the use of clustering algorithms and ML classifiers to enable divide-and-conquer parallel search approaches to handle vast search spaces (>100 million compounds) as well as new applications of our genetic algorithm searches. Such properties include compounds with low Marcus reorganization energies for efficient charge transport, non-fullerene acceptors for multi-chromaphore organic photovoltaics, and π-conjugated oligomers with low-lying and ground state triplet states. Molecular targets from all searches will be used to test both current electronic structure methods as well as machine learning strategies as efficient surrogates for accurate electronic structure predictions.

Grant Numbers and Grant Titles

DE-SC0019335 Genetic Algorithms for Rapid Molecular Materials Screening

Student(s): Dakota Folmsbee

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

None so far, project started September 2018

DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION

Christine Isborn[1] (PI), Aurora Clark (co-PI)[2], Thomas Markland (co-PI)[3]
1. University of California Merced, Email: cisborn@ucmerced.edu
2. Washington State University, Email: auclark@wsu.edu
3. Stanford University, Email: tmarkland@stanford.edu

The development of next generation energy conversion and catalytic systems requires 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 energy transfer in the presence of solvent fluctuations. Our team is developing accurate and efficient theoretical models for solution phase reactions. These developments provide an improved understanding of photo-initiated excitations, electron transfer, and proton coupled electron transfer processes. Our research team brings together expertise in electron and nuclear dynamics (classical and quantum), electronic structure, and analysis of solvation networks. We are developing and validating techniques for modeling condensed phase charge and energy transfer and to simulate the methods to monitor them using optical and vibrational spectroscopy.

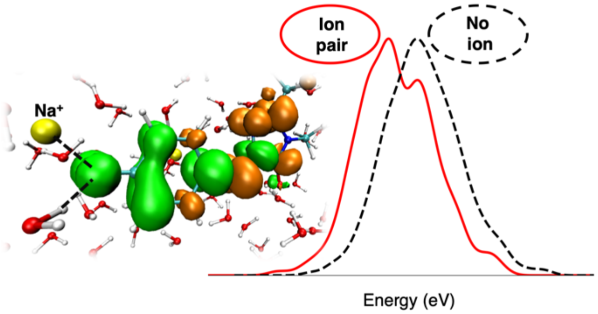


Figure 1: Comparison of the computed absorption spectra for a chromophore in pure water and for contact ion pairs.

EXCITED STATES IN THE CONDENSED PHASE: One of the goals in our group is accurately modeling absorption spectra in complex environments. Reproducing experimental condensed phase spectra serves as a good way to validate the ground state sampling of solute-solvent configurations, the ground and excited state methodology, and the importance of what causes spectral broadening, including lifetime and vibronic effects. By gaining a better understanding of which effects are necessary to reproduce absorption spectra, we will know which effects are important for a correct model of condensed phase reactivity. We have developed a combined ensemble plus vibronic approach to model the absorption spectrum of semi-flexible chromophores in solution that includes full sampling of solute-solvent degrees of freedom at the desired temperature using a large QM region for the calculation of vertical excitation energies, and then combines this ensemble sampling with the zero temperature Franck-Condon vibronic shape function to simulate the vibronic contributions to the spectrum at a particular solvent configuration. This combined approach models the full inhomogeneous broadening of the explicit solvent environment and is also able to reproduce the high-energy tail of the spectrum due to vibronic transitions. We have compared absorption spectra computed from configurations from ab initio molecular dynamics (AIMD) to those including nuclear quantum effects via path integral molecular dynamics (AI-PIMD), finding that the inclusion of nuclear quantum effects broadens the spectrum through three different mechanisms: (i) by softening the heavy-atom bonds of the chromophore that couple strongly to the bright transition, (ii) by creating a more diverse solvation environment, and (iii) by redistributing spectral weight to higher energy vibronic transitions through the formation of stronger hydrogen bonds between the chromophore and the solvent. Recently submitted work analyzes how the presence of ions in solution leads to formation of chromophore-ion pairs that shift and broaden the computed absorption spectrum by disrupting the hydrogen bond network (Figure 1).

Work is underway to explore and develop new methods for simulating absorption spectra that can account for both dynamic effects and explicit solvent / environment effects. We are benchmarking the regimes of validity of various spectral methods: ensemble, harmonic Franck-Condon, our newly developed E-ZTFC approach, and the cumulant expansion at second and third order truncation (Figure 2). Future work entails examining how these methods perform for an anionic chromophore in strongly hydrogen-bonding aqueous solution and extending these techniques for nonlinear spectroscopy.

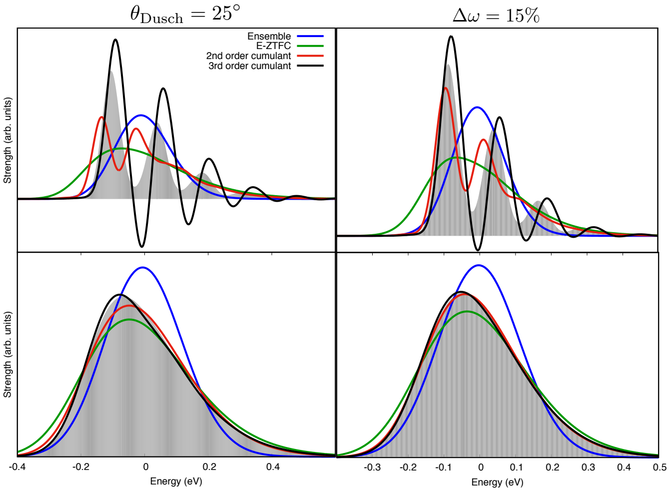


Figure 2: Absorption spectra computed in the ensemble, E-ZTFC, and cumulant approaches for a two-mode generalized Born oscillator model to explore the effects of the Duschinsky rotation θ, change in ground and excited state frequency ω, and weak vs strong coupling to solvent (top vs bottom figures).

ANALYSIS OF PROTON TRANSFER EVENTS IN ACIDIC SOLUTIONS: From the path integral molecular dynamics trajectories produced using the *ab initio* ring polymer contraction approached developed previously in this project it is possible to study the shapes of the ring polymers and examine their behavior as a function of different molecular processes. Specifically, we have examined the changes to the topological homology of the ring polymers of hydrogen atoms that are transferred during proton transfer events versus non-reactive hydrogen atoms within solutions of 4M aqueous HCl. Using persistent homology analysis, events that have all beads within the H-atom ring polymer (32 beads) involved in a proton transfer within a 50 fs winder were found and their persistant homology compared to H-atoms that did not undergo proton transfer. The Betti numbers were then determined and the Wasserstein distance of the two distributions were compared. As observed in Figure 2, there is significantly more variation in the persistence homologies of the H-atoms that are not undergoing proton transfer relative to those actively transitioning from one eigen/zundel to another. This indicates that the ring polymers actively reacting H-atoms have a more consistent "shape" during the reaction event.

EXACT CARTESIAN MAPPING OF FERMIONS FOR INVESTIGATING ELECTRODE PROCESSES: The exact treatment of real time nonadiabatic quantum dynamics in condensed phase chemical systems remains a significant challenge that spurs the ongoing development of approximate methods that are accurate, efficient, and can treat large systems with a wide range of different forms of interactions. Quantum-classical (semiclassical) trajectory-based methods provide some of the most appealing solutions to this problem and offer a hierarchy of approaches with different balances between accuracy and computational cost. We have shown how quantum-classical approaches can be made both more accurate and efficient by combining them with the formally exact quantum master equation framework. This combination of quantum-classical theory and master equation (ME) techniques makes it possible to obtain the accuracy of much more computationally expensive approaches at a cost an order of magnitude lower than even the most efficient trajectory-based approaches, providing the ability to treat the quantum dynamics of atomistic condensed phase systems for long times. Our most recent work has focused on extending the developments of quantum-classical GQME-based dynamics to many-fermion problems where the discrete energy levels are so numerous as to create continua, as is the case for processes near metallic and semiconducting interfaces. To achieve the accuracy benefits from the GQME approach one must have a prescription to generate the initial conditions exactly. In cases where one can write the Hamiltonian in terms of Cartesian positions and momenta, this can usually be achieved straightforwardly using path integral approaches. For Hamiltonians containing discrete states, the Meyer-Miller-Stock-Thoss protocol can be used, however, for those that include fermionic creation and annihilation operators an exact Cartesian mapping has remained elusive. In our recent work, we have therefore derived a rigorous, quantum mechanical map of fermionic creation and annihilation operators to continuous Cartesian variables that exactly reproduces the matrix structure of the many-fermion problem. We have shown how our scheme can be used to map a general many-fermion Hamiltonian and then consider two specific models that encode the fundamental physics of many fermionic systems: the Anderson impurity and Hubbard models. We used these models to demonstrate how efficient mappings of these Hamiltonians can be constructed using a judicious choice of index ordering of the fermions. For example, we have shown how the 1D Hubbard Hamiltonian can be exactly mapped from its usual form in terms of fermionic creation and annihilation operators to an isomorphic form in terms of Cartesian positions and momenta. Most remarkably in this case, by using an appropriate choice of index ordering, one can eliminate the need to treat the nonlocal operator that imposes the fermionic anticommutivity. This development provides an alternative exact route to calculate the static and dynamical properties of fermionic systems and sets the stage to exploit the quantum-classical and semiclassical hierarchies to systematically derive methods offering a range of accuracies, thus enabling the study of problems where the fermionic degrees of freedom are coupled to complex anharmonic nuclear motion and spins which lie beyond the reach of most currently available methods. These extensions should now allow us to simulate the GQME dynamics using memory kernels generated from a wide variety of quantum-classical approaches for large quantum subsystems coupled to fully atomistic environments. These developments are essential for treating problems such as proton coupled electron transfer in solution and at interfaces.

Award Number DE-SC0014437: Development of Approaches to Model Excited State Charge and Energy Transfer in Solution

Up to Ten Publications Acknowledging this Grant

1. Beyond Badger's Rule: the Origins and Generality of the Structure-Spectra Relationship of Aqueous Hydrogen Bonds. *M. A. Boyer, J. P. Heindel, T. E. Markland, A. B. McCoy, and S. S. Xantheas. J. Phys. Chem. Lett., 10, 918-924 (2019)*

2. Unraveling Electronic Absorption Spectra using Nuclear Quantum Effects: Photoactive Yellow Protein and Green Fluorescent Protein Chromophores in Water. *T. J. Zuehlsdorff, J. Napoli, J. Milanese, T. E. Markland, and C. M. Isborn. J. Chem. Phys., 149, 024107 (2018)*

3. On the Exact Continuous Mapping of Fermions. *A. Montoya-Castillo, T. E. Markland. Nature Sci. Rep., 8, 12929 (2018)*

4. The Quest for Accurate Liquid Water Properties from First Principles. *L. R. Pestana, O. Marsalek, T. E. Markland and T. Head-Gordon J. Phys. Chem. Lett., 9, 5009-5016 (2018)*

5. Combining the Ensemble and Franck-Condon Approaches for Calculating Spectral Shapes of Molecules in Solution. *T. J. Zuehlsdorff and C. M. Isborn. J. Chem. Phys. 148, 024110 (2018)*

6. Modeling Absorption Spectra of Molecules in Solution. *T. J. Zuehlsdorff and C. M. Isborn. Int. J. Quant. Chem. e25719. (2018)*

7. Combining Explicit Quantum Solvent with a Polarizable Continuum Model. *M. R. Provorse and C. M. Isborn. J. Phys. Chem. B 121, 10105-10117 (2017)*

8. Convergence of Computed Aqueous Absorption Spectra with Explicit Quantum Mechanical Solvent. *J. M. Milanese, M. R. Provorse, E. Alameda, C. M. Isborn. J. Chem. Theory Comput. 13, 2159-2171 (2017)*

9. Generalized Quantum Master Equations In and Out of Equilibrium: When Can One Win? *A. Kelly, A. Montoya-Castillo, L. Wang and T. E. Markland, J. Chem. Phys. 144, 184105 (2016)*

10. Simulating Nuclear and Electronic Quantum Effects in Enzymes. *L. Wang, C. M. Isborn, and T. E. Markland, Methods in Enzymology, 577, 389-418 (2016)*

The FLO-SIC Center: Progress towards efficient density functional theory calculations without self-interaction

Koblar A. Jackson
Physics Department, Central Michigan University, Mt. Pleasant, MI 48859
jacks1ka@cmich.edu

Abstract

Overview

The goal of FLO-SIC Center is to enable accurate and efficient density functional theory (DFT) calculations that are free of unphysical electron self-interaction, a problem that plagues essentially all DFT methods. The Center is a collaboration of investigators from Central Michigan University, the University of Texas at El Paso, Temple University, the University of Pittsburgh, and the University of Florida (a full list of personnel appears below). It has two main research thrusts and two additional validation initiatives. The first thrust involves developing a new theoretical approach for removing unwanted self-interaction errors (SIE) in situations where they are most problematic, for example, in describing stretched bonds. But the errors must be corrected without degrading the performance of sophisticated DFT methods such as the SCAN (strongly constrained and appropriately normed) meta-GGA (generalized gradient approximation) that give excellent predictions for the properties of molecules and solids near their equilibrium structures. The existing Perdew-Zunger self-interaction correction (PZ-SIC) method is known to worsen predictions of critical properties like molecular atomization energies and bond lengths. The framework for developing the new approach is the Fermi-Löwdin orbital self-interaction correction (FLO-SIC), a unitarily invariant alternative to PZ-SIC that also scales more favorably with system size in terms of computational effort. The second thrust is to develop a software package that implements the FLO-SIC methodology efficiently on advanced, massively parallel computing systems. The resulting FLOSIC package will be made available for free public download.

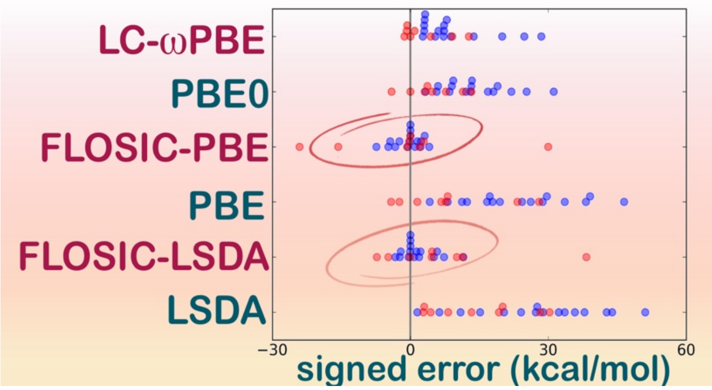


Fig. 1 Signed errors in kcal/mol for reaction energiess in self-interaction error test sets for several DFT methods. FLO-SIC significantly reduces errors relative to corresponding uncorrected methods.

The work of the Center also includes combined experimental and theoretical research into metal organic framework (MOF) -based catalysis and molecular magnets. This work targets problems that are important to the mission of the Department of Energy, including developing energy-efficient alternatives to synthesizing and purifying key chemical reagents and creating molecular-scale circuit components for quantum information science applications.

Recent results

A key objective during the current funding period was benchmarking the performance of FLO-SIC in situations where SIE are known to be pronounced. Fig. 1 summarizes the results of a recent study showing that the use of FLO-SIC significantly reduces errors relative to uncorrected DFT methods for a set of reaction energies and dissociation energies known to be strongly impacted by self-interaction problems. In other work, we demonstrated that FLO-SIC calculations give results that are similar to, but distinct from, traditional PZ-SIC calculations, and we derived and tested an expression for computing atomic forces in FLO-SIC calculations. Finally, we also showed that predicted magnetic exchange couplings in DFT can be significantly improved using FLO-SIC. Full descriptions of these studies can be found in the recent publications listed below.

Additional research being done in the FLO-SIC Center will be presented elsewhere at this meeting. This includes the first results of FLO-SIC-SCAN calculations, an explanation for why predicted atomization energies are worse in FLO-SIC-DFT than in uncorrected DFT, and the demonstration that FLO-SIC causes errors in the description of the exchange energy of the uniform electron gas, which uncorrected DFT describes exactly. It also includes a proposed catalytic pathway for the formation of formaldehyde on open metal sites in a MOF. Finally, applications of FLO-SIC to water clusters, long hydrocarbon chains, and transition metal-oxygen molecules will also be presented.

Future evolution

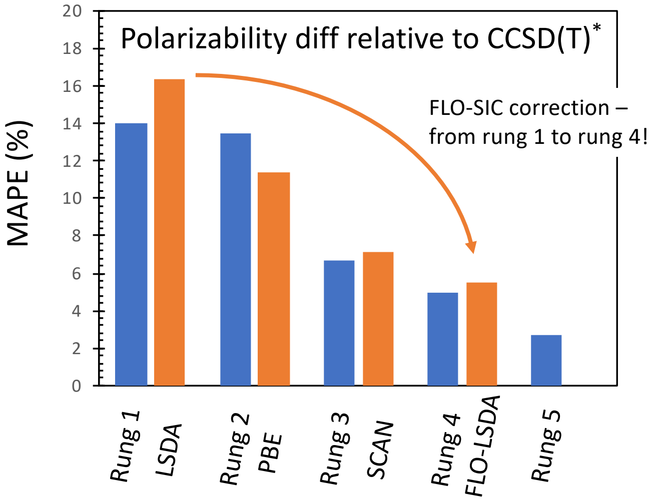


Fig 2. Mean absolute percentage error of atomic polarizabilities computed using various DFT methods. FLO-SIC improves the performance of local density approximation methods to roughly that of hybrid functionals that incorporate a fraction of exact exchange.

Benchmarking work in the Center continues, with studies on the impact of SIE on properties such as atomic polarizabilities (see figure at left), and molecular dipole moments. Also continuing are efforts to quantify the effects of self-interaction on the computed binding of important reactants on open metal sites in MOFs, as well as the DFT-based description of reaction pathways, and to compare FLO-SIC predictions to corresponding measurements made by experimentalists in the Center. On-going projects also include using FLO-SIC to predict key properties of molecular magnets for comparison with experimental measurements made in the Center. Theoretical work on improved approaches to remove self-interaction from DFT is also continuing, as is the development of a method to remove self-interaction effects from time dependent DFT, which will improve the description of properties beyond the ground state, particularly for charge-transfer excitations. Finally, development work continues to make FLO-SIC calculations more efficient. Both algorithmic and numerical improvements are being investigated, as are methods for initializing and optimizing the Fermi orbital descriptor parameters that determine the orbitals used in FLO-SIC calculations. An initial public release of FLOSIC is expected during the summer of 2019.

Grant Number and Title
DE-SC0018331 "FLO-SIC: Efficient Density Functional Calculations without Self-Interaction"

Project Personnel
Lead PI: Koblar A. Jackson, Central Michigan University (jacks1ka@cmich.edu)

PI's: Koblar A. Jackson and Juan E. Peralta, Central Michigan University (CMU); Tunna Baruah and Rajendra Zope, University of Texas-El Paso (UTEP); John P. Perdew and Adrienn Ruzsinszky, Temple University (TU); J. Karl Johnson, Nathanial Rosi, and Götz Veser, University of Pittsburgh (Pitt), and George Christou, University of Florida (UF)

Postdocs: Kai Trepte and Kamal Sharkas (CMU); Yoh Yamamoto, Jorge Vargas Teller, Luis Basurto (UTEP); Biswajit Santra and Hemanadhan Myneni (TU); Lin Li and Mona Mohamed (Pitt).

Students: Kushantha Withanage, Rajendra Joshi, and Alex Johnson (CMU); Sharmin Akther and Carlos Diaz (UTEP); Kamal Wagle, Chandra Shahi, Puskar Bhattarai, Niri Nepal, and Santosh Adhikari (UT); Yahui Yang and Shen Zhang (Pitt); Rahul Kumar and Preet Mahalay (UF).

Publications

1. *Self-consistent self-interaction corrected density functional theory calculations for atoms using Fermi-Löwdin orbitals: Optimized Fermi-orbital descriptors for Li – Kr.* D-y. Kao, K. Withanage, T. Hahn, J. Batool, J. Kortus, and K. Jackson, J. Chem. Phys. **147**, 164107 (2017).

2. *The Effect of Topology in Lewis Pair Functionalized Metal Organic Frameworks on CO2 Adsorption and Hydrogenation,* J. Ye, L. Li, and J. K. Johnson, Catal. Sci. & Tech. **8**, 4609 (2018) (Cover article)

3. *Shrinking Self-Interaction Errors with the Fermi-Löwdin Orbital Self-Interaction Corrected Density Functional Approximation.* K. Sharkas, L. Li, K. Trepte, K. P. K. Withanage, R. P. Joshi, R. R. Zope, T. Baruah, J. K. Johnson, K. A. Jackson, and J. E. Peralta, J. Phys. Chem. A **122**, 9307-9315 (2018) DOI: 10.1021/acs.jpca.8b09940

4. *Fermi- Löwdin orbital self-interaction correction to magnetic exchange couplings.* R. P. Joshi, K. Trepte, K. P. K. Withanage, K. Sharkas, Y. Yamamoto, L. Basurto, R. R. Zope, T. Baruah, K. A. Jackson, and J. E. Peralta, J. Chem. Phys. **149**, 164101 (2018). doi: 10.1063/1.5050809

5. *On the question of the total energy in the Fermi- Löwdin orbital self-interaction correction method.* Kushantha P. K. Withanage, Kai Trepte, Juan E. Peralta, Tunna Baruah, Rajendra Zope, and Koblar A. Jackson, J. Chem. Theory Comput. **14**, 4122 (2018).

6. *Energy Efficient Formaldehyde Synthesis by Direct Hydrogenation of Carbon Monoxide in Functionalized Metal–Organic Frameworks,* L. Li, S. Zhang, J. P. Ruffley, and J. K. Johnson, ACS Sustainable Chem. Eng. **7**, 2508 (2019)

7. *Analytic Atomic Gradients in the Fermi- Löwdin orbital self-interaction correction.* K. Trepte, S. Schwalbe, T. Hahn, J. Kortus, D-y. Kao, Y. Yamamoto, T. Baruah, R. R. Zope, K. P. K. Withanage, J. E. Peralta, and K. A. Jackson, J. Comp. Chem. **40**, 820-825 (2019). DOI**:**10.1002/jcc.25767

8. *Stretched or noded orbital densities and self-interaction correction in density functional theory.* Chandra Shahi, Puskar Bhattarai, Kamal Wagle, Biswajit Santra, Sebastian Schwalbe, Torsten Hahn, Jens Kortus, Koblar A. Jackson, Juan E. Peralta, Kai Trepte, Susi Lehtola, Niraj K. Nepal, Hemanadhan Myneni, Bimal Neupane, Santosh Adhikari, Adrienn Ruzsinszky, Yoh Yamamoto, Tunna Baruah, Rajendra R. Zope, and John P. Perdew, to appear in J. Chem. Phys.

9. *Perdew-Zunger self-interaction correction: How wrong for uniform densities and large-Z atoms?,* B. Santra and J. P. Perdew, to appear in J. Chem. Phys. (arXiv.1902.00117)

10. *Comment: "Additional Insights between Fermi- Löwdin Orbital SIC and the Localization Equation Constraints in SIC-DFT"*, K. A. Jackson, K. P. K. Withanage, and J. E. Peralta, to appear, Journal of Physical Chemistry

Presentation Title

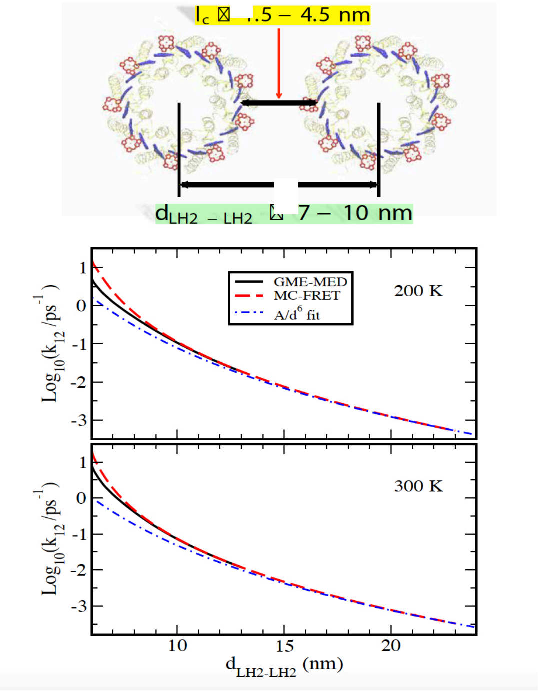
PI: Seogjoo J. Jang

Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30
Kissena Boulevard, Queens, NY 11367

Abstract

Program Scope:

The objective of this research project is to identify and test novel design principles for *efficient* and *robust* exciton and charge migration in molecular systems. In particular, understanding and quantifying major quantum effects crucial for such principles is the primary focus of this project. The criteria for successful design principles we are seeking for are those that can offer new physical insights and help identify controllable molecular characteristics intimately related to the functionality. Successful design principles can also offer practical guidance for experimentalists' efforts to develop cost-effective energy conversion and storage materials. In order to achieve these goals, we pursue three complementary subprojects. First, we conduct detailed computational modeling and analyses of the exciton dynamics in natural photosynthetic light harvesting complexes and elucidate design principles of natural systems through theoretical analysis. Second, we conduct computational modeling of conjugated oligomers so as to develop coarse-grained models applicable for large-scale quantum dynamics calculations. Third, we apply coarse-grained simulation and path integral approaches for the modeling and calculation of charge transport in disordered and complex environments. Integration and further development of these three branches of efforts can help develop new kinds of energy conversion materials either utilizing some design principles identified from biological systems or based on novel quantum dynamics mechanisms intrinsic to synthetic systems.



Enhancement of exciton transfer rates between (LH2) complexes from purple bacteria [8].

Recent Progress:

Exciton Dynamics in Aggregates of LH2 complexes and related model systems: We have completed a comprehensive computational modeling of light harvesting 2 (LH2) complex of purple photosynthetic bacteria and its natural variant LH3 complex [6]. Comparison of theoretical absorption lineshapes with experimental ones confirmed that the exciton-bath models developed through the computation and simulation reproduce major features of experimental lineshapes with reasonable accuracy. I have completed a review article [7] titled "Delocalized excitons in natural light harvesting complexes" in collaboration with Benedetta Mennucci. This article was published as a cover article for the Reviews of Modern Physics in

August, 2018, and offers comprehensive information on various computational and experimental aspects of three major light harvesting complexes. Most importantly, important design principles have been clarified in this work.

I have also completed a computational study of inter-LH2 exciton dynamics examining how quantum effects and the disorder influence the dependences of inter-LH2 exciton transfer rates on key energetic and structural features [8]. The results show that combined effects of dark exciton states and multipolar contributions enhance the rate significantly, up to about a factor of 10 for the closest distance tested, when compared to the prediction based on transition-dipole interactions. The disorder reduces the average rate by about a factor of 4, but does not change appreciably the distance dependence of the quantum enhancement due to delocalized excitons.

Computational study and modeling of organic conjugated molecules: We have recently completed a computational study [10] of neutral and charged oligothiophene (OT) molecules, OT_n, OT_n^+, and OT_n^-, with the repeat unit n=2-6. Both semi-empirical and time dependent density functional (TD-DFT) methods were tested against experimental results, and all of the computational and experimental data were analyzed further based on simple exciton and free electron models. These results show that TD-DFT with M06-2X functional is fairly reliable in reproducing the distance dependence of excitation energies and that the fitting with the exciton model provides a simple way to assess the performance of different computational methods. The fitting with the exciton model also suggests the feasibility of developing a simple exciton-bath model to describe singlet excitons in both neutral and charged OTs.

Simulation of charge transport in quantum environments: In parallel with molecular-level computations, kinetic Monte Carlo (KMC) simulation suitable for large scale exciton and charge transport dynamics have been tested for both one dimensional and two dimensional model systems. Application of these methods for models with gradient in site energies, which is designed to investigate the effect of external field on the charge transport in disordered quantum environments, is currently in progress.

Future Plans:

Our effort in the future will be focused on the following research tasks and objectives.

- Further validation of results on LH2 complexes through more refined model parameters from recent computational study and advanced lineshape theories currently being explored. Extension of these simulations for larger scale aggregates of LH2 complexes will be conducted.
- Computational study on a phenylene-vinylene system called DEH-PPV. The major experimental data for this system are unpublished single molecule spectroscopy data. We will then complete the development of exciton-bath models for both the OT and oligo-phenylene-vinylene systems Ultimately, the exciton-bath models for these systems will be employed for the modeling of the spectroscopy and energy/charge transport dynamics in their aggregates and related systems in the future.
- We will employ the KMC simulation method to investigate the effects of detailed quantum features of the environment and the disorder on large scale charge and exciton dynamics. The focus of this study will be finding the relationship between the characteristics of rate kernels and the mobility at large length scales.
- We will continue working on path integral simulation of excess electrons in hydrocarbon liquids.

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

Postdoc(s): Eva Rivera, Daniel Montemayor, Marta Kowalczyk

Student(s): Ning Chen, Taner M. Ture

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

1. Seogjoo Jang, Eva Rivera, and Daniel Montemayor, "Molecular level design principle behind optimal sizes of photosynthetic LH2 complex: Taming disorder through cooperation of hydrogen bonding and quantum delocalization," *Journal of Physical Chemistry Letters* **6**, 928 (2015)

2. Seogjoo Jang and Andres Montoya-Castillo, "Charge hopping dynamics along a disordered chain in quantum environments: Comparative study of different rate kernels," *Journal of Physical Chemistry B* **119**, 7659 (2015)
3. Seogjoo Jang and Gregory A. Voth, "Can quantum transition state theory be defined as an exact t=0+ limit?," *Journal of Chemical Physics* **144**, 084110 (2016)

4. Seogjoo Jang, "Generalized quantum Fokker-Planck equation for photo induced nonequilibrium processes with positive definiteness condition," *Journal of Chemical Physics* **144**, 214102 (2016)

5. Seogjoo Jang and Gregory A. Voth, "Non-uniqueness of quantum transition state theory and general dividing surfaces in the path integral space," *Journal of Chemical Physics* **146**, 174106 (2017)

6. Daniel Montemayor, Eva Rivera, and Seogjoo J. Jang, "Computational modeling of exciton-bath Hamiltonians for light harvesting 2 and light harvesting 3 complexes of purple photosynthetic bacteria at room temperature," *Journal of Physical Chemistry B* **122**, 3815-3825 (2018)

7. Seogjoo J. Jang and Benedetta Mennucci, "Delocalized excitons in natural light harvesting complexes," *Reviews of Modern Physics* **90**, 035003 (2018)

8. Seogjoo J. Jang, "Robust and fragile quantum effects in the transfer kinetics of delocalized excitons between B850 units of LH2 complexes," *Journal of Physical Chemistry Letters* **9**, 6576-65 83 (2018)

9. Seogjoo J. Jang, "Effects of donor-acceptor quantum coherence and non-Markovian bath on the distance dependence of resonance energy transfer," *Journal of Physical Chemistry C* **123**, 5767-5775 (2019)

10. Marta Kowalczyk, Ning Chen, and Seogjoo J. Jang, "Comparative computational study of electronic excitations of neutral and charged small oligothiphenes and their extrapolations based on simple models," *ACS Omega* **4**, 5758-5767 (2019)

A Polarizable Frozen-Density Embedding Method

Lasse Jensen

Department of Chemistry, The Pennsylvania State University, 104 Chemistry Building,
University Park, PA 16802, Email: jensen@chem.psu.edu

Abstract

Assemblies of molecular switches at surfaces are of great interest for applications in solar energy conversion, optoelectronic and optomechanical devices. Experimental studies have demonstrated that it is possible to optically probe photoactive molecules in well-defined nanoscale environments. The goal of this research project is to obtain a microscopic understanding of the electronic and geometric effects on the photochemistry of molecules in well-defined environments. First-principles simulations based on a quantum embedding model will be used to understand the photochemistry of prototypical photochemical reactions.

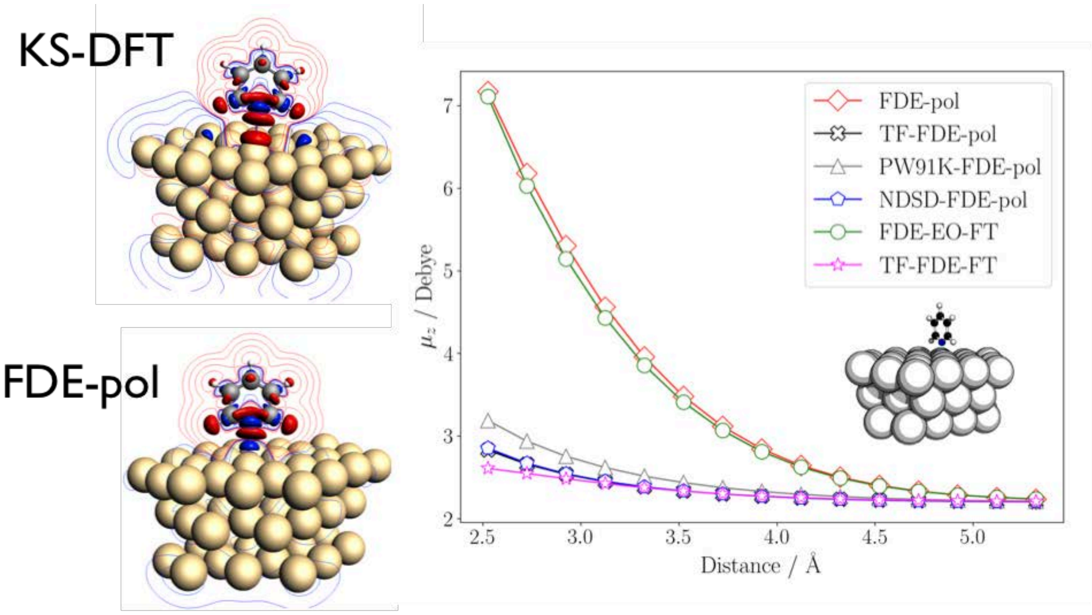


Fig 1: Dipole moment of pyridine on a small silver cluster as calculated using several different embedding methods.

Recent progress

We report a polarizable subsystem density functional theory to describe electronic properties of molecules embedded on a metal cluster. Interaction between the molecule and metal cluster is described using the frozen density embedding (FDE). Substituting the non-additive kinetic potential (NAKP) by approximate functionals is circumvented by enforcing external orthogonality (EO) through a projection operator. The computationally expensive freeze/thaw (FT) cycles is bypassed by including a polarization term in the embedding operator. Furthermore, the combination of polarization and EO permits supermolecular basis set calculations, which was not possible for strongly interacting systems with existing kinetic energy functional. We find that the density is reproduced to within 10^{-4}e and the dipole and quadrupole moments are within 6-18% of the reference points for subsystem separations ranging from bonding to non-interacting distances. Additionally, our formalism allows the flexibility of incorporating different density functionals to the molecular and the metallic subsystems reducing the overall computational cost. Current efforts are focused on extending the FDE-pol method to automatic determination of the polarization parameters and inclusion of larger metal substrates. Additional effectors aim at extending the FDE-pol method to describe excited states of molecules using time-dependent density functional theory (TDDFT). FDE-EO has been extended to TDDFT and thus can serve as a benchmark for FDE-pol.

Grant Numbers and Grant Titles

DE-SC0018038 - Electronic and Geometric effects on Photochemistry of Molecules in Well-Defined Environments

Postdoc: Partha Pratim Pal

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

1. Polarizable Frozen Density Embedding with External Orthogonalization, Partha Pratim Pal, Pengchong Liu, and Lasse Jensen, Submitted, 2019

Synthesis of Formaldehyde from Syngas via Catalytic Condensation in Functionalized Metal Organic Frameworks

Lin Li[1], Sen Zhang[1], Jonathan Ruffley[1], J. Karl Johnson[1], Kushantha Withanage[2], Juan Peralta[2], PI: Koblar Alan Jackson[2]
[1]Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania, UNITED STATES
[2]Department of Physics, Central Michigan University,
Mt Pleasant, Michigan, UNITED STATES

Formaldehyde is a highly desirable platform chemical with an annual demand of over 30 megatons. The most common commercial way of generating formaldehyde is energy intensive, with 57% exergy loss. Formaldehyde is produced by oxidation of methanol, which is typically produced by the partial oxidation of methane to syngas, followed by the reduction of CO to methanol via Fischer-Tropsh synthesis. This is a complex, multi-step process, involving oxidation, then reduction, followed by another oxidation step. In this work, we will present a more efficient pathway for converting CO to formaldehyde through hydrogenation of CO in catalytic metal organic frameworks (MOFs). The catalytic sites within the MOFs are produced by incorporating Lewis acid base pairs (LPs), which are excellent catalysts for heterolytic splitting of hydrogen, as we have previously shown.[1-2]

We used density functional theory (DFT) to construct and evaluate LP-functionalized MOFs for their activity toward CO hydrogenation. We computed reaction pathways for hydrogen splitting on the LP, followed by reduction of CO to formaldehyde by addition of the hydridic and protic hydrogens on the LP in the MOF. It is known that DFT often underestimates reaction barriers, and this may be due to self-interaction errors, which are manifest when bonds are stretched in transition state geometries. We have therefore used a variety of levels of DFT to evaluate the transition states, complemented with post Hartree-Fock ab initio methods on cluster models.[3] We have used the FLOSIC code[4] to estimate the magnitude of the self-interaction error in this system. Periodic DFT results have been calculated using the GPAW code, with the BEEF-vdW

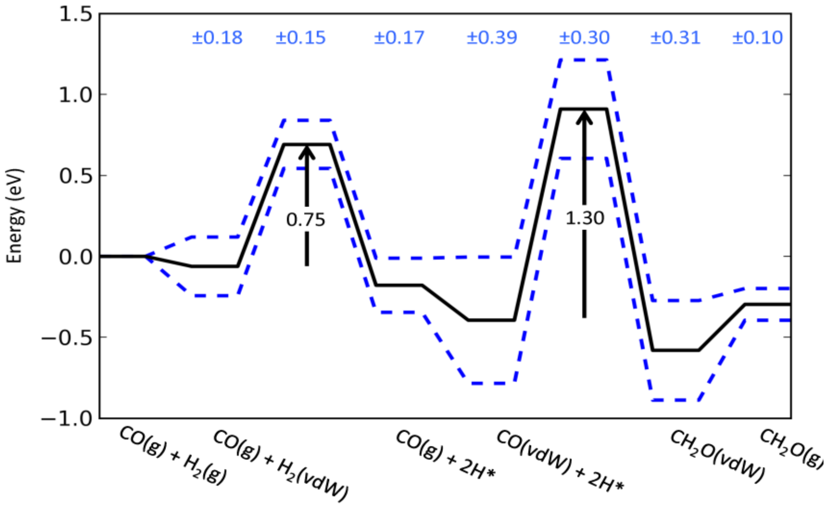


Fig. 1. Reaction energy diagram for the CO hydrogenation pathway. The solid line represents total energies calculated using BEEF-vdW. The blue dashed lines represent the standard deviations computed from the BEEF ensemble for the relative energy between the reference state and the corresponding state.

functional to describe the exchange-correlation energy. We also quantified the uncertainly associated with each DFT calculation due to the choice of exchange-correlation functional using the BEEF ensemble.

We have computed the reaction pathway for CO hydrogenation in gas phase, inside LP functionalized UiO-67, and on a freestanding fragment containing the LP. The rate-limiting step is the hydrogenation of CO, with a barrier of 1.30 ± 0.15 eV, which is an improvement of about 2 eV relative to the uncatalyzed reaction. We believe that conversion of CO to formaldehyde will be further enhanced in the MOFs due to the increase in effective pressure inside confined pores. Additionally, this confinement effect also reduces translational degrees of freedom, which makes the free energy of the overall reaction more favorable. Catalytic conversion of CO to formaldehyde in the MOF overcomes the equilibrium limitation of gas phase synthesis of formaldehyde by making the overall reaction irreversible, since the products desorb with a barrier much lower than the reverse reaction. Moreover, separation of the product from reactants can be carried out by condensing the formaldehyde. This is much more energy efficient than the current method of distillation from the aqueous phase synthesis now in common use.

Grant Number and Title

DE-SC0018331 "FLO-SIC: Efficient Density Functional Calculations without Self-Interaction"

Project Personnel

Lead PI: Koblar A. Jackson, Central Michigan University (jacks1ka@cmich.edu)

PIs: Koblar A. Jackson and Juan E. Peralta, Central Michigan University (CMU); Tunna Baruah and Rajendra Zope, University of Texas-El Paso (UTEP); John P. Perdew and Adrienn Ruzsinszky, Temple University (TU); J. Karl Johnson, Nathanial Rosi, and Götz Veser, University of Pittsburgh (Pitt), and George Christou, University of Florida (UF)

Postdocs: Kai Trepte and Kamal Sharkas (CMU); Yoh Yamamoto, Jorge Vargas Teller, Luis Basurto (UTEP); Biswajit Santra and Hemanadhan Myneni (TU); Lin Li and Mona Mohamed (Pitt).

Students: Kushantha Withanage, Rajendra Joshi, and Alex Johnson (CMU); Sharmin Akther and Carlos Diaz (UTEP); Kamal Wagle, Chandra Shahi, Puskar Bhattarai, Niri Nepal, and Santosh Adhikari (UT); Yahui Yang and Shen Zhang (Pitt); Rahul Kumar and Preet Mahalay (UF).

Publications

1. Ye, J.; Li, L.; Johnson, J. K., The effect of topology in Lewis pair functionalized metal organic frameworks on CO2 adsorption and hydrogenation. *Catalysis Science & Technology* **2018,** *8*, 4609-4617.
2. Ye, J.; Yeh, B. Y.; Reynolds, R. A.; Johnson, J. K., Screening the activity of Lewis pairs for hydrogenation of CO2. *Molecular Simulation* **2017,** *43*, 821-827.
3. Li, L.; Zhang, S.; Ruffley, J. P.; Johnson, J. K., Energy Efficient Formaldehyde Synthesis by Direct Hydrogenation of Carbon Monoxide in Functionalized Metal–Organic Frameworks. *ACS Sustainable Chemistry & Engineering* **2019,** *7*, 2508-2515.
4. Sharkas, K.; Li, L.; Trepte, K.; Withanage, K. P. K.; Joshi, R. P.; Zope, R. R.; Baruah, T.; Johnson, J. K.; Jackson, K. A.; Peralta, J. E., Shrinking Self-Interaction Errors with the Fermi–Löwdin Orbital Self-Interaction-Corrected Density Functional Approximation. *The Journal of Physical Chemistry A* **2018,** *122*, 9307-9315.

2019 CTC PI MEETING May 22 - 24, 2019

ABSTRACT

- **Program Title**: Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies.
- **Principal Investigator**: Khanna, Shiv
- **Mailing Address**: Physics Department, Virginia Commonwealth University, Box-2000, Richmond, VA 23284-2000, USA
- **Email**: snkhanna@vcu.edu
- **Program Scope**: An exciting development in nanoscience is the formation of materials whereby size selected clusters serve as the building blocks. This interest stems from the developments over the past 30 years that indicate that the physical, chemical, electronic or magnetic properties of small clusters change with size and composition. This diversity is further fueled by the addition of ligands that can protect the cluster against reactivity and also provides further tuning of properties by the nature of ligands. In this regard, cluster assemblies offer the attractive proposition of forming materials with novel combination of chosen properties. The proposed work is directed towards developing cluster materials with magnetic building blocks with tunable band gaps using a variety of clusters. We are particularly interested in identifying clusters with large magnetic anisotropy to develop magnetic storage and permanent magnets.

We propose to undertake a comprehensive program starting from electronic structure, stability, and magnetic properties of various classes of clusters including mixed transition metal clusters, chalcogenide superatoms, and silicon transition metal clusters. Our objective is to propose novel materials including clusters supported on reduced graphene with high magnetic anisotropy energy (MAE), superatom doped semiconductors with adjustable gap and control over nature of carriers and p-n junctions, and silicon transition metal motifs for magnetic silicon based materials. The requested DOE program will involve four interrelated areas of study, namely: A) motivated by our preliminary findings, we will investigate magnetic anisotropy in mixed transition metal carbide $TM1_nTM2_mC_l$ (TM=Cr, Mn, Fe, Co, Ni) clusters to identify those with unusually high MAE. We will investigate transition metal clusters supported on reduced graphene following our preliminary studies that indicate that such a support could considerably increase the MAE; B) investigate the origin of stability of metal chalcogenide superatoms including electron donors $Co_6Se_8(PEt_3)_6$, $Cr_6Se_8(PEt_3)_6$, $Ni_9Te_6(PEt_3)_8$, $Ni_9Te_6(PMe_3)_8$, $Co_6Te_8(PEt_3)_6$, $Co_6Te_8(PEt_2Ph)_6$ and electron acceptor clusters $Co_{11}Te_7(CO)_{10}$, and $Co_9Te_6(CO)_8$. We shall investigate how the donor/acceptor characteristics and magnetic character can be transformed by the choice of ligands. Finally, we will carry out theoretical studies on the doping of MoS_2 and WSe_2 semiconductors with metal chalcogenide superatoms not only to provide insight into the recent experiments in the group of Nuckolls but also to predict the properties of such doped semiconductors containing donor and acceptor superatoms including magnetic superatoms; C) study the magnetic character in assemblies of Si_nTM (n=12-16) clusters and the electronic character of charge transfer complexes of Si_nTM_m (n=12-16, m=1-2, TM: Cr, Mn, Fe, Co, Ni) clusters with C_{60}; D) continue studies on ligated clusters to explore the possibility of forming p-n junctions and intense internal electric fields that could separate electrons and holes.

- **Recent Progress :** Our recent work has proceeded along various directions. In this report we have highlighted three directions.

1. Magnetic Behaviour of Assemblies of Interacting Cobalt-Carbide Nanoparticles

One approach to design rare earth free permanent magnets is to examine nano-assembled materials where magnetic nonoparticles serve as building blocks. For ordinary ferromagnetic materials, the reduction in size leads to a decrease in the magnetic anisotropy, resulting in superparamagnetic relaxations at nanoscopic sizes. One of the fundamental questions is if the anisotropy could be enhanced in reduced sizes. In a joint experimental/theory effort we had demonstrated that using synthetic chemical methods, it was possible to stabilize a new cobalt carbide phase where nanoparticles have blocking temperatures exceeding 570 K even for particles as small as 8 nm. The assembled material demonstrated high coercivity and magnetic moment in cobalt carbide nanoparticle assemblies and we had suggested that the high coercivity probably stems from the high magnetocrystalline anisotropy.

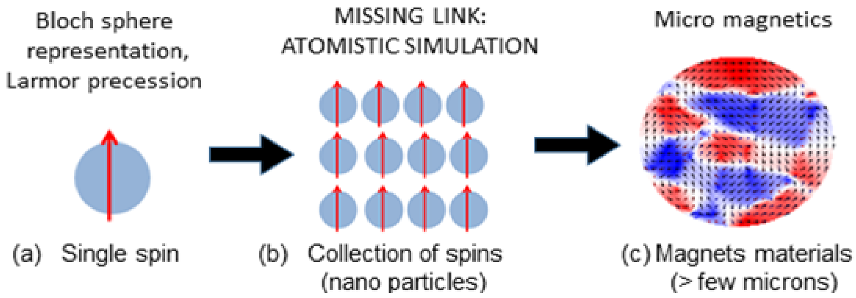


Fig. 1: Studies on assemblies of magnetic nanoparticles are a key to transforming properties of individual nanoparticles to bulk magnetic behaviors with pre-ordained properties.

In this work, we undertook a theoretical study of the collective behavior of a magnetic nanoparticles assembly to systematically understand the effect of particle size, distribution of the orientations of the nanoparticles magnetocrystalline anisotropy axis with respect to the applied magnetic field, and dipole coupling between nanoparticles, on the temperature dependent magnetic behavior of the magnetic coercivity of the assembly (Fig. 1). The studies indicate that while the magnetic behavior is extremely sensitive to particle size and orientation, the effect of dipole coupling is less significant. This suggests that one could pack nanoparticles with high densities in such assemblies to achieve high net magnetization without degrading the hard magnetic behavior (coercivity) significantly. Furthermore, particle size and distribution of orientation of the easy axis (of magneto crystalline anisotropy) can be used to optimize the magnetic properties of such assemblies. Finally, the temperature dependent behavior is qualitatively predicted and hysteresis is explained by magnetocrystalline anisotropy but the reduction in hysteresis with increasing temperature is significantly over predicted by the model. This suggests that magnetocrystalline anisotropy alone cannot describe the temperature dependent hysteresis. Defects that pin the magnetization could potentially enhance the hysteresis (and therefore coercivity) of these magnetic nanoparticles, making them retain favorable coercivity even at elevated temperatures. Further studies are needed to examine this point.

2. Transforming Redox Properties of Clusters Using Organic Ligands:

We have developed a novel approach to design clusters and nanoparticles with remarkable oxidative or reductive properties that would have potential applications such as dopants to develop two dimensional semiconductors with tunable band gaps, carriers for batteries, catalysis, and pre-programmed motifs for forming ionic cluster assembled solids when combined with counter-ions.

The electronic properties of bulk surfaces are usually modified by depositing a doped surface layer in which charge transfer and the intrinsic dipole moment of the layer results in band bending that can change the work function of the surface. In our work, we demonstrated how the interaction between ligands and particles can be used to alter their redox properties leading to particles with low ionization energies (I.E.). To show how ligation can act to lower the I.E., we considered the Trimethylphosphine, PMe_3 ligand which is a strong σ-donor that generally increases the electron density in the cluster core through the lone pair of the phosphorus.

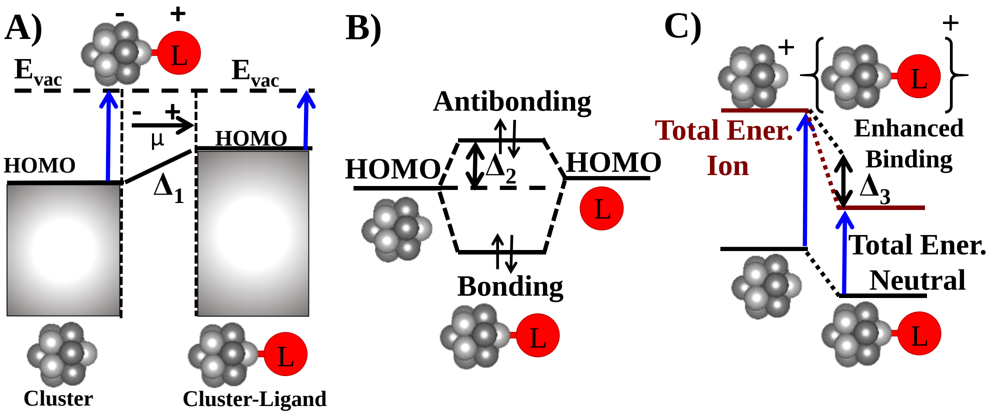


Figure 2. Mechanisms that affect the ionization energy of a cluster after ligation. A) Dipole induced shift of the Electronic Levels. B) Bonding and antibonding shifts in the HOMO, C) Enhanced binding of the ligand to a charged species, and electronic relaxation after ionization.

We examined the change in I.E. of a variety of clusters including simple and noble metal clusters, Au_7, Au_{11}, $Au_{13}Cl_2$, Ag_{11}, and Al_7; an Al_4O_6 cluster corresponding to an insulator; $Ga_{12}N_{12}$, and $Zn_{12}O_{12}$ as representative of semiconductor clusters; Co_6, Pd_6, and Pd_7 as representative of transition metal clusters; and Mo_6Te_8 corresponding to the important metal-chalcogenide clusters recently synthesized by Roy and co-workers. We found that the I.E. of the ligated clusters universally decrease as compared to the bare clusters. The mechanism by which this shift in I.E. occurs is different from bulk where the formation of dipole layer leads to a reduction in the work function, and in the atomic case where the filling of electronic shells controls I.E. Here, attaching ligands form charge transfer complexes. While part of the reduction can be associated with a cluster version of band bending, the formation of bonding/anti-bonding pairs and the binding enhancement in the cation and the stabilization of the charged state of the cluster by the ligands also play an important role (Fig. 2). We find that the type of cluster core effects how the I.E. is reduced. In the simple metal and noble metal clusters, the initial state effect is most important in which the antibonding orbitals formed between phosphine and the metal increase in the HOMO of the neutral cluster. In transition metal clusters, the electronic relaxation of the cluster core prevents the HOMO from increasing as much as in simple metal and noble metal clusters, and after the electron is removed the covalent binding may be enhanced through further electronic relaxation. The ligand effect in finite sizes has several additional features. The I.E. can be controlled by changing the number of ligands and ligands can create donors that can donate multiple electrons.

3. Bimetallic Clusters supported on graphene as catalysts for cross-coupling reactions:

We had earlier carried out computational studies to support the experimental results in providing a fundamental understanding of how a graphene support may activate both oxidative and reductive reaction steps in the catalytic cycle of Suzuki-Miyaura palladium-catalyzed cross-coupling reactions. The high catalytic activity was shown to be linked to the ability of a graphene support to act as both an efficient charge donor and acceptor. In this work, we performed a series of calculations to investigate the electronic properties and activation energies for the different steps in the Suzuki cross-coupling reaction in first row transition metal clusters (Fe, Ni, and Cu). Investigations into bimetallic Palladium-Nickel clusters revealed they may act as co-catalysts to further reduce activation energies due to the charge transfer from Ni to Pd resulting in the Ni sites acting as improved charge acceptors, and the Pd sites acting as improved charge donors. These calculations also revealed that the activation energy of the supported Ni cluster can be further curtailed even lower than the activation energy of supported Pd cluster by reducing the size of the Ni cluster and mixing Pd atoms into the Ni cluster. Thus, our investigations reveal that bimetallic Pd/Ni clusters supported on defected graphene, and small Ni_4 clusters supported on defected graphene are potential strategies towards improving catalysis and reducing metal costs in cross-coupling catalysts.

- **Future Plans**:

We are proceeding along several directions. We are working with experimental groups at Johns Hopkins and Columbia University to support our prediction that the redox properties of clusters can be altered by attaching organic ligands. The initial experimental results support our findings. We have examined the properties of a molecule composed of two identical clusters but with donor and acceptor ligands on the two sides. The system develops a giant dipole moment and an intense electric field that could separate electron hole pairs. Such super-molecules also have the potential of acting as nano p-n junctions. We also plan to continue our effort to use the new building blocks as dopants to modify create semiconductors with tunable band gaps and semiconductors with magnetic units. We plan to continue studies of metal silicon clusters containing multiple transition metal atoms.

- **Selected References:**

(1) Bista, D.; Reber, A. C.; Chauhan, V.; Khanna, S. N. Electronic and Magnetic Properties of Fe_2Si_n $(1 \leq n \leq 12)^{+/0/-}$ Clusters. *Chemical Physics Letters* **2018**, *706*, 113–119. https://doi.org/10.1016/j.cplett.2018.05.079.

(2) Sutradhar, P.; Khanna, S. N.; Atulasimha, J. Magnetic Behaviour of Assemblies of Interacting Cobalt-Carbide Nanoparticles. *Journal of Magnetism and Magnetic Materials* **2019**, *469*, 128–132. https://doi.org/10.1016/j.jmmm.2018.08.026.

(3) Prabha, S.; Reber, A. C.; Khanna, S. N. The Structure and Stability of Cr_nTe_m $(1 \leq n \leq 6, 1 \leq m \leq 8)$ Clusters. *Chemical Physics Letters* **2019**, *720*, 76–82. https://doi.org/10.1016/j.cplett.2019.02.003.

(4) Reber, A. C.; Khanna, S. N. The Effect of Chalcogen and Metal on the Electronic Properties and Stability of Metal–Chalcogenides Clusters, $TM_6X_n(PH_3)_6$ (TM = Mo, Cr, Re, Co, Ni; X = Se, Te; n = 8,5). *Eur. Phys. J. D* **2018**, *72* (11), 199. https://doi.org/10.1140/epjd/e2018-90223-7.

(5) Yang, Y.; Reber, A. C.; Gilliland, S. E.; Castano, C. E.; Gupton, B. F.; Khanna, S. N. Donor/Acceptor Concepts for Developing Efficient Suzuki Cross-Coupling Catalysts Using Graphene-Supported Ni, Cu, Fe, Pd, and Bimetallic Pd/Ni Clusters. *J. Phys. Chem. C* **2018**, *122* (44), 25396–25403. https://doi.org/10.1021/acs.jpcc.8b07538.

(6) Jash, M.; Reber, A. C.; Ghosh, A.; Sarkar, D.; Bodiuzzaman, M.; Basuri, P.; Baksi, A.; Khanna, S. N.; Pradeep, T. Preparation of Gas Phase Naked Silver Cluster Cations Outside a Mass Spectrometer from Ligand Protected Clusters in Solution. *Nanoscale* **2018**, *10* (33), 15714–15722. https://doi.org/10.1039/C8NR04146F.

(7) Reber, A. C.; Khanna, S. N. $Co_6Se_8(PEt_3)_6$ Superatoms as Tunable Chemical Dopants for Two-Dimensional Semiconductors. *npj Computational Materials* **2018**, *4* (1), 33. https://doi.org/10.1038/s41524-018-0092-9.

(8) Chauhan, V.; Khanna, S. N. Strong Effect of Organic Ligands on the Electronic Structure of Metal-Chalcogenide Clusters. *J. Phys. Chem. A* **2018**, *122* (28), 6014–6020. https://doi.org/10.1021/acs.jpca.8b03355.

(9) Reber, A. C.; Bista, D.; Chauhan, V.; Khanna, S. N. Transforming Redox Properties of Clusters Using Phosphine Ligands - *J. Phys. Chem. C* **2019**, 123, 8983-8989. https://doi.org/10.1021/acs.jpcc.9b00039

Shiv N. Khanna

Transforming Redox Properties of Clusters Using Ligands to Create Super Dopants for Two-Dimensional Semiconductors and to Synthesize Nano p- n- junctions.

S. N. Khanna, V. Chauhan, A. C. Reber and D. Bista
Physics Department, Virginia Commonwealth University, Richmond, VA 23284-2000

Abstract

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 using ligands to transform the redox properties of a variety of clusters and their use as dopants to design novel semiconductors where the location of Fermi energy and n- and p- characteristics can be controlled. I will end my talk with a recent discovery where we have used ligands to induce intense electric fields and dipole moments in molecules of homo-atomic clusters. Such units have the characteristics of nano p- n- junctions.

Organic ligands that protect the surfaces of clusters and nanoparticles against reactions and control the rate of growth are generally considered to be inert passive coatings. I will demonstrate that the ligands can also strongly affect the redox properties of clusters.

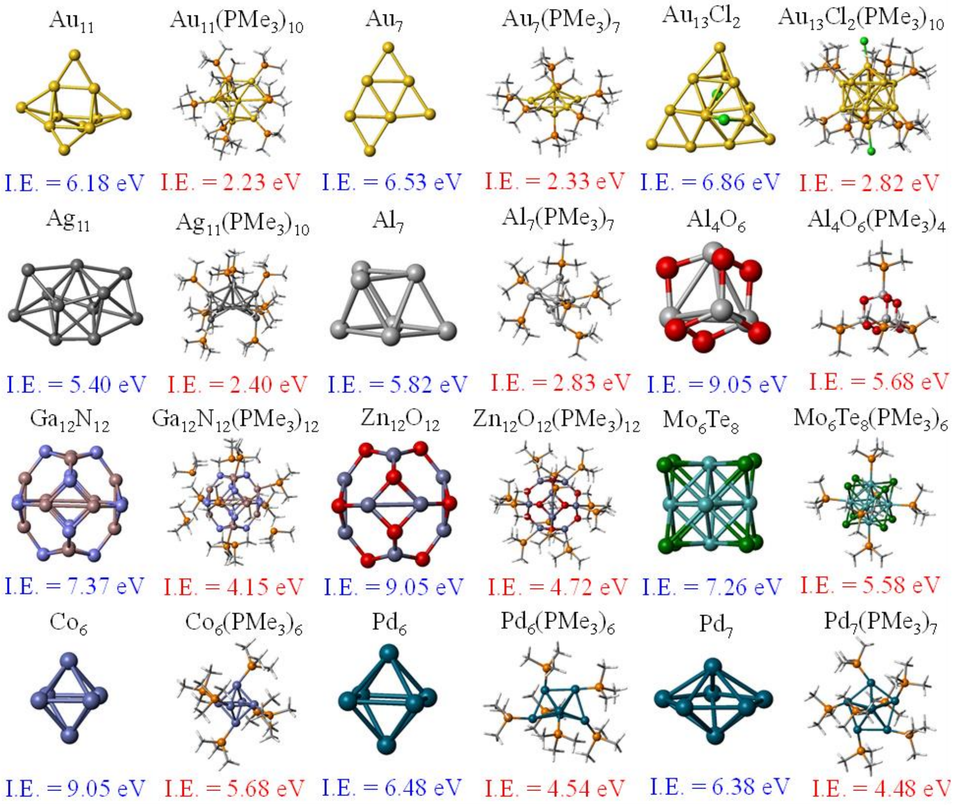


Fig. 1. Reduction in I.E. upon ligation in a variety of Clusters.

I will present our results of the effect of ligation on the ionization energy (I.E). of a variety of clusters including simple and noble metal clusters, Au_7, Au_{11}, $Au_{13}Cl_2$, Ag_{11}, and Al_7; an Al_4O_6 cluster corresponding to an insulator; $Ga_{12}N_{12}$, and $Zn_{12}O_{12}$ as representative of semiconductor clusters; Co_6, Pd_6, and Pd_7 as representative of transition metal clusters; and Mo_6Te_8 corresponding to the important metal-chalcogenide clusters recently synthesized by Roy and co-workers. For all cases, the ionization energy is reduced (Fig. 1). In many cases, ligated clusters are transformed into super donors with ionization energies nearly half that of cesium atoms, and extremely low second and third ionization energies creating super donors that can donate multiple electrons.. I will show that the reduction in ionization energy can be split into initial and final state effects. The initial state effect derives in part from the surface dipole, but primarily through the formation of bonding/antibonding orbitals that shifts the HOMO. The final state effect derives from the enhanced binding of the donor ligand to the charged cluster.

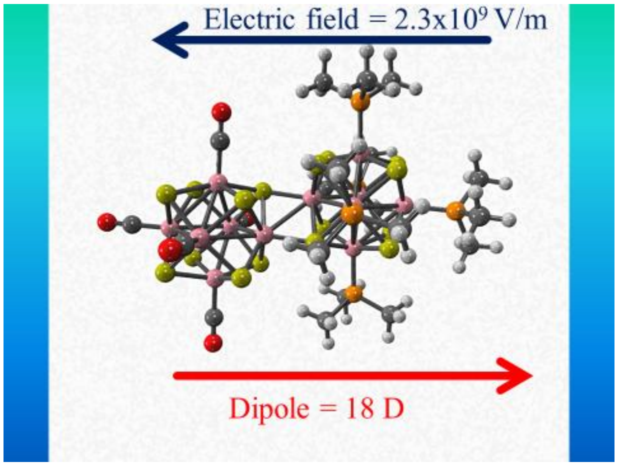


Fig. 2. Intense electric field in a ligated super molecule

I will then show how organic ligands can be used to modulate the chemical potential of clusters and then join identical clusters to create giant dipoles and electric fields even in symmetric clusters. We first show that even weakly bound ligands can significantly change the chemical potential of the cluster and that the direction of change can be controlled by the nature of ligands. While the charge donating ligands raise the chemical potential, charge accepting ligands lower the chemical potential. Even though, the ligands bind weakly, the effect is so intense that the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) can shift by 0.5 – 1.0 eV. We then show that a composite molecule of two identical clusters with different ligands can exhibits an intense permanent dipole moment as the clusters are joined to form a molecule. Investigations into the electric field required to create a similar dipole in no-ligated system indicates that the effect is equivalent to applying intense electric field ranging to 10^9 V/m (Fig. 2 shows the field required to destroy the original dipole). An investigation into the absorption spectra reveals that such units could absorb even visible light to create electron hole pairs that can be separated by the intense field.

Finally, I will show how ligated clusters with multiple low I.E. can lead to semiconductors with tunable band gaps. I will present results of our recent work on using $Co_6Se_8(PEt_3)_5$ clusters as donors to dope a WSe_2 film by binding dopants to the surface. Our investigations show such a doping allows several new features for the doped species. First, the Fermi energy of the doped system can be varied over a wide range by selectively replacing the PEt_3 ligands by CO ligands. Such a control is important for optoelectronic properties and even for creating semiconductors where the dopants carry magnetic moments. We are now investigating more ligands and clusters to build on the above findings.

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.

PI: S. N. Khanna 0.12 month of salary

Post Doc: Vikas Chauhan
Arthur Reber Research associate Professor (Partially)
Student:

Daniel Rabayda	Graduate Student (partially)
Albert Armstrong	Graduate Student (partially)

Selected Publications:

(1) Bista, D.; Reber, A. C.; Chauhan, V.; Khanna, S. N. Electronic and Magnetic Properties of Fe_2Si_n $(1 \leq n \leq 12)^{+/0/-}$ Clusters. *Chemical Physics Letters* **2018**, *706*, 113–119. https://doi.org/10.1016/j.cplett.2018.05.079.
(2) Sutradhar, P.; Khanna, S. N.; Atulasimha, J. Magnetic Behaviour of Assemblies of Interacting Cobalt-Carbide Nanoparticles. *Journal of Magnetism and Magnetic Materials* **2019**, *469*, 128–132. https://doi.org/10.1016/j.jmmm.2018.08.026.
(3) Prabha, S.; Reber, A. C.; Khanna, S. N. The Structure and Stability of Cr_nTe_m $(1 \leq n \leq 6, 1 \leq m \leq 8)$ Clusters. *Chemical Physics Letters* **2019**, *720*, 76–82. https://doi.org/10.1016/j.cplett.2019.02.003.
(4) Reber, A. C.; Khanna, S. N. The Effect of Chalcogen and Metal on the Electronic Properties and Stability of Metal–Chalcogenides Clusters, $TM_6X_n(PH_3)_6$ (TM = Mo, Cr, Re, Co, Ni; X = Se, Te; n = 8,5). *Eur. Phys. J. D* **2018**, *72* (11), 199. https://doi.org/10.1140/epjd/e2018-90223-7.
(5) Yang, Y.; Reber, A. C.; Gilliland, S. E.; Castano, C. E.; Gupton, B. F.; Khanna, S. N. Donor/Acceptor Concepts for Developing Efficient Suzuki Cross-Coupling Catalysts Using Graphene-Supported Ni, Cu, Fe, Pd, and Bimetallic Pd/Ni Clusters. *J. Phys. Chem. C* **2018**, *122* (44), 25396–25403. https://doi.org/10.1021/acs.jpcc.8b07538.
(6) Jash, M.; Reber, A. C.; Ghosh, A.; Sarkar, D.; Bodiuzzaman, M.; Basuri, P.; Baksi, A.; Khanna, S. N.; Pradeep, T. Preparation of Gas Phase Naked Silver Cluster Cations Outside a Mass Spectrometer from Ligand Protected Clusters in Solution. *Nanoscale* **2018**, *10* (33), 15714–15722. https://doi.org/10.1039/C8NR04146F.
(7) Reber, A. C.; Khanna, S. N. $Co_6Se_8(PEt_3)_6$ Superatoms as Tunable Chemical Dopants for Two-Dimensional Semiconductors. *npj Computational Materials* **2018**, *4* (1), 33. https://doi.org/10.1038/s41524-018-0092-9.
(8) Chauhan, V.; Khanna, S. N. Strong Effect of Organic Ligands on the Electronic Structure of Metal-Chalcogenide Clusters. *J. Phys. Chem. A* **2018**, *122* (28), 6014–6020. https://doi.org/10.1021/acs.jpca.8b03355.
(9) Reber, A. C.; Bista, D.; Chauhan, V.; Khanna, S. N. Transforming Redox Properties of Clusters Using Phosphine Ligands -. *J. Phys. Chem. C* **2019,** 123, 8983-8989. https://doi.org/10.1021/acs.jpcc.9b00039

Embedding Quantum Computing into Many-body Frameworks: Hamiltonian downfolding techniques based on the double unitary coupled-cluster Ansatz

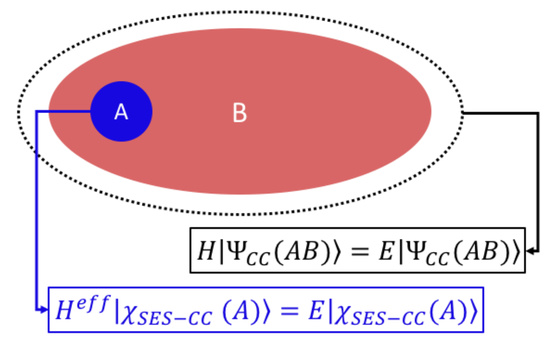
Eric J. Bylaska, Wibe A. de Jong, Travis Humble, Sriram Krishnamoorthy, Mekena Metcalf, Dominika Zgid, Karol Kowalski

Pacific Northwest National Laboratory
Lawrence Berkeley National Laboratory
Oak Ridge National Laboratory
University of Michigan

Abstract

Many aspects of the DOE-BES scientific portfolio cannot function without support from predictive many-body models that can provide valid information relevant to various types of chemical transformations, spectroscopies, and materials properties. Novel and predictive modeling tools capable of overcoming exponential computational barriers of conventional computing are needed to describe chemical transformations that involve quasi-degenerate electronic states and corresponding potential energy surfaces that are relevant for comprehensive understanding of challenges in the areas of catalysis, actinide chemistry and nuclear-waste storage, nitrogen fixation, and energy storage materials. The “Embedding Quantum Computing into Many-body Frameworks for Strongly Correlated Molecular and Materials Systems” project will focus on accurate many-body methods that seamlessly integrate quantum and classical computations to describe complex electron correlation effects for strongly correlated molecular and materials systems.

We will outline the extension of recently introduced sub-system embedding sub-algebras coupled cluster (SES-CC) formalism to the unitary CC formalism. In analogy to the standard single-reference SES-CC formalism, its unitary CC variant allows one to include the dynamical (outside the active space) correlation effects in an SES induced complete active space (CAS) effective Hamiltonian. In contrast to the standard single-reference SES-CC theory, the unitary CC approach results in a Hermitian form of the effective Hamiltonian. Additionally, for the double unitary CC formalism (DUCC) the corresponding CAS eigenvalue problem provides a rigorous separation of external cluster amplitudes that describe dynamical correlation effects - used to define the effective Hamiltonian - from those corresponding to the internal (inside the active space) excitations that define the components of eigenvectors associated with the energy of the entire system. The proposed formalism can be viewed as an efficient way of downfolding many-electron Hamiltonian to the low-energy model represented by a particular choice of CAS. The Hermitian character of low-dimensional effective Hamiltonians makes them an ideal target for quantum computing.



The proposed hybrid classical and quantum computing approach will enable researchers to use combined power of classical and quantum computing in studies of complex chemical processes using novel coupled cluster techniques for downfolding electronic Hamiltonians.

To illustrate the performance and feasibility of the DUCC formalism and the level of dimensionality reduction provided by the DUCC approach, we will provide preliminary results obtained with the Quantum Phase Estimator (using Quantum Development Kit) for benchmark molecular systems described by Gaussian basis sets. We will also outline extensions of the DUCC formalism towards the utilization of plane wave basis and Variational Quantum Eigensolver (VQE) formalism.

Grant Numbers and Grant Titles

This work was supported as part of the Quantum Information Science Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division at the Pacific Northwest National Laboratory (project title "Embedding Quantum Computing into Many-body Frameworks for Strongly Correlated Molecular and Materials Systems").

Postdoc(s):

Dr. Mekena Metcalf

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

1. Nicholas P Bauman, Eric J Bylaska, Sriram Krishnamoorthy, Guang Hao Low, Nathan Wiebe, Karol Kowalski, "Downfolding of many-body Hamiltonians using active-space models: extension of the sub-system embedding sub-algebra approach to unitary coupled cluster formalism," J. Chem. Phys. (submitted) https://arxiv.org/abs/1902.01553 .
2. Guang Hao Low, Nicholas P. Bauman, Christopher E. Granade, Bo Peng, Nathan Wiebe, Eric J. Bylaska, Dave Wecker, Sriram Krishnamoorthy, Martin Roetteler, Karol Kowalski, Matthias Troyer, Nathan A. Baker, "Q# and NWChem: Tools for Scalable Quantum Chemistry on Quantum Computers," Comp. Phys. Commun. (submitted) https://scirate.com/arxiv/1904.01131 .

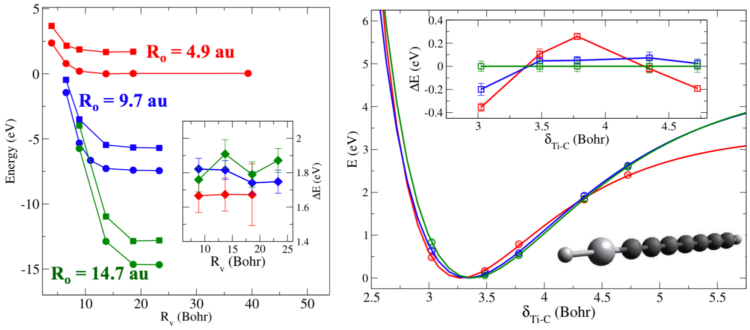
Quantum Monte Carlo calculations for chemical bonding and reactions

Henry Krakauer and Shiwei Zhang

College of William & Mary
Williamsburg, VA 23187

Abstract

This project 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 wave function 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). The AFQMC algorithm has the form of an entangled ensemble of mean-field calculations, so it is computationally more costly than traditional DFT calculations. A main objective of this project is to develop computational strategies to achieve improved speed and even better scaling with system size.



Local embedding and effective downfolding approach in AFQMC. Left panel: H-Ti-C_{29}-H energy for two Ti-C bond lengths (3.4 and 4.35 au), for three occupied orbital cutoff values R_o as a function of the unoccupied orbital cutoff R_v. The inset shows the well-converged energy difference. Right panel: PECs for (R_o, R_v) = (4.9, 8.9), (9.7, 13.7), and (14.7, 18.6), respectively red, green, and green. Solid lines are Morse fits; an energy offset aligns the Morse fit minima. The inset shows deviations from the (14.7, 18.6) reference, indicating rapid convergence, at greatly reduced computational cost. (Eskridge, Krakauer, and Zhang, arxiv.org/abs/1812.05471.)

Recent progress includes:

- the development of a downfolding approach which allows realistic quantum-chemistry- like calculations in solids, including transition metal oxides
- implemented recently developed multiple-projector pseudopotentials into the plane-wave-based AFQMC, which achieves all-electron accuracy while reducing planewave cutoffs, increasing its reach to larger and more complicated systems
- an algorithm for accurate, systematic and scalable computation of interatomic forces within AFQMC, and first implementation of molecular geometry optimization
- implementation of the AFQMC method on GPUs and demonstration of the achievement of systematic chemical accuracy in a set of about 40 transition metal dimers

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. We will continue to integrate AFQMC into the toolkit for quantum chemistry.

Grant Numbers and Grant Titles

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

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

Postdoc(s): Fengjie Ma (partial)

Student(s): Brandon Eskridge

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

1. Purwanto, Wirawan, Shiwei Zhang, and Henry Krakauer, 2016. "Auxiliary-Field Quantum Monte Carlo Calculations of the Molybdenum Dimer." *The Journal of Chemical Physics* 144, 244306 (2016); doi:10.1063/1.4954245.
2. Ma, Fengjie, Shiwei Zhang, and Henry Krakauer, 2017. "Auxiliary-Field Quantum Monte Carlo Calculations with Multiple-Projector Pseudopotentials." *Physical Review B* 95, 165103 (2017); doi:10.1103/PhysRevB.95.165103.
3. J. Shee, S. Zhang, D. R. Reichman, and R. A. Friesner, "Chemical Transformations Approaching Chemical Accuracy via Correlated Sampling in Auxiliary-Field Quantum Monte Carlo," *J. Chem. Theory Comput.* 13, 2667, May (2017); http://pubs.acs.org/doi/abs/10.1021/acs.jctc.7b00224.
4. M. Motta, D. M. Ceperley, G. K.-L. Chan, J. A. Gomez, E. Gull, S. Guo, C. A. Jiménez-Hoyos, T. N. Lan, J. Li, F. Ma, A. J. Millis, N. V. Prokof'ev, U. Ray, G. E. Scuseria, S. Sorella, E. M. Stoudenmire, Q. Sun, I. S. Tupitsyn, S. R. White, D. Zgid, and S. Zhang, "Towards the Solution of the Many-Electron Problem in Real Materials: Equation of State of the Hydrogen Chain with State-of-the-Art Many-Body Methods," Phys. Rev. X 7, 031059 (2017); link.aps.org/doi/10.1103/PhysRevX.7.031059.
5. M. Motta and S. Zhang, "Communication: Calculation of interatomic forces and optimization of molecular geometry with auxiliary-field quantum Monte Carlo," J. Chem. Phys. 148, 181101 (2018); aip.scitation.org/doi/10.1063/1.5029508.
6. B. Eskridge, H. Krakauer, and S. Zhang, "Local embedding and effective downfolding in the auxiliary-field quantum Monte Carlo method," arXiv.cond.mat (2019); arxiv.org/abs/1812.05471.
7. J. Shee, B. Rudshteyn, E. J. Arthur, S. Zhang, D. R. Reichman, and R. A. Friesner, "On Achieving High Accuracy in Quantum Chemical Calculations of 3 d Transition Metal-Containing Systems: A Comparison of Auxiliary-Field Quantum Monte Carlo with Coupled Cluster, Density Functional Theory, and Experiment for Diatomic Molecules," J. Chem. Theory Comput. 15, 2346 (2019); pubs.acs.org/doi/10.1021/acs.jctc.9b00083.

Theoretical Framework for New Magnetic Materials for Quantum Computing and Information Storage

Anna I. Krylov
Department of Chemistry, University of Southern California,
Los Angeles, CA 90089-0482; krylov@usc.edu

Program Scope

The focus of this project is on molecular magnetic materials for information storage and quantum computing. We are developing robust, first-principle methods for computing relevant electronic and magnetic properties of molecular building blocks (SMMs) of novel magnetic materials and quantum computers. These tools will enable theoretical modeling of SMMs' behavior, facilitating the interpretation of experimental studies and aiding the design of novel magnetic materials. Our strategy is based on the spin-flip (SF) approach, which extends the hierarchy of black-box single-reference methods to strongly correlated systems. Specifically, we develop general scalable algorithms and computer codes for calculating molecular properties, with an emphasis on spin-related properties, such as zero-field splittings, hyperfine couplings, g-tensors, and asymmetric Dzyaloshinksii-Moriya interactions. While our primary focus is on SF wave functions and SF-TDDFT, the underlying theory and computer codes are formulated using reduced density matrices, such that these tools are applicable to a broader class of methods. To extend the scope of applicability of wave-function-based SF methods to larger systems, we develop reduced-scaling approaches for the equation-of-motion coupled-cluster (EOM-CC) methods and continue developing libtensor (our open-source general tensor contraction library for many-body methods) for high-performance computations.

Summary of recent major accomplishments

During the past year, we were primarily focusing on method development for calculations of molecular properties within the EOM-CC framework. We developed theoretical framework and computer code for computing spin-orbit couplings (SOCs) for the entire multiplet from reduced spinless density matrix of just one multiplet component. The approach greatly simplifies SOCs calculations and takes care of the phase problem inherent to Born-Oppenheimer's separation of the nuclear and electronic degrees of freedom. The theory is formulated using density matrices and is wave-function agnostic. We already applied the theory to the EOM-CCSD wavefunctions; the paper is now being finalized for publication. We also initiated collaboration with Professors D. Casanova and N. Mayhall, with an aim to combine our approach with the RAS-CI methods. We also developed formal expressions for computing g-tensors. To extend the EOM-CC framework to large systems, we implemented RI/Cholesky analyic gradient (the paper has been submitted to the Journal of Chemical Physics).

The code for Cholesky/RI gradients and for SOCs is included in the upcoming 5.2 release of the Q-Chem electronic structure program. The requisite developments within opensource libtensor library are on github. The results have been presented on several major conferences.

Highlight: Magnetic anisotropy in single-center Fe-containing SMM

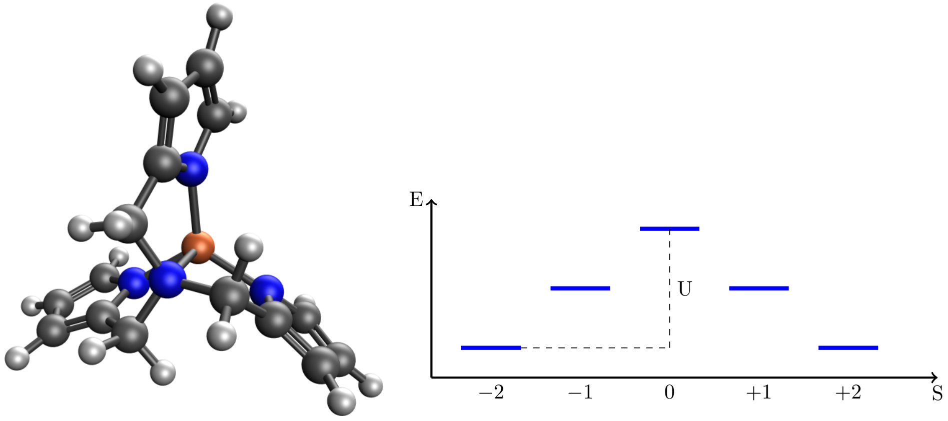


Figure 1: Left: Structure of (tpa)Fe ($C_{15}N_4H_{15}Fe$) in the hextet neutral state. Iron is shown in red, nitrogens in blue, carbons in gray, and hydrogens in white. Right: The lowest spin-split levels of quintet anionic (tpa)Fe^-, showing a spin-reversal barrier U (the energy gap between the lowest and the highest spin-split states within the ground state multiplet).

Figure 1 shows the structure of a single-center Fe-containing SMM. Using our new codes for SOC calculations, we computed the spin-reversal barrier (spin-splitting gap in the multipletl). The state energies and SOCs were computed with EOM-EA-MP2/cc-pVDZ. Spin–orbit splittings were computed in state-interaction approach with varying number of electronic states. Depending on the number of sates included in the state-interaction calculation, the computed barrier ranges between 157-173 cm^{-1}, in excellent agreement with the experimental value of 158 cm^{-1}.

Current developments and future plans

In the near future, we plan to complete the following:
(i) Finalize the paper on "General framework for calculating spin–orbit couplings using spinless one-particle density matrices: Theory and application to the equation-of-motion coupled-cluster wave functions"; (ii) Complete the implementation of SOCs within RAS-CI; (iii) Complete the implementation of the g-tensors; (iv) Develop the Bloch equation based framework for automatic generation of model Hamiltonians; (v) Continue benchmark studies and illustrative calculations of SMMs.

Grant numbers and grant titles

Theoretical Framework for New Magnetic Materials for Quantum Computing and Information Storage, DE-SC0018910.
Postdocs: Dr. Alexandre Barrozo.
Students: Pavel Pokhilko.

Heather J. Kulik

Recovering exact conditions at semi-local DFT cost to mitigate energy and density errors for transition metal chemistry

Heather J. Kulik
Department of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, MA 02139
email: hjkulik@mit.edu

Abstract

Program scope: Accurate prediction of electronic properties of open-shell transition metal complexes is essential for solving outstanding challenges in resource utilization and energy storage through materials and catalyst design. Nevertheless, the properties that make these materials and molecules so compelling also make them extremely challenging to study accurately with any computational model. Although density functional theory (DFT) remains the method of choice for its balance of speed and accuracy in computational screening, semi- local approximations in DFT, such as the generalized gradient approximation (GGA), suffer from many electron self-interaction errors (MESIE) that causes them to predict erroneous spin states and geometries, barrier heights and dissociation energies, and orbital energies, to name a few. The primary aim of this work is to understand and decouple some such errors, aiming to eliminate or avoid increasing some of the more challenging errors (e.g., density delocalization error, static correlation error) rather than focusing on a single number (e.g., relative energy error) (Figure 1). Additionally, we aim to understand how recovering piecewise linearity (i.e., eliminating energetic delocalization error) impacts density properties with respect to accurate correlated wavefunction theory references, which we refer to here as density delocalization error. We then define relative energy errors as residual errors in semi-local functionals that remain, even when static correlation errors, deviations from piecewise linearity, and density errors are all eliminated.

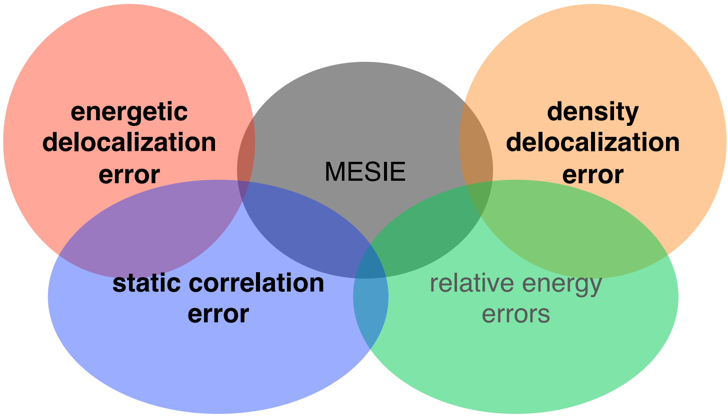


Figure 1. Range of coupled errors present in approximate density functional theory studied in this work.

Recent Progress: We aim to both understand and correct approximate DFT errors for predictive modeling of transition metal chemistry through the following:

i) We have examined how common approximations to recover the derivative discontinuity (e.g., hybrid functionals) affect the density properties of transition metal complexes and in turn affect their geometries and spin-state ordering. We have observed that a localization of the density away from the metal in transition metal complexes occurs with incorporation of Hartree-Fock (HF) exchange. This incorporation of HF exchange improves agreement with higher level wavefunction theory results (i.e., from CCSD(T) densities). In particular, nominally non-bonding δ orbitals delocalize to form bonds with the neighboring oxygen atoms in PBE more than when HF exchange is incorporated. Tuning the functionals to eliminate this density delocalization leads to significant, qualitative changes in the angular potential energy curve (PEC) of the MO_2 molecules. As an example, the ground state of MnO_2 has a relative bent/linear energy difference of 0.6 eV with PBE but the linear molecule is only destabilized by half that in the case of 40% exact exchange (Figure 2). At the same time, in some cases, incorporating HF exchange will worsen spin state ordering, indicating that there is no one-size fits all approach to getting density, geometry, and spin splitting properties accurately within a generalized Kohn-Sham framework.

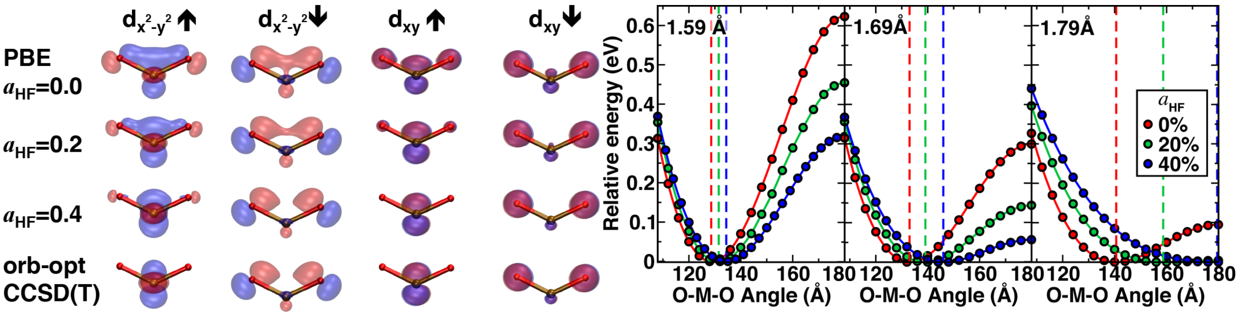


Figure 2. (Left) Orbitals in MnO_2 and how their shapes change with increasing HF exchange in comparison to CCSD(T) (bottom) for increasing fractions of HF exchange. (Right) Angular potential energy curves of MnO_2 with fixed bond lengths annotated in inset and how those bond lengths change with incorporation of HF exchange.

ii) We continue to extend our method to demonstrate recovery of the flat-plane condition that is a union of the requirement of piecewise linearity with electron removal or addition as well as unchanged energy when changing the spin of an electron in isoenergetic orbitals. We accomplish this at no computational cost over semi-local DFT by building from scratch our judiciously-modified DFT (jmDFT) functionals designed to oppose errors inherent in semi-local functionals. New accomplishments this year are fully non-empirical evaluation of the coefficients and demonstration on p and d-electron configurations. Our method reduces fractional spin line errors (i.e., static correlation errors) while improving deviations from piecewise linearity at no computational cost (Figure 3). The present method is also being tested on both improving dissociation energies without introducing static correlation error and on recovering predictive spin state ordering.

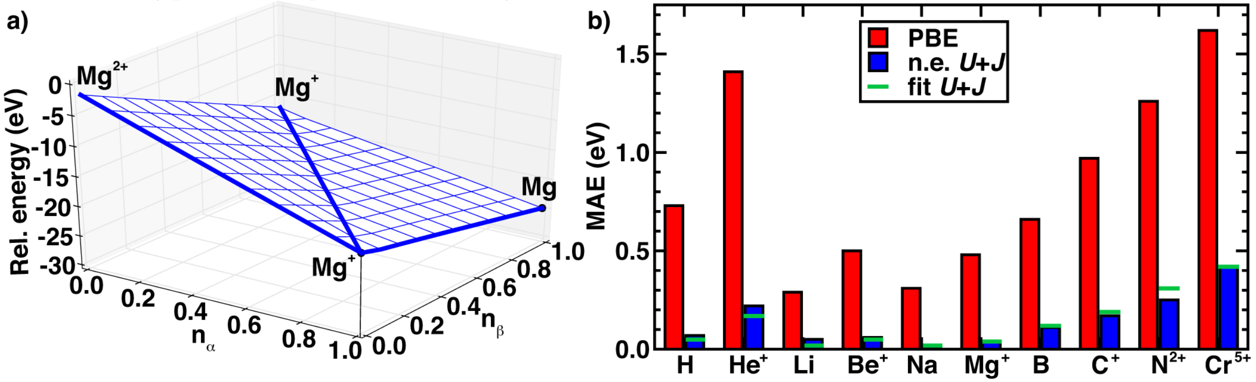


Figure 3. a) Example of non-empirical jmDFT (*U*+*J*/*J*′) recovery of the Mg^{+} flat plane with energies in eV and the Mg^{2+} relative energy set to zero. The x- and y-axis values correspond to number of spin up (n_α) and spin down (n_β) 3*s* electrons, respectively, and charge states of Mg^{2+} are annotated on the plot. b) The mean absolute error (MAE, in eV) over the *N*-1- to *N*-electron portion of the flat plane for ten ions from PBE (red bars), non-empirical jmDFT (*U*+*J*) coefficients (n.e. *U*+*J*, blue bars), and the result from fit *U*+*J* coefficients (green horizontal lines).

iii) Finally, we make efforts to overcome approximate DFT errors through the development of data-driven structure-method relationships, including in artificial neural networks that can predict sensitivity of spin-state ordering in transition metal complexes to changes in the exchange-correlation functional. These data-driven models have allowed us to examine how sensitive lead compounds are to the exchange-correlation approximation.

Future Plans: Now that we have accurate non-empirical coefficients in our method, we are looking at using a Wannier orbital basis to overcome limitations in the prior projection techniques as well as to improve densities (e.g., where anions were poorly bound and in improving densities of delocalized states).

DE-SC-0018096: "Simultaneous mitigation of density and energy errors in approximate DFT for transition metal chemistry"
Postdoc: Fang Liu
Ph.D. Students: Akash Bajaj, Qing Zhao (Ph.D. 2018)

Publications acknowledging this grant (since 9/1/17):

1. A. Bajaj, J. P. Janet, and H. J. Kulik "Communication: Recovering the flat-plane condition in electronic structure theory at semi-local DFT cost", *Journal of Chemical Physics*, **147**, 191101 (2017). http://dx.doi.org/10.1063/1.5008981
2. Q. Zhao and H. J. Kulik "Where Does the Density Localize in the Solid State? Divergent Behavior for Hybrids and DFT+U", *Journal of Chemical Theory and Computation*, **14**, 670-683 (2018). http://dx.doi.org/10.1021/acs.jctc.7b01061
   ACS Editors' Choice
3. J. P. Janet, L. Chan, and H. J. Kulik "Accelerating Chemical Discovery with Machine Learning: Simulated Evolution of Spin Crossover Complexes with an Artificial Neural Network", *The Journal of Physical Chemistry Letters,* **9**, 1064-1071 (2018). http://dx.doi.org/10.1021/acs.jpclett.8b00170
   Featured in Chemical & Engineering News February 19, 2018
   https://cen.acs.org/articles/96/i8/Machine-learning-identifies-potential-inorganic.html
4. A. Nandy, C. Duan, J. P. Janet, S. Gugler, and H. J. Kulik "Strategies and Software for Machine Learning Accelerated Discovery in Transition Metal Chemistry", *Industrial & Engineering Chemistry Research*, **57**, 13973-13986 (2018). http://dx.doi.org/10.1021/acs.iecr.8b04015
5. F. Liu, T. Yang, J. Yang, E. Xu, A. Bajaj, and H. J. Kulik "Bridging the homogeneous-heterogeneous divide: modeling spin and reactivity in single atom catalysis" *Frontiers in Chemistry*, **7**, 219 (2019). https://doi.org/10.3389/fchem.2019.00219
   Invited article for "Rising Stars" special topic.
6. J. P. Janet, F. Liu, A. Nandy, C. Duan, T. Yang, S. Lin, and H. J. Kulik "Designing in the Face of Uncertainty: Exploiting Electronic Structure and Machine Learning Models for Discovery in Inorganic Chemistry", *Inorganic Chemistry*, ASAP. http://dx.doi.org/10.1021/acs.inorgchem.9b00109
   Invited article for "Celebrating the Year of the Periodic Table: Emerging Investigators in Inorganic Chemistry"
7. A. Bajaj, F. Liu, H. J. Kulik "Non-empirical, low-cost recovery of exact conditions with model-Hamiltonian inspired expressions in jmDFT" *Journal of Chemical Physics*, **150**, 154115 (2019). https://doi.org/10.1063/1.5091563

Designing and Screening of Organic Sensitizers for Highly Efficient Dye-Sensitized Solar Cells: *In Silico* Approaches

Jerzy Leszczynski (PI)

Interdisciplinary Center for Nanotoxicity, Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, MS 39217
E-mail: jerzy@icnanotox.org

ABSTRACT

Our study has the following two primary objectives: (1) To understand the basic electron transfer mechanism along with optical properties of two different type of solar cells viz. organic/polymer solar cells (PSCs) and dye-sensitized solar cells (DSSCs) via Quantitative Structure-Property Relation (QSPR) analysis and quantum chemical calculations and (2) To design new sensitizers based on QSPR model and screen them via the state of the art Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations. This project also focuses on examining a variety of factors impinging short-circuit current density (JSC) and open-circuit voltage (VOC) characteristics through the critical assessment of charge transfer bands as well as optical and electrochemical properties of photoexcited dyes as a function of dye's building block to gain insight into the photophysical properties of the organic dye-sensitizer based DSSCs. As the result we designed and screened potential lead organic dye-sensitizers for DSSCs with higher photo-conversion efficiency.

Two families of organic dye-sensitizers: Tetrahydroquinoline (THQ) and Indoline (IND) we considered. Based on the comprehensive analysis, modeling and design followed by the structural and electronic properties evaluation we proposed new, efficient lead dyes for future dye-sensitized solar cells (DSSCs). In the case of THQ, all the dyes were screened rationally through different computational approaches to explore their potential applications as photosensitizers for DSSCs. Compelling photophysical properties such as electron injection driving force, electron injection time, and dye regeneration were studied for the isolated dyes under the DFT and TD-DFT frameworks. Index of spatial extent (S, D, and Δq), the strength of charge transfer and separation along with the charge transfer process were explored. First principle approach including van der Waals density functional calculation of dye@TiO2 interface indicates that all of the designed dyes have optimal interfacial behavior. Bader charge analysis, the partial density of state (PDOS), charge density and electrostatic potential difference calculations confirm that THQ7 and THQ9 are the most efficient dye-sensitizers. The other five designed dyes also possess the required properties to emerge as effective dye-sensitizers potentially better than those already utilized — performance and energy conversion efficiency of sensitizers[1].

To ensure the balance between VOC and JSC, we designed D−A−π−A-based IND family dyes taking guidance from the QSPR model. An array of optoelectronic properties of the isolated dye and dyes adsorbed on a TiO2 cluster that simulates the semiconductor was explored by density functional theory (DFT) and time-dependent DFT methods. Light absorption spectra, vertical dipole moment, the shift of conduction band of the semiconductor, excited state lifetime,

the driving force of electron injection, the photostability of the excited state, and exciton binding energy were computed. Our study showed that the presence of an internal acceptor such as pyrido[3,4-b]pyrazine (pyrazine) would increase the VOC, compared to the benzothiadiazole moiety. Considering the balance between the VOC and JSC (short circuit current) along with the all calculated characteristics, the IND3, IND5, and IND10 are the most suited among the designed dyes to be used as potential candidates for the photo-efficient DSSCs. This study provides the results of rational molecular design followed by an exploration of photophysical properties that could be used as a valuable reference for the synthesis of photo-efficient dyes for DSSCs [2].

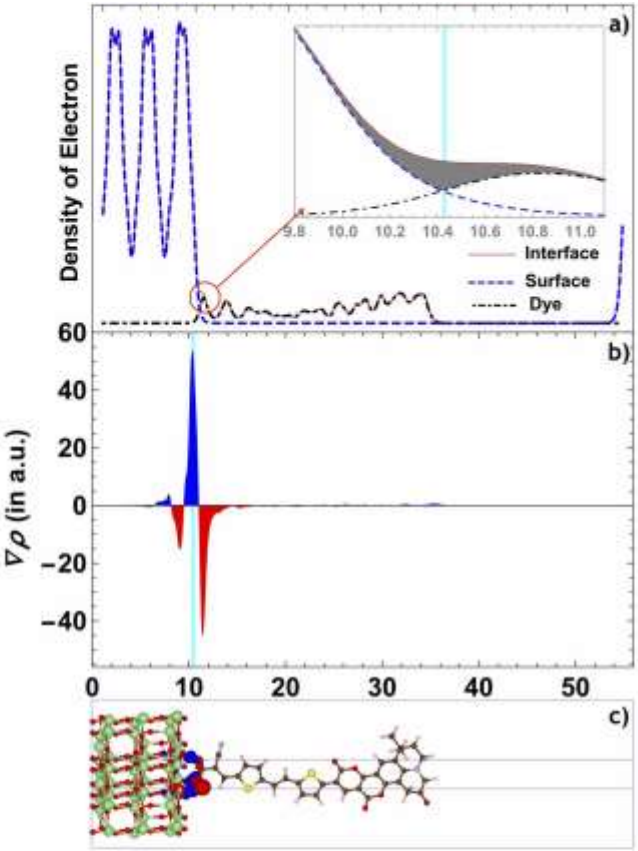


Figure 1. For THQ1 (a) Planar averaged charge density of dye@TiO2 system after absorption (red), isolated dye (dashed) and surface (dotted) at the same relative positions. It is clear that there is no significant charge redistribution away from the interface region. Inset: magnifying the interface region and yellow part showing the amount of injected charge. (b) Planar average charge density difference as a function of position in the Z-direction, in Å. (c) 3D charge density difference with an isovalue of 0.006e/Å3. Blue and red color represents charge accumulation and depletion in space. The vertical cyan line indicates the interface line of dye@TiO2 system. Ref [1]

We will continue our study to unveil the physical insights of the mechanism of photoinduced charge transfer, electron injection and recombination process at the semiconductor-dye-sensitizers (N,N-dialkylaniline, Triphenylaniline) interface in organic dye-sensitized solar cells. These processes are pivotal to increase the photo-conversion efficiency of DSSCs. Determination of the nature of the fluorescent state of the dye-sensitizers is one of the crucial tasks because the stability of this state (in terms of a lifetime) endows a significant role in the electron mobilization process, electron coupling strength in the cell.The prediction of quantum yield for electron injection procedure that requires the estimations of rate constant for radiative and non-radiative decay of the excited state of isolated dye molecule as well as the rate constant for electron transfer from a specified state of the photosensitizer to the many acceptor states of the semiconductor will be carried out based on the Marcus electron transfer theory.

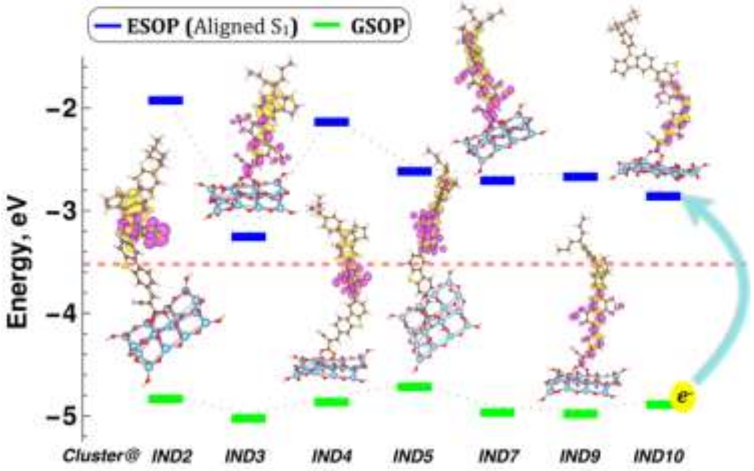


Figure 2: Energy alignment of the IND dyes on TiO2 along with the CDD of the dyes@cluster complex and CB of TiO2. Magenta (yellow) indicates positive and negative region with the isovalue of 0.0009 eV/Å.

Grant Numbers and Grand Title

DE-SC0018322: Development of efficient solar cells using combination of QSPR and DFT approaches

Postdoc(s): Dr. Supratik Kar

Student(s): Juganta K. Roy

Publications Acknowledging this Grant

1. Juganta K. Roy, Supratik Kar, Jerzy Leszczynski, Insight into the optoelectronic properties of designed efficient tetrahydroquinoline dye-sensitizers on TiO2(101) surface for solar cells: first principles approach. Scientific Reports, 8, 10997 (2018). DOI: 10.1038/s41598-018-29368-9

2. Juganta K. Roy, Supratik Kar, Jerzy Leszczynski, Electronic Structure and Optical Properties of Designed Photo- Efficient Indoline-Based Dye-Sensitizers with D−A−π−A Framework, J. Phys. Chem. C, 123, 6, 3309-3320 (2019). DOI: 10.1021/acs.jpcc.8b10708

Toward Ab Initio Quantum Molecular Dynamics in Dense Manifolds of Electronic States

Dmitry A. Fedorov, Andrew Durden, Benjamin G. Levine
Department of Chemistry, Michigan State University, East Lansing, MI 48824

Abstract

In recent years, ab initio nonadiabatic molecular dynamics methods have arisen as valuable tools for modeling the dynamics of electronically excited molecules and materials, especially when prior knowledge of the reaction mechanism of interest is not available. However, existing methods are typically limited to systems where the dynamics are restricted to relatively few (<10) electronic states. Many interesting chemical problems, however, require modeling dynamics on a much larger number of states, or even in a continuum of states. Examples include dynamics of plasmonic materials, optoelectronic materials, molecules in strong laser fields, atmospheric chemistry, and radiation damage to molecules and materials. The broad goals of the present project are to develop an ab initio nonadiabatic molecular dynamics method that can accurately and efficiently model dynamics in dense manifolds of electronic states and to apply that method to model light-matter interactions in plasmonic nanomaterials and other systems. We are developing both molecular dynamics and electronic structure tools to achieve these broad goals.

With regard to modeling molecular dynamics, many methods exist for modeling dynamics on a few (up to ~10) electronic states, but most of these become impractical for systems with dense manifolds of states. In such cases, difficulties arise because explicit calculation of a large number of electronic states becomes intractable. Ehrenfest molecular dynamics, on the other hand, does not require explicit knowledge of the electronic eigenspectrum, and therefore is a practical tool for modeling dynamics on many states. Unfortunately, Ehrenfest suffers from well-known issues with overcoherence, resulting in unphysical predictions of chemical outcomes. Several methods exist to incorporate decoherence into Ehrenfest dynamics, but these methods again require explicit calculation of the full electronic eigenspectrum.

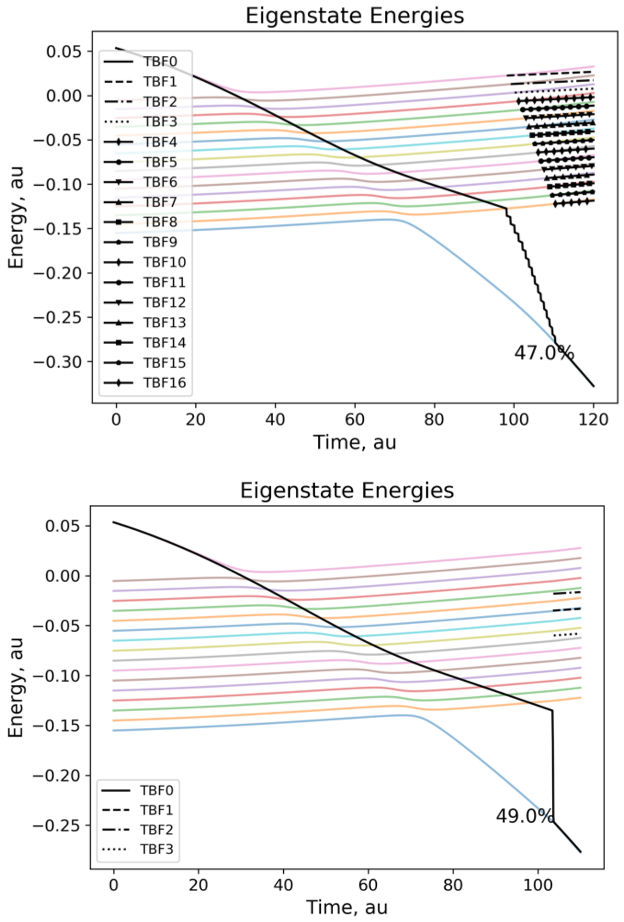


Figure 1. Energies of several trajectory basis functions (TBFs; in black) from MCDMS simulations of a trajectory crossing a dense band of states using exact eigenstates (top) and two approximate eigenstates (bottom). Exact adiabatic energies are shown with collored lines. The probabilities of transmission through the dense bands of states are nearly identical: 47.0% and 49.0% with the full eigenspectrum and a minimal number of approximate eigenstates, respectively.

To solve these problems, we have developed a variant of the full multiple spawning nonadiabatic molecular dynamics method capable of accurately modeling dynamics on many electronic states: multiple cloning in dense manifolds of states (MCDMS). Like its parent method, MCDMS is a fully quantum dynamical approach capable of modeling dynamics without preconceptions about the reaction path. It treats decoherence between populations on different electronic states in a fully ab initio way. The key advance in MCDMS is that it does not require calculation of the full electronic eigenspectrum during the simulation. Instead, cloning (basis set expansion) is based on a set of approximate eigenstates. The level of approximation is systematically improvable from extremely computationally inexpensive to exact, thus enabling the modeling of accurate dynamics on many electronic states. To date, we have implemented MCDMS in the pySpawn software package, and it has been tested on several model systems. We have found that the probability of transmission of a wavepacket through a dense band of states can be accurately predicted while calculating very few approximate eigenstates (often as few as two; see Figure 1).

A second challenge arises when modeling electronic dynamics in a light field, as is important in plasmonics and strong field chemistry/physics. The rate of decoherence depends on the difference in nuclear kinetic energy between populations evolving on different electronic states. In an isolated system, this rate is well approximated from the potential energy difference between electronic states. This approximation is used, for example, in the rescaling of momentum after hopping in fewest switches surface hopping. However, when an electronic transition arises from an external field, it is wrong to use the energy gap between states to define the decoherence time. The energy of the absorbed photon must also be considered. Our solution to this problem must be extremely computationally efficient, as integration of the electronic wave function over 10^5-10^7 time steps will be required in typical simulations.

To enable accurate treatment of decoherence in a light field, we have developed a GPU-accelerated time-dependent Floquet configuration interaction (TD-F-CI) method for modeling light matter interactions. GPU-acceleration enables efficient application to relatively large systems. Time-dependent configuration interaction has many advantages over the more widely used time-dependent density function theory, e.g. correct prediction of Rabi oscillations and systematic improvability. Our approach utilizes direct configuration interaction strategies familiar from time-independent electronic structure theory, eliminating the need to form or store any data structures that are the full dimension of the Hamiltonian. The Floquet (dressed state) formalism is necessary to accurately treat decoherence in our dynamics simulations, which requires that light absorption be treated as an energy-conserving process, as described above. We have implemented TD-F-CI in the TeraChem software package. Performance is found to be excellent, scaling linearly with the number of photons. Early results show that Rabi oscillations can be accurately computed in the Floquet formalism.

Having developed the two methodological building blocks that we need to perform ab initio quantum molecular dynamics in dense manifolds of electronic states, our next step will be to integrate them. After integration, we will apply MCDMS/TD-F-CI to model nonlinear optical processes and nonradiative dynamics in plasmonic nanomaterials.

DE-SC0018432 – A Multireference Approach to Electron and Electron-Nuclear Dynamics in Nanomaterials

Postdoc(s): Dmitry A. Fedorov

Student(s): Andrew Durden

Machine Learning for Excited-State Dynamics

James P. Lewis

P.O. Box 6315, 135 Willey St., Department of Physics and Astronomy,
West Virginia University, Morgantown, WV 26506-6315
Email: james.lewis@mail.wvu.edu; Web: http://fireball.phys.wvu.edu

Co-Investigators: Aldo Romero, West Virginia University; Oleg Prezhdo,
University of Southern California; Marcus Hanwell, Kitware, Inc.

Program Scope

The primary objective of this computational chemistry sciences team is to design a machine-learning NAMD environment that will utilize current petascale and future exascale computational capabilities to advance understanding of charge and energy flow in materials. Our machine-learning NAMD environment will 1) integrate advanced NAMD capabilities directly into electronic structure software (e.g., ABINIT, Quantum Espresso, VASP, etc.); 2) merge the preparatory tools of Pychemia into PYXAID and Avogadro environments so that massive data collection from NAMD simulations can be rapidly utilized by machine-learning analysis of excited-state-dynamic ensembles.

Recent Progress

The proposed integrated machine-learning environment will provide the opportunity to understand charge- and energy-transfer dynamics within a variety of photo-activated materials. During the initial stages of this award, we have developed a roadmap for observing pattern recognition in charge- and energy-transfer dynamics. Primarily, we are developing algorithms for observing pattern recognition in electronic, molecular orbital, densities from nonadiabatic molecular dynamics simulations. Observing and recognizing these electron-dynamic patterns will enable a comprehensive understanding in electron- and energy-transfer in materials.

Applications and Results. We explore electron-dynamic pathways in a variety of materials. Initially, to understand these processes, we consider Pt nanocrystals on the MoS_2 substrate as a prototypical system (see Fig. 1). A significant challenge is to understand how the configurations of catalysts and photocatalysts may influence the charge-transfer dynamics at the interface of the catalyst and its substrate. Here, we utilized a neural network potential (DeepPOT-SE) to explore various configurations from which to build models of Pt nanocrystals on a MoS_2 substrate; we utilize the structural configuration exploration to map many different potential energy surfaces. From these initial configurations and their respective potential energy surfaces, we investigate electron-dynamics pathways from nonadiabatic molecular dynamics simulations.

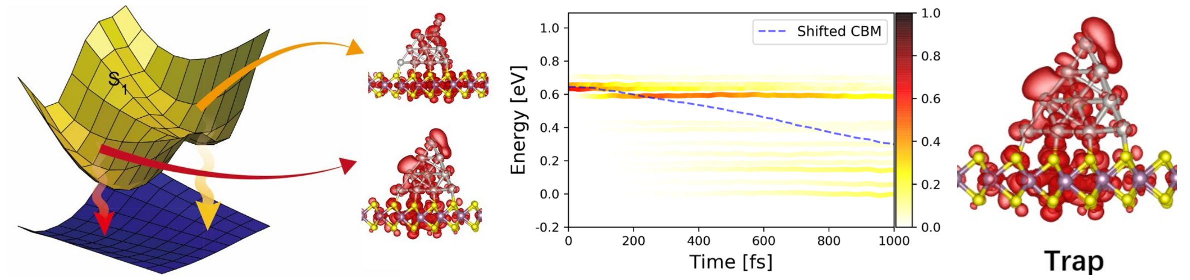


Figure 1. Machine learning approach to evaluate electron-dynamics pathways in Pt- MoS_2 system. First, we use a neural network potential (DeepPOT-SE) to explore structural configurations from which to map out various potential energy surfaces and discover configuration with the most efficient processes (*left panel*). Subsequent nonadiabatic molecular dynamics simulations reveal a trapped state (orange probability density in *central panel*); a probability density of a trapped state is shown.

Pattern Recognition for Charge- and Energy-Transfer Dynamics - Marching Cubes. Probability densities, molecular orbital states, are represented visually as isosurfaces; these isosurfaces may be plotted in terms of a marching cubes algorithm (a marching square algorithm is shown in Fig. 2). The advantage of a marching cubes algorithm is that the isosurface can be uniquely defined anywhere in terms of the 15 marching cubes representation (there are actually 256 marching cubes, but this reduces to a set that is rotationally equivalent). Therefore, the representation of an isosurface is defined by a finite, and small, basis set representation of these well-defined marching cubes. Such a small basis set is perfect for evaluating kernels or similarities between different isosurfaces because of the reduced dimensionality (the curse of machine learning algorithms).

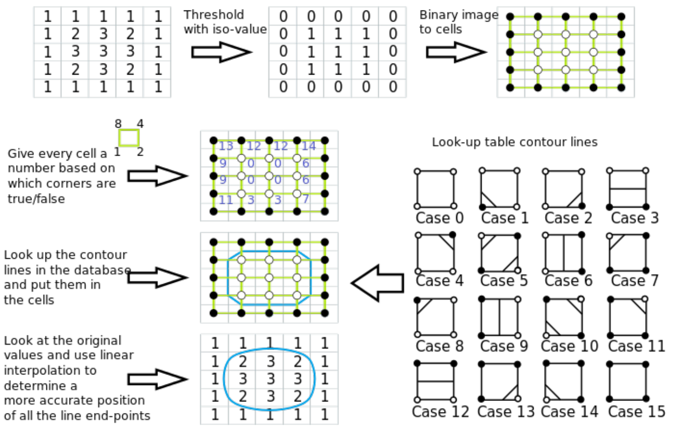


Figure 2. Diagram of marching cubes algorithm; marching cubes for the basis set of utilizing kernel regression formalisms in machine-learning algorithms.

There are many ways to represent a kernel within machine-learning. As we modelling charge-transfer pathways which are quantum mechanical events, and hence probabilistic, we choose to use kernels derived from probabilistic generative models.[77] The probability product kernel, generally used for comparing strings of data, is defined as

$$\kappa(x_i, x_j) = \int p(x|x_i)^{\rho} p(x|x_j)^{\rho} dx,$$

where $\rho > 0$, and $p(x|x_i)$ may be approximated by $p(x|\boldsymbol{\theta})$; $\boldsymbol{\theta}$ is a parameter (model) estimate. Evaluating these kernels are necessary for machine-learning algorithms that utilize kernals (*e.g.* kernel regression) for evaluating similarities, or pattern recognition, in complex data. Because the isosurfaces can be expanded as a linear combination of marching cubes, then evaluating the probabilities $p(x|x_i)$ is computationally very efficient. Currently, we have developed a machine-learning formalism using these kernel expressions and marching cubes to evaluate pattern recognition in electron densities.

Grant DE-SC0019491: Machine-Learning for Excited-State Dynamics

Postdoctoral Associates Supported: Pengju Ren
Students Supported: Weibin Chu, Arturo Hernandez, Gihan Panapitiya, Ike Tan, and Guoqing Zhou

Publications

1. G. Panapitiya, G. Avenaño-Franco, P. Ren, X. Wen, Y. Li, and J.P. Lewis. 2018. “Machine-learning prediction of CO adsorption in thiolated Ag-alloyed Au nanoclusters,” *J. Am. Chem. Soc.* 140, 17508-17514.
2. P. Tavadze, G. Avenaño-Franco, P. Ren, X. Wen, Y. Li, and J.P. Lewis. 2018. “A machine-driven hunt for global reaction coordinates of azobenzene photoisomerization,” *J. Am. Chem. Soc.* 140: 285-290.
3. J.I. Mendieta-Moreno, D.G. Trabada, J. Mendieta, J.P. Lewis, P. Gómez-Puertas, and J. Ortega. 2016. “Quantum mechanics/molecular mechanics free energy maps and nonadiabatic simulations for a photochemical reaction in DNA: Cyclobutane thymine dimer. *J. Phys. Chem. Lett.* 7:4391-4397.
4. V. Zobač, J.P. Lewis, and P. Jelínek. 2016. “Nonadiabatic molecular dynamics simulations of opening reaction of molecular junctions,” *Nanotechnology* 27:285202.
5. O. Ranasingha, H. Wang, V. Zobač, P. Jelínek, G. Panapitiya, A. Neukirch, O.V. Prezhdo, and J.P. Lewis. 2016. “Slow relaxation of surface plasmon excitations in Au_{55}: The key to efficient plasmonic heating in Au/TiO2. *J. Phys. Chem. Lett.* 7: 1563-1569.

Modeling Magnetic Field Effects with Variational Electronic Structure Methods

Xiaosong Li*

Department of Chemistry, University of Washington, Seattle, WA, 98195

E-mail: xsli@uw.edu

Abstract

Electron spin is a fundamental physical property that is important to a wide array of science and technological applications such as energy storage, quantum computing, and chemical catalysis. An atomic or molecular system has a spin-dependent many-electron response that can be perturbed by an external electromagnetic field. Although effective model Hamiltonians with perturbative treatments of external fields have their merits, they are limited in their description of spin-dependent processes in the strong perturbation limit. While molecular response to external electric fields has been a subject of extensive theoretical work, computational frameworks for modeling finite magnetic field effects have been lagging behind mainly due to three challenges; the gauge-origin problem, spin non-collinearity, and necessity of complex arithmetic.

It is well known that certain symmetry breaking, such as an external static magnetic field breaking time reversal symmetry and geometric frustration breaking continuous translation symmetry, will cause noncollinear spin configurations to arise (see Fig. 1). Thus, a proper description of spin processes must come from a solution of the first-principles spin-dependent Hamiltonian that allows a variational treatment of non-collinear spin. The generalized Hartree-Fock (GHF) method removes the spin collinear constraint from conventional restricted and unrestricted Hartree-Fock (RHF and

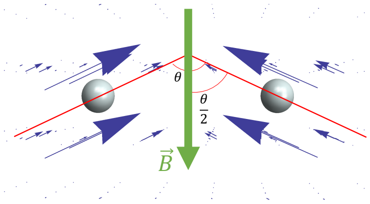


Figure 1. Illustration of noncollinearity of two spin vectors.

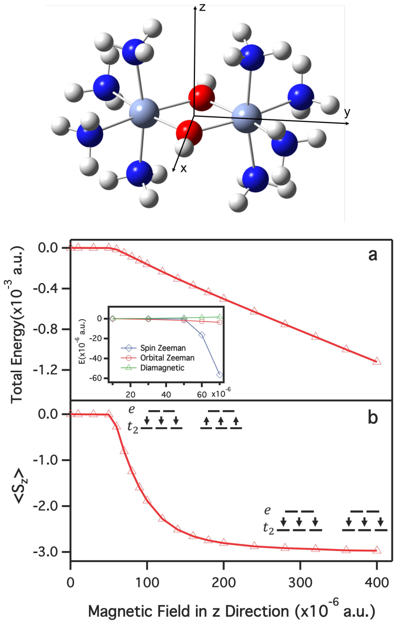


Figure 2. (**a**) Total energy of di-Cr(III) complex in a finite magnetic field. (**b**) The expectation value of S_z of the $\mathbb{C}$-GHF solution. The magnetic field is applied in the $+z$ direction, perpendicular to the Cr-O-Cr-O plane.

UHF) methods so that spins are allowed to rotate freely in a non-collinear framework. The GHF approach has been shown to be a convenient and inexpensive computational platform to simulate spin dynamics of a single spin center in a static magnetic field and in a dissociated reaction. In this talk, I introduce a variational spin non-collinear approach using the complex GHF ($\mathbb{C}$-GHF) method with London orbitals in the presence of a strong magnetic field. The method implemented herein is able to model both spin-collinear and noncollinear phenomena as well as the processes underlying the magnetic field induced spin phase transition.

In order to probe the spin phase transition in a complex magnetic molecular system, we study the spin characteristics of a di-chromium molecular complex, $[(H_3N)_4Cr(OH)_2Cr(NH_3)_4]^{4+}$, in a uniform magnetic field (Fig. 2) In the di-Cr(III) molecular complex, the octahedral ligand field splits Cr d orbitals into e and t_2 sets where three unpaired electrons occupy the t_2 manifold. The ground state of the di-Cr(III) molecular complex exhibits a magnetic $\mathbb{C}$-GHF solution. In the absence of an external magnetic field, the ground state wave function of the di-Cr(III) molecular complex obtained from the $\mathbb{C}$-GHF calculation is antiferromagnetic. Figure 2 plots the relative total energy compared to that in the absence of a magnetic field and the expectation value of S_z as a function of applied magnetic field strength. When the magnetic field is relatively weak, the system is in the antiferromagnetic state. In this region, the super-exchange coupling is constant and the small energy change is solely due to the orbital Zeeman and diamagnetic terms. As the magnetic field reaches a critical point ($\sim 60 \times 10^{-6}$ a.u.) where a small change in spin alignment can give rise to a spin Zeeman term strong enough to overcome the antiferromagnetic super-exchange coupling, the system starts to undergo a spin phase transition. As the magnetic field strength increases, the energy of the molecule decreases due to the increasing spin Zeeman contribution. The change of expectation value of S_z indicates that the spin state gradually switches from the antiferromagnetic $\langle S_z \rangle = 0$ to ferromagnetic $\langle S_z \rangle = -3$ configuration. This case study suggests that $\mathbb{C}$-GHF calculations with London atomic orbitals can be used to investigate magnetic phase transitions in transition metal complexes.

The variational $\mathbb{C}$-GHF method with London orbitals can also be used to compute magnetic phase transitions in molecular complexes driven by an external magnetic field. Results show that there exists a critical point where the spin Zeeman is large enough to compete with the super-exchange coupling so that the spin phase transition takes place and drives the magnetic phase transition. The method presented in this work is based on the single Slater determinant wave function ansatz which lacks important electron correlation effects. Future developments will use the variational $\mathbb{C}$-GHF reference for correlated electronic structure methods which will provide more accurate descriptions of spin and magnetic phase transitions.

Grant Number: DE-SC0006863

Program Title: Ab Initio Relativistic Electron Spin Dynamics

Principal Investigator: Xiaosong Li, Department of Chemistry, University of Washington, Seattle, WA 98195

Program Scope: New spin-based technologies hold tremendous promise for a diverse range of applications, including high-efficiency energy harvesting, quantum computing, and molecular sensing. Spin is a quantum property that is increasingly important in materials design, as scientists seek to utilize the spin of electrons to store or process quantum information, to elucidate complex molecular structure, and to maximize the quantum yield of solar cells. Essential to these applications is the dynamics of the electrons including time-dependent spin-spin and spin-orbit couplings, which are crucial to describe key phenomena that manipulate spin properties such as intersystem crossing, thermal-activated spin-crossover, spin-coherence, and spin-dephasing. In particular, a detailed understanding of how these spin systems are affected by external perturbations (e.g. magnetic field, fluctuation in crystal field) is needed. In this project, we further expand the power of time-dependent relativistic electronic structure theory with strategic introductions of spin couplings. A central goal of this work is to generate the theoretical and computational tools necessary to disentangle the importance of two-electron spin coupling terms in the physics describing chemical processes. This research has the potential to design and optimize new materials with unprecedented properties and functionality through the control of multiple spin centers for sensing, energy, and spintronic applications.

Recent Progress: During this funding period, we have published 12 peer-reviewed articles and released a new version of the open-source software package (ChronusQ) that includes new algorithms and methods developed under the support of this grant. Highlights of our research achievement in this funding period include: (1) a variational relativistic TDDFT method that satisfies the zero-torque theorem for generalized gradient functionals (2) a variational relativistic TDDFT method to compute $L_{2,3}$-edge X-ray absorption spectrum, (3) a well-tempered eigensolver to obtain high-energy excited states in a dense manifold of spectral region, and (4) a variational approach to treat the effects of magnetic fields in electronic structure theories.

New methods, algorithms, and research findings were published in peer-reviewed journals. The PI has presented 12 invited talks in national and international conferences, including the American Chemical Society (ACS) National Conference, Gordon Research Conference, Telluride Scientific Research Conference (TSRC). In addition, the PI?s students have presented five contributed talks and three posters at professional conferences, including ACS and TSRC.

Future Plans: There are three specific plans: (1) We will complete the development of integral engines that can compute two-electron spin-orbit couplings; (2) We will complete the development of a DFT grid engine that can support complex atomic orbitals; (3) We will validate the real-time time-dependent relativistic theory framework for simulating the L-edge spectroscopy.

Postdoc(s): Andrew Jenkins

Student(s): Lauren Koulias, Shichao Sun

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

(1) Sun, S.; Williams-Young, D.; Stetina, T. F.; Li, X. Generalized Hartree-Fock with Nonperturbative Treatment of Strong Magnetic Field: Application to Molecular Spin Phase Transition. *J. Chem. Theory Comput.* **2019**, *15*, 348–356.

(2) Wildman, A.; Donati, G.; Lipparini, F.; Mennucci, B.; Li, X. Nonequilibrium Environment Dynamics in a Frequency-Dependent Polarizable Embedding Models. *J. Chem. Theory Comput.* **2019**, *15*, 43–51.

(3) Petrone, A.; Williams-Young, D. B.; Sun, S.; Stetina, T. F.; Li, X. An Efficient Implementation of Two-Component Relativistic Density Functional Theory with Torque-Free Auxiliary Variables. *Eur. Phys. J. B* **2018**, *91*, 169.

(4) Egidi, F.; Fusè, M.; Baiardi, A.; Bloino, J.; Li, X.; Barone, V. Computational Simulation of Vibrationally Resolved Spectra for Spin-Forbidden Transitions. *Chirality* **2018**, *30*, 850–865.

(5) Donati, G.; Lingerfelt, D. B.; Aikens, C.; Li, X. Anisotropic Polarizability-Induced Plasmon Transfer. *J. Phys. Chem. C* **2018**, *122*, 10621–10626.

(6) Kasper, J. M.; Lestrange, P. J.; Stetina, T. F.; Li, X. Modeling $L_{2,3}$-Edge X-ray Absorption Spectroscopy with Real-Time Exact Two-Component Relativistic Time-Dependent Density Functional Theory. *J. Chem. Theory Comput.* **2018**, *14*, 1998–2006.

(7) Kasper, J. M.; Williams-Young, D. B.; Vecharynski, E.; Yang, C.; Li, X. A Well-Tempered Hybrid Method for Solving Challenging Time-Dependent Density Functional Theory (TDDFT) Systems. *J. Chem. Theory Comput.* **2018**, *14*, 2034–2041.

(8) Lestrange, P. J.; Williams-Young, D. B.; Petrone, A.; Jimenez-Hoyos, C. A.; Li, X. An Efficient Implementation of Variation After Projection Generalized Hartree-Fock. *J. Chem. Theory Comput.* **2018**, *14*, 588–596.

(9) Goings, J. J.; Lestrange, P. J.; Li, X. Real-Time Time-Dependent Electronic Structure Theory. *WIREs Computational Molecular Science* **2018**, *8*, e1341.

(10) Goings, J. J.; Egidi, F.; Li, X. Current Development of Non-collinear Electronic Structure Theory. *Int. J. Quant. Chem.* **2018**, *118*, e25398.

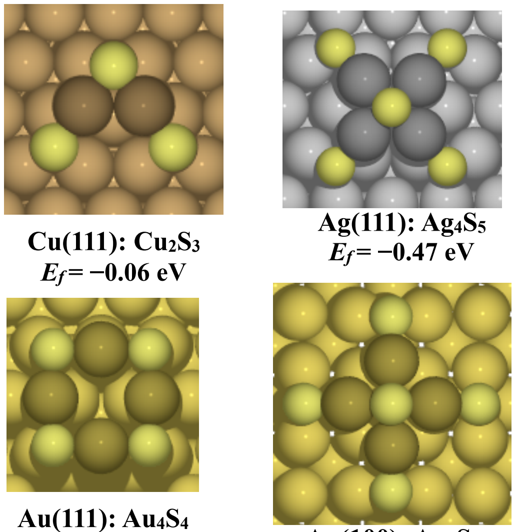
Energetic and Statistical Mechanical Analysis of Complexation on Metal Surfaces

Da-Jiang Liu, Theresa L. Windus, and Jim Evans
Ames Laboratory – USDOE, Division of Chemical & Biological Sciences

Abstract

We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes, M_mS_n, with M=Cu, Ag, and Au, both in the gas-phase and also for these complexes adsorbed on the (111) and (100) surfaces of the same coinage metal. An early influential theoretical study on S/Cu(111) proposed that the Cu_3S_3 complex being the most stable copper containing species. Later combined low temperature STM and DFT studies suggest that a heart-shaped Cu_2S_3 and its concatenations being more stable. Larger and even more complex Ag-S complexes have being observed for S/Ag(111). No complexation have been observed for S/Cu(100) and S/Ag(100). On the other hand, a Au_4S_5 complex and its fragmentations have being observed for S/Au(100), but no complexation is observed for S/Au(111) at low S coverage. We select a set of nine types of complexes, chosen for their proposed existences, intrinsic stabilities, and affinities for adsorption on metal surfaces. For the adsorbed species, we calculate various aspects of their energetics including their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that Ag_2S_3, Ag_3S_3 and many larger complexes on Ag(111) are strongly stable, Cu_2S_3 is stable and some larger complexes are marginally stable on Cu(111), but only Au_4S_4 on Au(111) is stable. In contrast, no complex is stable on Cu(100) and Ag(100), but a group of complex is stable on Au(100), with Au_4S_5 . DFT results are consistent with experiments with the apparent exception of Au(111).[i] This comprehensive assessment of energetics provides key input for statistical mechanical analysis of S adlayer ordering in the absence of complexation, and of the kinetics of complex formation and associated enhanced mass transport and surface dynamics.

Stable adsorbed M-S complexes predicted by DFT



Cu(111): Cu_2S_3
$E_f = -0.06$ eV

Ag(111): Ag_4S_5
$E_f = -0.47$ eV

Au(111): Au_4S_4
$E_f = -0.24$ eV

Au(100): Au_4S_5
$E_f = -0.57$ eV

PROGRAM SCOPE

The 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 and non-equilibrium statistical mechanical and multi-scale modeling*. The former includes quantum chemistry studies for large systems, and for homogeneous & heterogeneous catalysis. The latter, described in part, below explores molecular-level descriptions of: (i) the interplay between anomalous transport and catalytic reaction in functionalized mesoporous materials; (ii) chemisorption and heterogeneous catalysis on metal surfaces and nanoclusters. These studies also connect molecular-level treatments to mesoscale spatiotemporal mesoscale behavior, and analysis of fundamental non-equilibrium behavior in reaction-diffusion systems.

RECENT PROGRESS

Complexation on metal surfaces. While it has been long postulated that metal-ligand complexes could form on metal surfaces, and actively participate in surface transport and catalysis, conclusive evidence of these complexes have been elusive. Recently a body of experiments by collaborators (Thiel @ ISU, Kim @ Riken), mostly based at low temperature (~5 K) scanning tunneling microscope (STM) of sulfur on coinage metals (Cu, Ag, and Au) at low dosage, show complexation on Cu(111), Ag(111), Ag(110), and Au(100), but not on Cu(100), Ag (100), and Au(111).[ii] In the latter case, sulfur adatoms appear as protrusions, sombreros, and depressions, depending on the tunneling bias voltage. Density-functional theory (DFT) calculations are used to model the STM experiments and reproduce this change of contrast.[iii] We also use DFT to elucidate the structures of the complexes. We use codes with Gaussian-type-orbitals (GTO) and plane-waves (PW) basis sets respectively to study the stabilities of gas-phase and adsorbed complexes. A set of small complexes, which can be standalone or part of larger complexes or surface sulfides, are studied systematically. We obtain reliable energetics by effectively mitigating the quantum-size effects so that structures with different orderings can be compared. The relative stabilities of various structures are generally in good agreement with experiments, especially for Cu and Ag surfaces.[iv,v] Detailed characterization of energetics in the above systems provides key input for comprehensive statistical mechanical modeling of ordering of sulfur adlayers in the absence of complex formation, and of potential enhanced surface mas transport and dynamics in the presence of (and mediated by) complexes.

Catalytic Reactions in Functionalized Nanoporous Materials. Recent efforts have considered catalytic conversion reactions occurring inside linear nanopores. Inhibited transport inside the pores leads to development of strong spatial correlations and thus the breakdown of mean-field reaction-diffusion equation (RDE) treatments. A key parameter is the propensity, P, for reactants and products to pass each other in the pore. We employ multi-scale modeling strategy to elucidate the 20 fold increase in yield with a modest increase in pore diameter, d, for conversion of PNB to an aldol product in amine functionalized mesoporous silica observed by Igor Slowing and Marek Pruski in the Ames Lab catalysis group. PNB and aldol must align orientationally inside narrow pores in order to pass, but Langevin simulations suitably treating coupled translational and rotational diffusion can reliably determine $P(d)$. This quantity provides input to KMC simulations of a spatially coarse-grained model for the overall reaction-diffusion process which show that the strong increase in P with d accounts for the increase in yield.[vi]

Fundamentals of Catalytic Poisoning Transitions. For catalytic surface reactions under high-pressure conditions the corresponding high reactant coverages imply limited mobility of the reactant adlayer. This leads to strong non-equilibrium spatial correlations and large fluctuations resulting in a break-down of mean-field kinetics and predictions for catalytic poisoning. We analyze a basic Schloegl model for autocatalysis to provide fundamental insight into such far-from-equilibrium reaction systems including elucidation of generic two-phase coexistence.[vii]

Synthesis and stability of catalytic nanomaterials. Advances in shape-controlled synthesis of metallic nanocrystals (NCs) are often driven by applications to catalysis. However, synthesized shapes are metastable, and NC catalyst degradation often occurs by sintering. We have developed a realistic atomistic-level treatment of reshaping and sintering of single-component NCs mediated by surface diffusion, and quantified the kinetics of these processes via KMC simulation.[viii,ix]Bimetallic NCs often have optimal catalytic properties, and intermetallic NCs are particularly desirable because of well-defined surface structure. These are often synthesized in solution by adding a precursor of the second component to a NC "seed" of the first component. However, little is understood of the kinetics of conversion to the intermetallic. Our recent work combined rate equation modeling and DFT analysis to elucidate this process for PtSn NCs.[x] Finally, there is extensive interest in strategies to stabilize NCs against coarsening. We have performed both DFT analysis and stochastic modeling to elucidate observed intercalation of metal NCs underneath the "protecting" top layer of layered materials, specifically graphite.

FUTURE PLANS

Future research efforts will include the following: **(i)** 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 has involved collaboration with the *Windus group*. **(ii)** Development of realistic and predictive models for catalytic reactions on extended surfaces of metals, oxides, etc. For metal surfaces in collaboration *Zahariev and Gordon,* we will address limitations of DFT predictions for energetics, and incorporating the local environment dependence of barriers for reactions and of the dynamics of dissociative adsorption, etc. **(iii)** Development of 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 catalytic poisoning transitions and related phenomena. **(iv)** Development of more detailed system-specific models for catalysis in functionalized nano- and meso-porous materials, including detailed modeling of the mesoporous material, the solution phase, the solid-solution interface, and key transport and reaction processes. With *Windus*, we may explore functionalization kinetics. With the *Gordon group*, we aim to apply MD analysis to assess both the solvent-mediated diffusivity and interactions of reactant and product species.

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

Staff Scientists: D.-J. Liu (dajiang@ameslab.gov), F. Zahariev
PIs: J.W. Evans (evans@ameslab.gov), M.S. Gordon, K.R. Ruedenberg, T.L. Windus.

Selected Publications Acknowledging this Grant from 2016-present

[i] Lee, J.; Windus, T.L.; Thiel, P.A.; Evans, J.W.; Liu, D.-J.; Coinage metal-sulfur complexes: statbility on metal(111) surfaces and in the gas phase, *J. Phys. Chem. C*, 2019, accepted.

[ii] Walen, H; Liu, D.-J.; Oh, J.; Yang, H.J.; Spurgeon, P.M.; Kim, Y.; and Thiel, P.A.; Sulfur atoms adsorbed on Cu(100) at low coverage: characterization and stability against complexation, *J. Phys. Chem. B*, 2018, *122*, 963.

[iii] Spurgeon, P.M., Liu, D.-J.; Walen, H.; Oh, J.; Yang, H.J.; Kim, Y.; Thiel, P.A.; Characteristics of sulfur atoms adsorbed on Ag(100), Ag(110), and Ag(111) as probed with scanning tunneling microscopy: experiments and theory, *Phys. Chem. Chem. Phys.* Accepted 2019.

[iv] Liu, D.J.; Lee, J.; Windus, T.L.; Thiel, P.A.; Evans, J.W.; Stability of M_3S_3 complexes on fcc M(111) surfaces: M=Au, Ag, Cu, and Ni, *Surf. Sci.* 2018, *676*, 2.

[v] Lee, J.: Boschen, J.S.; Windus, T.L.; Thiel, P.A.; Liu, D.-J.; Stabilization of X-Au-X complexes on the Au(111) surface: a theoretical investigation and comparison of X=S, Cl, CH_3S, and SiH_3S, *J. Phys. Chem. C*, 2017, *121*, 3870.

[vi] Garcia, A.; Slowing, I.I.; Evans, J.W. Pore diameter dependence of catalytic activity: PNB conversion to an aldol product in amine-functionalized mesoporous silica, *J. Chem. Phys.* 2018, *149,* 024101.

[vii] Liu, D.-J.; Wang, C.-J.; Evans, J.W. Discontinuous phase transitions in non-local Schloegl models for autocatalysis: Loss and reemergence of a non-equilibrium Gibbs phase rule, *Physical Review Letters*, 2018, *121,* 120603.

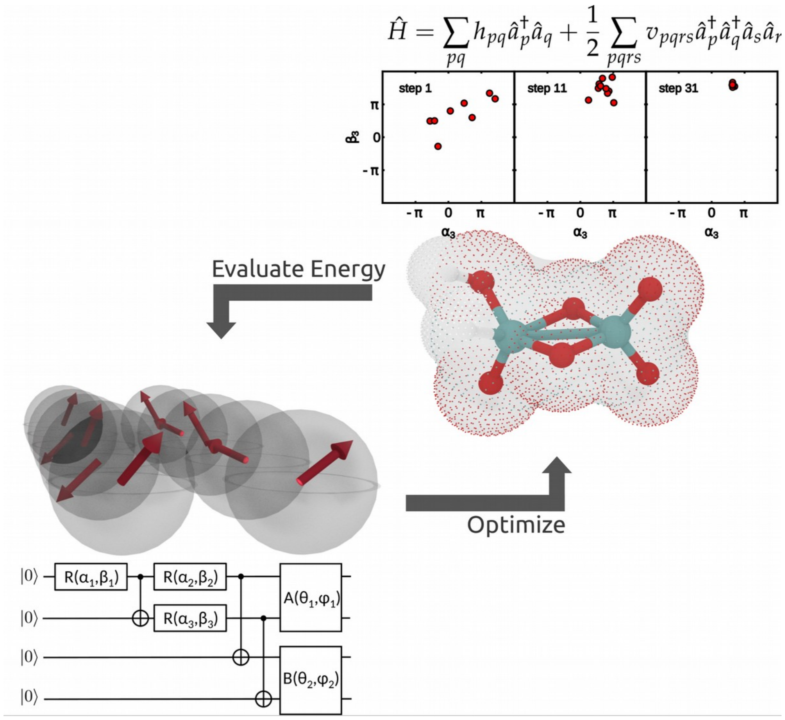
[viii] Lai, K.C.; Evans, J.W. Reshaping and sintering of 3D fcc metal nanoclusters: Stochastic atomistic modeling with realistic surface diffusion kinetics, *Phys. Rev. Materials* 2019, *3*, 026001.

[ix] Lai, K.C.; Han, Y.; Spurgeon, P.; Huang, W.; Thiel, P.A.; Liu, D.-J.; Evans, J.W. Reshaping, intermixing, and coarsening for metallic nanocrystals: Non-equilibrium statistical mechanical and coarse-grained modeling, *Chemical Reviews*, 2019, in press. 10.1021/acs.chemrev.8b00582

[x] Chen, M.; Han, Y.; Goh, T.W.; Sun, R.; Maligal-Ganesh, R.V.; Pei, Y.; Frank Tsung, F.; Evans, J.W.; Huang, W. Kinetics, Energetics, and Size-dependence of the Transformation from Pt to Ordered PtSn Intermetallic Nanoparticles, *Nanoscale*, 2019, *11*, 5336-5345

Simulating strongly correlated molecules with a superconducting quantum processor
PI: Nick Mayhall
Virginia Polytechnic Institute and State University

Many of the biggest challenges in expanding the nation’s access to clean and low-cost energy resources are fundamentally chemistry or materials challenges. An important case is the development of new catalysts for the up-conversion of cheap and readily available materials such as methane or water into materials suitable for use as a fuel such as methanol or oxygen. To understand and exploit such processes, computer simulations of chemical reactions provide a natural complement to experimental studies. Unfortunately, most catalytic reactions involve so-called “strongly correlated” molecules which are notoriously difficult to study with simulation algorithms that can be executed on existing (classical) computers. The recent growth in quantum information science offers a promising alternative route for simulating these difficult systems. As a result, an increasing number of computational chemists are becoming interested in quantum computing. At the same time, quantum information scientists have identified chemistry simulation as a possible first demonstration of a quantum computer providing an improvement over a classical computer. The objective of this project is to accurately simulate strongly correlated molecules on a superconducting quantum processor. To meet the high challenges of this objective, new hybrid quantum/classical algorithms will be co-designed with advanced quantum gate developments and implemented on customized quantum hardware. The developed techniques will have broad applicability to other molecular systems and other quantum hardware, while the project as a whole will help define better strategies for advancing the quantum simulation of matter more generally.



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

Alexander M. Mebel
Department of Chemistry and Biochemistry, Florida International University
Miami, Florida 33199. E-mail: mebela@fiu.edu

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 and advanced statistical reaction rate theoretical methods (TST, VRC-TST, and RRKM-Master Equation) to compute absolute reaction rate constants and product branching ratios.

Recent Progress

Since the last progress report in 2018, we continued investigating potential energy surfaces, reaction mechanisms, and kinetics for the reactions of PAH growth via HACA (Hydrogen-Abstraction-aCetylene-Addition) and HAVA (Hydrogen-Abstraction-Vinylacetylene-Addition) mechanisms. For HACA, we considered the reactions on various types of PAH edges, zigzag and armchair, including pentacenyl + C_2H_2 and phenanthrenyl + C_2H_2 forming acepentacene and pyrene, respectively. Our theoretical studies were combined with experimental measurements in pyrolytic microreactor with photoionization mass spectroscopy detection (PIMS) of reaction products (R. I. Kaiser's and Musahid Ahmed's groups at the University of Hawaii and LBNL, respectively) to identify pyrene in the reaction of 4-phenanthrenyl radical with acetylene. For HAVA, we have studied the reactions of phenyl, naphthyl, as well 4- and 9-phenanthrenyl radicals with vinylacetylene C_4H_4 forming a variety of products including two-, three-, and four-ring PAHs, respectively, such as naphthalene, phenanthrene and anthracene, [4]-helicene, and triphenylene. Here, our theoretical calculations were carried out jointly with experimental PIMS studies in the microreactor and with computational fluid dynamics (CFD) and kinetic modeling of physical and chemical processes performed in Samara University, which allowed us to unravel the reaction mechanism in a great detail.

Rates of two mechanisms, HACA and C_2H_2 (carbon) addition hydrogen migration (CAHM), were intercompared with each other at postflame conditions of a laminar premixed flame of ethylene. The analysis showed that HACA is substantially faster than CAHM, in contrast with the conclusions reached in a recent study of Zhang et al. [J. Phys. Chem. A 120 (2016) 683]. The difference between the two studies is largely due to dissimilar assignments of the thermodynamics of the H abstraction and of the islands of stability pulling the HACA reaction sequence. In support of this conclusion, the kinetics and thermodynamics of the key HACA reaction step were recalculated at a reliable level of quantum and reaction-rate theories. The implication of our results is that both HACA and CAHM mechanisms can explain formation of aliphatic groups chemisorbed at edges of aromatics; however, a quantitative relationship is yet to be established with the experimental observations. This work provided updated rate expressions for kinetic modeling of PAH growth both in the gas phase and on graphene-edges of soot particles.

By exploring the reaction of the 4-phenanthrenyl radical ($[C_{14}H_9]^\bullet$) with acetylene (C_2H_2) under conditions prevalent in carbon-rich circumstellar environments, we provided testimony on a facile, isomer-selective formation of pyrene ($C_{16}H_{10}$). Along with the HAVA mechanism, molecular mass growth processes from pyrene may lead through systematic ring expansions not only to more complex PAHs, but ultimately to two-dimensional graphene-type structures. These fundamental reaction mechanisms are of crucial significance to facilitate an understanding of the origin and evolution of the molecular universe and in particular of carbon in our galaxy.

The formation of the simplest PAH – naphthalene ($C_{10}H_8$) - was explored in a high-temperature chemical reactor under combustion-like conditions in the phenyl (C_6H_5) - vinylacetylene (C_4H_4) system. The products were probed utilizing tunable vacuum ultraviolet light by scanning the photoionization efficiency (PIE) curve at a mass-to-charge m/z = 128 ($C_{10}H_8^+$) of molecules entrained in a molecular beam. The data fitting with PIE reference curves of naphthalene, 4-phenylvinylacetylene ($C_6H_5CCC_2H_3$), and trans-1-phenylvinylacetylene ($C_6H_5CHCHCCH$) indicates that the isomers were generated with branching ratios of 43.5±9.0%:6.5±1.0%:50.0±10.0%. Kinetics simulations agree nicely with the experimental findings with naphthalene synthesized via HAVA pathway and through hydrogen-assisted isomerization of phenylvinylacetylenes. The HAVA route to naphthalene at elevated temperatures represents an alternative pathway to the HACA forming naphthalene in flames and circumstellar envelopes, whereas in cold molecular clouds, HAVA synthesizes naphthalene via a barrier-less bimolecular route.

By unravelling the chemistry of the 9-phenanthrenyl radical ($[C_{14}H_9]^\bullet$) with vinylacetylene, we found the first compelling evidence of a barrier-less pathway leading to a prototype tetracyclic PAH - triphenylene ($C_{18}H_{12}$) - via an unconventional HAVA mechanism operational at temperatures as low as 10 K. The barrier-less, exoergic nature of the reaction reveals HAVA as a versatile reaction mechanism that may drive molecular mass growth processes to PAHs and even two dimensional, graphene-type nanostructures in cold environments in deep space thus leading to a better understanding of the carbon chemistry in our universe through the untangling of elementary reactions on the most fundamental level. Also, exploiting the simplest helicene as a benchmark, the elementary gas phase reaction of the 4-phenanthrenyl radical ($[C_{14}H_9]^\bullet$) with vinylacetylene was shown to yield the primary reaction product [4]-helicene ($C_{18}H_{12}$) along with atomic hydrogen via a low-barrier reaction mechanism through a resonance-stabilized free radical (RSFR) intermediate ($C_{18}H_{13}$). This pathway potentially represents a versatile mechanism to build up even more complex polycyclic aromatic hydrocarbons (PAHs) such as [5]- and [6]-helicene via stepwise ring annulation through bimolecular gas phase reactions of an aryl radical with vinylacetylene in circumstellar envelopes of carbon-rich stars, whereas secondary reactions involving hydrogen atom assisted isomerization of thermodynamically less stable isomers of [4]-helicene might be important in combustion flames as well.

We exploited variable reaction coordinate transition state theory (VRC-TST) together with the RRKM-Master Equation approach to study the reactions of phenyl with allyl and benzyl with vinyl, which are expected to produce a precursor of another prototype two-ring PAH, indene. In this work, potential energy surfaces for the allyl + phenyl and benzyl + vinyl barrierless radical association reactions were studied at the CCSD(T)-F12/cc-pVTZ-f12//B3LYP/6-311G** level of theory. VRC-TST was employed to evaluate high-pressure limit rate constants for the barrierless channels and then, RRKM-ME calculations were performed to assess phenomenological rate constants and product branching ratios of various reaction channels at different temperatures and pressures. The initial step of both radical association reactions produces 3-phenylpropene which can further dissociate into a variety of bimolecular products including the indene precursor 1-phenylallyl + H. The results showed that at typical combustion conditions the collisional stabilization of 3-phenylpropene dominates both the phenyl + allyl and benzyl + vinyl reactions at temperatures below 1000 K and remains important at high pressures up to 2500 K. The main bimolecular products of the two reactions at high temperatures are predicted to be benzyl + vinyl and phenyl + allyl, respectively. The well-skipping mechanism to form 1-phenylallyl directly in the allyl + phenyl and benzyl + vinyl reactions appeared to be not significant, however, the reactions can provide some contributions into the formation of the indene precursor via the 3-phenylpropene stabilization/dissociation sequence and most of all, via the formation of 3-phenylpropene itself, which then can undergo H-abstraction by available radicals to produce 1-phenylallyl. The allyl + phenyl reaction can also contribute to the formation of two-ring PAH by producing benzyl radical at high temperatures, either by the well-skipping or stabilization/dissociation mechanisms; in turn, benzyl can readily react with acetylene or propargyl radical to form indene or naphthalene precursors, respectively. Rate expressions for all important reaction channels in a broad range of temperatures and pressures have been generated for kinetic modeling.

In the second segment of our research, we investigated the formation of resonantly stabilized free radicals (RSFR), which often serve as precursors of aromatic and polycyclic aromatic molecules, through reactions of atomic carbon, dicarbon, and the propynyl radical H_3CCC with unsaturated hydrocarbons. These theoretical calculations were carried jointly with experimental crossed molecular beams studies by Kaiser's group. In particular, during the last year we studied the C + pyridine, C_2 + CH_3CCH/C_2H_5CCH, and H_3CCC + C_2H_2/C_2H_4/C_4H_2/C_4H_6 reactions. Finally, in the third research facet, we continued theoretical calculations aimed on understanding the mechanism of PAH oxidation and considered the reactions of indenyl with O_2 and polycyclic aromatic $C_{15}H_9$ radicals with atomic oxygen.

Future Plans

The main goal of this project remains 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, in the next reporting period we will focus on the following systems: 1) reactions converting a five-member ring in PAH into a six-member ring, in particular, acenaphthyl radical + CH_3/C_2H_2 and indenyl + CH_3; 2) reactions potentially producing three-ring PAHs, such as indenyl + C_2H_2/C_4H_4, naphthyl + 1,3-butadiene, and naphthyl + C_3H_4 (allene and propyne); 3) formation of four-ring PAHs via vinylacetylene addition to various phenanthrenyl and anthracenyl radicals; 4) oxidation of PAH radicals such as indenyl and acenaphthyl with various oxidizers abundant in combustion flames, such as O_2, O, and O_2H; 5) formation or resonantly stabilized free radicals via reactions of the CH and H_3CCC

radicals with various unsaturated hydrocarbons. We will continue our collaboration with R. Kaiser's and M. Ahmed's groups on the studies of combustion and astrochemically relevant bimolecular reactions in crossed beams and in the pyrolytic reactor at LBNL. We will also collaborate with M. Frenklach (UC Berkeley) on implementation of the rate constants we generate in kinetic models of PAH and soot growth and oxidation.

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: Alexander N. Morozov
Visiting Research Associate: Galiya R. Galimova
Students: Juan Alarcon, Lotefa Binta Tuli

DOE/BES sponsored publications (2018-2019)
1. Galimova G.R., Azyazov V.N., Mebel A.M., "Reaction mechanism, Rate Constants, and Product Yields for the Oxidation of Cyclopentadienyl and Embedded Five-Member Ring Radicals with Hydroxyl", Combust. Flame 2018, 187, 147-164.
2. Frenklach M., Liu Z., Singh R.I., Galimova G.R., Azyazov V.N., Mebel A.M., "Detailed, Sterically-Resolved Modeling of Soot Oxidation: Role of O Atoms, Interplay with Particle Nanostructure, and Emergence of Inner Particle Burning", Combust. Flame 2018, 188, 284-306.
3. Oleinikov A.D., Azyazov V.N., Mebel A.M., "Oxidation of Cyclopentadienyl Radical with Molecular Oxygen: A Theoretical Study", Combust. Flame 2018, 191, 309-319.
4. Zhao L., Kaiser R.I., Xu B., Ablikim U., Ahmed M., Joshi D., Veber G., Fischer F.R., Mebel A.M., "On the Synthesis of Pyrene in Circumstellar Envelopes and Its Role in the Formation of Two-Dimensional Nanostructures", Nature Astron. 2018, 2, 403-419.
5. Zhao L., Kaiser R.I., Xu B., Ablikim U., Ahmed M., Zagidullin M V., Azyazov V.N., Howlader A.H., Wnuk S.F., Mebel A.M., "A VUV Photoionization Study on the Formation of the Simplest Polycyclic Aromatic Hydrocarbon: Naphthalene ($C_{10}H_8$)", J. Phys. Chem. Lett., 2018, 9, 2620-2626.
6. Zhao L., Kaiser R.I., Xu B., Ablikim U., Ahmed M., Evseev M.M., Bashkirov E.K., Azyazov V.N., Mebel A.M., "Low-temperature formation of polycyclic aromatic hydrocarbons in Titan's atmosphere", Nature Astron., 2018, 2, 973-979.
7. Frenklach M., Singh R.I., Mebel A.M., "On the low-temperature limit of HACA", Proc. Combust. Inst., 2019, 37, 969-976.
8. Morozov A.N., Mebel A.M., "Theoretical Study of the Reaction Mechanism and Kinetics of the Phenyl + Allyl and Related Benzyl + Vinyl Associations", J. Phys. Chem. A, 2019, 123, 1720-1729.
9. Zhao L., Kaiser R.I., Xu B., Ablikim U., Lu W., Ahmed M., Evseev M.M., Bashkirov E.K., Azyazov V.N., Zagidullin M. V., Morozov A.N., Howlader A.H., Wnuk S.F., Mebel A.M., Joshi D., Veber G., Fischer F.R., "Gas Phase Synthesis of [4]-Helicene", Nature Comm. 2019, 10, 1510.
10. Ghildina A.R., Porfiriev D.P., Azyazov V.N., Mebel A.M., "The Mechanism and Rate Constants for Oxidation of Indenyl Radical C_9H_7 with Molecular Oxygen O_2: A Theoretical Study", Phys. Chem. Chem. Phys., 2019, DOI: 10.1039/c9cp01122f.

Ab initio Molecular Dynamics Beyond Density Functional Theory

Fred Manby, Garnet Chan, Thomas Miller

University of Bristol
California Institute of Technology

Abstract

A density functional theory (DFT) description of electronic structure is currently synonymous with *ab initio* molecular dynamics (MD), due to DFT's reasonable compromise between accuracy and computational cost. However, the chemical sciences are permeated with systems for which the approximations of DFT fundamentally break down or for which the computational cost of DFT remains prohibitive for the MD simulation of necessary length- and timescales. Our project aims to move "beyond DFT" in both key dimensions of higher accuracy and lower computational cost, thereby bringing broad new chemical and materials application domains within the reach of *ab initio* MD simulation. Two central embedding frameworks will be extended in pursuit of these goals. The first is wavefunction-in-DFT embedding theory, where the electronic structure of the chemically interesting part of the system is described by a high-level wavefunction, while the remaining environment is described by DFT. The second is embedded mean-field theory (EMFT), where the chemically interesting part is described using a more costly mean-field method (such as hybrid DFT) and the environment is described using a lower-level mean-field method (such as local density approximation or DFTB). Within these embedding frameworks, we will pursue theoretical innovations that include coupling highly correlated system wavefunction methods with DFT environments, transferable machine-learning methods for electronic structure, and non-adiabatic dynamics methods based on the path-integral framework.

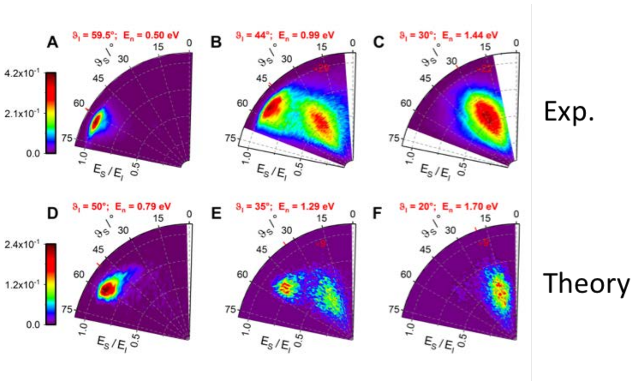


Figure 1. H-on-graphene scattering, showing energy loss and scattering angle for low (A,D), intermediate (B,E), and high (C,F) scattering incidence energies. Agreement between experiment (A-C) and theory (B-D) enables mechanistic analysis of the energy-loss mechanism and origin of efficient H-on-graphene sticking. (Science, 2019, *in press*.)

In the first year of activity, we have pursued these activities along multiple threads. In terms of methodology, we have completed, numerically demonstrated, and reported the analytical gradient theory for projection-based wavefunction-in-DFT embedding [1], along with a more general review of this quantum embedding approach [2]. In terms of software, we have made an initial report of the *entos* molecular simulation package [3] and are on pathway towards and open-source release in calendar year 2019. And in terms of application studies, we have worked in collaboration with the Wodtke group (Max Planck Institute) to study the scattering and sticking of hydrogen atoms from graphene surfaces [4]. New experiments reported in this work revealed that H sticking on graphene far exceeded the predictions of earlier theoretical studies. By using *entos* to combine EMFT with ring-polymer molecular dynamics studies of the H-on-graphene scattering process, excellent agreement with experiment was obtained (Fig. 1), and it was revealed that the unexpectedly high sticking probability arose due to efficient energy transfer due to transient C-H bond formation and accompanying transient re-hybridization of the graphene sheet at the point of the H-atom collision. Future work in this direction will explore the H/D isotope effect in these systems, as well as examining alternative metallic and semiconducting substrates that support the graphene surface.

Grant Numbers and Grant Titles

Postdoc(s): Feizhi Ding (Caltech)

Student(s): Jorge Rosa (Caltech)

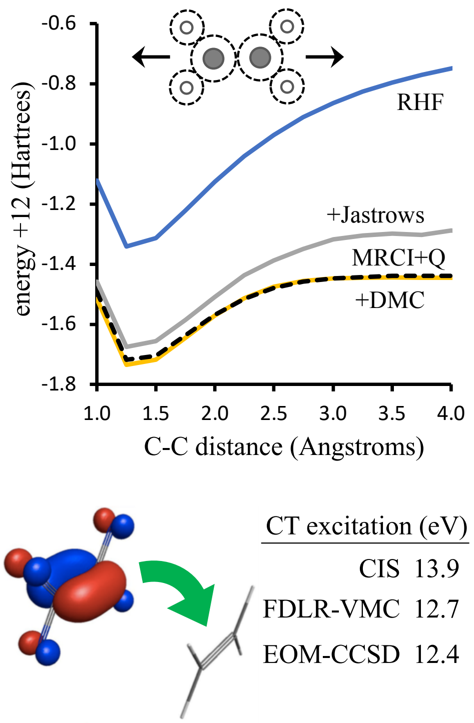
1. Analytical gradients for projection-based wavefunction-in-DFT embedding." S. J. R. Lee, F. Ding, F. R. Manby, T. F. Miller III, *arXiv:1093.05830* (2019).
2. "Projection-based wavefunction-in-DFT embedding." S. J. R. Lee, M. Welborn, F. R. Manby, T. F. Miller III, *Acc. Chem. Res.*, Article ASAP (2019). DOI: 10.1021/acs.accounts.8b00672
3. "entos: A quantum molecular simulation package." F. R. Manby, T. F. Miller III, P. J. Bygrave, F. Ding, T. Dresselhaus, F. A. Batista-Romero, A. Buccheri, C. Bungey, S. J. R. Lee, R. Meli, K. Miyamoto, C. Steinmann, T. Tsuchiya, M. Welborn, T. Wiles, and Z. Williams, *ChemRxiv.7762646* (2019). DOI: 10.26434/chemrxiv.7762646.v2
4. "Imaging covalent bond formation by H-atom scattering from graphene." H. Jiang, M. Kammler, F. Ding, Y. Dorenkamp, F. R. Manby, A. M. Wodtke, T. F. Miller III, A. Kandratsenka, O. Bunermann, *Science*, **364**, 379-382, 2019.

Variational Excited States, Quantum Monte Carlo, and Charge Transfer

Eric Neuscamman

Department of Chemistry, University of California, Berkeley, CA 94720
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
eneuscamman@berkeley.edu

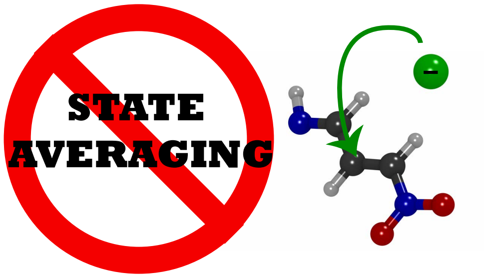
This research program explores the intersection of variational principles for excited states, quantum Monte Carlo (QMC) methods, and charge transfer processes. While the foundations for this research lie in our DOE-funded work over the past few years in the Gas Phase Chemical Physics program and the Computational Materials Science Program, funding from DOE's Early Career Research Program is now allowing us to explore the exciting opportunities that lie at the intersection of these three topics. Together, these research thrusts include work on enabling high-accuracy excited state simulation with QMC methods, making improvements to QMC wave function approximations, creating more robust and capable QMC optimization algorithms, and translating lessons learned about excited state variational principles out of QMC and into the world of quantum chemistry.

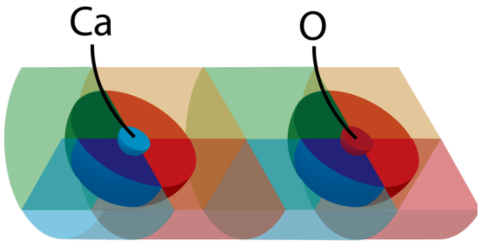


CT excitation (eV)	
CIS	13.9
FDLR-VMC	12.7
EOM-CCSD	12.4

Excited state variational principles

The foundation for this work began with our group's development of QMC methods capable of optimizing variational principles whose global minimums are not the ground state but excited states that can be selected based on their positions in the energy spectrum. The primary advantage of this approach is that the entire wave function ansatz, crucially including the molecular orbitals, can be tailored for the state in question rather than having to share some of its flexibility with the ground state or other excited states. In excitations that make large changes to the electronic structure, such as double excitations and charge-transfer excitations, we have demonstrated that these variational principles allow relatively compact wave functions to produce highly accurate results, as for example in the variational Monte Carlo (VMC) result for the quadruply-fluorinated-ethylene-to-ethylene charge transfer shown in the bottom part of the figure, where the primary difference between VMC and configuration interaction singles (CIS) is the state-specific optimization of the orbitals. These approaches have now been extended both to more sophisticated wave function forms and to deterministic quantum chemistry approaches that lie entirely outside of the QMC formalism, as we discuss below.





Improved QMC Wave Functions

In addition to our work on variational principles, we have also developed improvements in ansatz flexibility. In one area, we have derived and implemented efficient forms for number counting Jastrow factors (NCJFs) that can control how many electrons are present in sub-regions of a molecule. As seen in the top portion of the figure on the previous page, the combination of these NCJFs with the re-optimization of a single Slater determinant is sufficient, via the delivery of strong left-right correlation through the suppression of ionic configurations, to produce nodal surfaces leading to quantitatively accurate diffusion Monte Carlo (DMC) results for the double bond dissociation of ethylene. In the last year, we have now generalized this approach such that counting regions are guaranteed to be cleanly additive, meaning that the variational principle is free to combine adjacent regions when working to control particle concentrations without raising the kinetic energy and without the user needing to know what types of combinations would be important in advance. This formulation allows us to make more aggressive divisions of space in to local counting regions, as seen on the bottom of this page's figure for the CaO diatomic, where we again find that a single-reference wave function can deliver a surprising degree of strong electron correlation when combined with NCJFs.

In addition to these Jastrow factor improvements, we have implemented the fast multi-Slater orbital optimization methods of Filippi and coworkers in our QMC software and connected this methodology to our variational excited state optimization technology. The result is that we can now pursue state-specific multi-reference excited states without the need to settle for state averaged orbitals. Although state-averaging is often effective, it can run into trouble when different states have drastically different dipole moments and thus require substantial state-specific orbital relaxations. We have now demonstrated that in a challenging charge transfer example, shown in the top of this page's figure, our QMC methodology can outperform multi-reference quantum chemistry. In this case, state-averaged complete active space perturbation theory suffers from both intruder state issues and state-averaging limitations. Our methodology suffers from neither, and we have shown that with state-specific orbital optimization, its systematic improvability converges rapidly on to a high accuracy prediction for the charge transfer energy. For singly excited states, we have further shown that a simple linear-response-inspired two-determinant ansatz, rather than a more aggressive multi-Slater expansion, can be highly accurate when combined with state-specific optimization and diffusion Monte Carlo. Happily, this simple approach can import its initial guess from TD-DFT or CIS, making it much more user-friendly than many other current options in excited state QMC.

Improved QMC Optimization Methods

To fully exploit advances in QMC wave function methodology, we have also put significant effort in to improving the tools used for variational Monte Carlo (VMC) optimization. For more than a decade now, the leading method in this area has been constrained to work with about ten thousand variables or fewer, which by quantum chemistry standards is almost quaint. Of course, with exact cusp conditions satisfied and DMC waiting in the wings, a small number of variables goes farther in QMC than in quantum chemistry, but this cap which stems from memory constraints does prevent more aggressive applications of modern QMC wave functions. With the resurgence of selective CI methods, which can easily seed multi-Slater forms with millions of determinants, the ability to optimize much larger numbers of parameters has become especially pressing. We have implemented and published a low-memory variant of the leading linear method optimizer, which we have named the blocked linear method and which can easily handle variable numbers in the tens of thousands. More recently, preliminary work in which we have combined this approach with accelerated descent methods suggests that a hybridization of these approaches may be able to retain the strong performance of the linear method while reaching into the regime of hundreds of thousands of variables, although these results are quite new and much additional attention is merited to develop the idea into a production-level optimizer.

Excited State Mean Field Theory

Finally, we have discovered ways of extending the ideas behind excited state variational principles outside the realm of QMC. By combining approximations of these forms with automatic differentiation approaches, we have developed an excited state generalization of Hartree Fock theory that, like its ground state counterpart, can act as a platform upon which high-accuracy correlation methods can be built. In preliminary tests, we have combined this excited state mean field reference with an excited state generalization of MP2 theory and found that its accuracy rivals that of EOM-CCSD in a basket of tests involving valence excitations, charge transfer excitations, and one Rydberg excitation. Most excitingly, this mean field approach has a cost scaling that is the same as Hartree Fock theory. We are already pursuing multi-reference generalizations of this idea in hopes of being able to perform excited-state-specific multi-reference orbital optimization on the quantum chemistry side when preparing for high-accuracy QMC calculations, which would dramatically simplify the VMC optimizations.

Grant Numbers and Grant Titles:

DE-SC0017869 “Modeling Charge Transfer Excitations with Variation After Response Quantum Monte Carlo”

“Center for Predictive Simulation of Functional Materials” (grant number not known)

DE-AC02-05CH11231 “Lawrence Berkeley National Lab Gas Phase Chemical Physics”

Students:

Jacqueline A. R. Shea, Brett van der Goetz, Leon Otis, Luning Zhao, Sergio D. Pineda Flores

Post-docs:

Nicholas Blunt (now at Cambridge), Lan Tran

Up to Ten Publications Acknowledging these funding sources in the last 3-4 years:

Zhao, L.; Neuscamman, E., An Efficient Variational Principle for the Direct Optimization of Excited States. J. Chem. Theory Comput. 2016, 12 (8), 3436. DOI: 10.1021/acs.jctc.6b00508

Neuscamman, E., Communication: Variation after Response in Quantum Monte Carlo. J. Chem. Phys. 2016, 145, 081103. DOI: 10.1063/1.4961686

Goetz, B. V. D.; Neuscamman, E., Suppressing Ionic Terms with Number-Counting Jastrow Factors in Real Space. J. Chem. Theory Comput. 2017, 13 (5), 2035
DOI: 10.1021/acs.jctc.7b00158

Zhao, L. and Neuscamman, E., A Blocked Linear Method for Optimizing Large Parameter Sets in Variational Monte Carlo. J. Chem. Theory Comput. 2017, 13 (6), 2604
DOI: 10.1021/acs.jctc.7b00119

Shea, J. A. R. Neuscamman, E., Size Consistent Excited States via Algorithmic Transformations between Variational Principles. J. Chem. Theory Comput., 2017, 13 (12), 6078
DOI: 10.1021/acs.jctc.7b00923

Wei, H. and Neuscamman, E. Reduced Scaling Hilbert Space Variational Monte Carlo.
J. Chem. Phys. 2018, 149, 184106 DOI: 10.1063/1.5047207

Shea, J. A. R. and Neuscamman, E. Communication: A Mean Field Platform for Excited State Quantum Chemistry. J. Chem. Phys. 2018, 149, 081101 DOI: 10.1063/1.5045056

Blunt, N. S. and Neuscamman, E. Excited-state diffusion Monte Carlo calculations: a simple and efficient two-determinant ansatz. J. Chem. Theory Comput. 2019, 15, 178
DOI: 10.1021/acs.jctc.8b00879

Goetz, B. V. D.; Otis, L.; and Neuscamman, E. Clean and Convenient Tessellations for Number Counting Jastrow Factors. J. Chem. Theory Comput. 2019, 15, 1102
DOI: 10.1021/acs.jctc.8b01139

Pineda Flores, S. D. and Neuscamman, E. Excited State Specific Multi-Slater Jastrow Wave Functions. J. Phys. Chem. A 2019, 123, 1487 DOI: 10.1021/acs.jpca.8b10671

Excited State Phenomena in Correlated Nanostructures: Transition Metal Oxide Clusters and Nanocrystals
(DE-SC0017824)

Serdar Ogut
University of Illinois at Chicago, Department of Physics
845 W Taylor Street (M/C 273), Chicago, IL 60607
ogut@uic.edu

Postdoc: Young-Moo Byun
Student: Meisam Rezai

PROGRAM SCOPE

The primary goal of our research program is to apply state-of-the-art density functional and many-body perturbation theory techniques, which employ the *GW* approximation and the Bethe Salpeter equation (BSE), to predict electronic and optical properties of a variety of transition metal oxide clusters and nanocrystals. These include 3*d* transition metal monoxide and dioxide clusters, small-to-medium size anionic clusters of the form $M_xO_y^-$ with M = Cu, V, and Cr containing up to ~25 atoms, and bulk-truncated Cu_2O and Ag_2O nanocrystals. The enhanced electron correlations inherent in these systems make it very challenging to model their excited state properties within a first principles approach. Our overall goal is to investigate the impact of computational and theoretical approaches employed within the *GW*-BSE framework on the electronic and optical excitations of these systems. Comparing several variants of the *GW*-BSE formalism as applied to transition metal oxide nanostructures with each other, available photoelectron spectroscopy data, and high-level quantum chemistry computations will help us identify the level of theory and approximations that are needed to achieve a reasonable balance between accuracy and computational demand. Our computations will involve applying several flavors of the *GW* approximation, including partial and quasiparticle self-consistency, the effects of a two-point vertex for occupied and unoccupied states, as well as one-shot G_0W_0 calculations performed on top of hybrid DFT starting points and self-consistent COHSEX approximation.

RECENT PROGRESS

Electronic Structure of 3d-Transition Metal Monoxide Anions

We have computed the quasiparticle spectra of closed- and open-shell 3*d*-transition metal (TM) anion monoxides using various levels of *GW* theory to evaluate the performance of the *GW* approximation. We have applied perturbative non-self-consistent *GW* (G_0W_0) with PBE and hybrid functional starting points and the eigenvalue-only self-consistent *GW* (ev*GW*) (with two types, G_nW_0 and G_nW_n, which update eigenvalues only in *G* and in both *G* and *W*, respectively)

Our results for the first ionization energy (IE) and lowest 3*d* binding energies (corresponding to the orbital with 100% 3*d* character) for TMO anions are plotted in Fig. 1. Note that the highest occupied molecular orbitals (HOMOs) of TMO anions have different strengths of TM 3*d* character: HOMOs of NiO^- and CuO^- have moderate (~50%), and those of other anions have weak (~10%) 3*d* character. We observe several trends in Fig. 1. First, G_0W_0@PBE underestimates the IE by ~1 eV and the 3*d*-electron BE by ~2 eV, which is significantly more than the typical underestimation of the IE of *sp*-bonded molecules (~0.5 eV). Note that the IEs of NiO^- and CuO^- are outliers, because HOMOs of NiO^- and CuO^- are more strongly hybridized with 3*d* orbitals than those of the other anions.

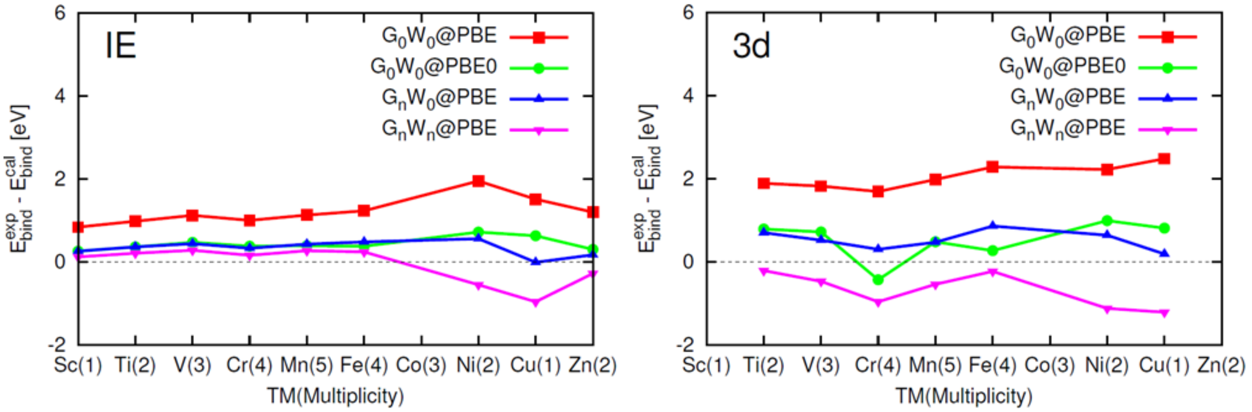


Fig. 1: First ionization energies (left) and lowest 3d binding energies (right) of TMO (TM = Sc, Ti, …, Cu, Zn) anions. The vertical axis represents the difference between experimental and calculated binding energies. The numbers in parentheses on the horizontal axis represent the multiplicity of TMO anions.

Second, both G_0W_0@PBE0 and G_nW_0@PBE lead to much improved predictions, which underestimate the IE and the 3*d*-electron BE by ~0.1-0.5 eV independently of the orbital character. We argue that G_nW_0@PBE is practically more favorable than G_0W_0@PBE0 because it is parameter-free, as it does not need the system-dependent optimal amount of exact exchange, and does not suffer from the SCF convergence problems of open-shell systems with hybrid functionals. Third, G_nW_n@PBE overestimates the IE and the 3*d*-electron BE by ~0.1-1 eV independently of the orbital character. Note that for molecules, G_nW_0@PBE is a better choice than G_nW_n@PBE because G_nW_0@PBE works well for both the IE and 3*d*-electron BE, whereas G_nW_n@PBE works well only for the IE. Note also that for solids, G_nW_0@PBE is a better choice than G_nW_n@PBE because of a practical reason: G_nW_0@PBE and G_nW_n@PBE give similar results for both bandgaps and 3*d*-electron BEs, but G_nW_0@PBE is computationally cheaper than G_nW_n@PBE. We attributed the good performance of G_nW_0@PBE to the fortuitous cancellation effect: the over-screening due to the screened Coulomb interaction produced by PBE is cancelled by the under-screening due to the neglect of vertex corrections.

Multiplet Splittings in Open-Shell Molecules from GW theory

In open-shell systems, the coupling of the orbital and spin angular momenta of electrons can result in multiple energy eigenstates of the electronically excited system leading to the characteristic multiplet structures observed in photoemission experiments. While DFT is not capable of determining the resulting multiplet splittings accurately, there have been some recent studies that have shown that the *GW* approximation can describe the multiplet structure with reasonable accuracy. Since multiplet splittings are a common occurrence in many transition-metal oxide clusters, in which enhanced electron correlation increases the computational cost significantly, we have been investigating the performance of *GW* theory in predicting the multiplet splittings in simpler (moderately correlated) *sp*-bonded open-shell molecules such as NO_2, NF_2, O_2, ClO_2, and single atoms.

In *GW* theory, multiplet solutions appear in the solution of the quasiparticle equation for orbital *j* given by $\varepsilon_j+\Sigma_{jj}(E)-V_{jj}^{xc} = E$, where ε_j is the Kohn-Sham eigenvalue, E is the quasiparticle energy (for which the equation is being solved), and $\Sigma_{jj}(E)$ and V_{jj}^{xc} are the matrix elements of the self-energy (at energy E) and exchange-correlation potential in orbital *j*, respectively. If the removal of an electron from orbital *j* leads to a multiplet structure, the above non-linear equation has at least two solutions. For example, as shown in the inset of the upper left panel of Fig. 2, the removal of an electron from HOMO leads to a singlet configuration, and the graphical solution of the quasiparticle equation accordingly has a single root (shown by the peak in the spectral function A_{jj}). The removal of an electron from HOMO-1 in the majority-spin channel, on the other hand, (lower left panel) could lead to either a singlet or a triplet configuration. Accordingly, the graphical solution of the quasiparticle equation has two roots (shown by the two peaks in the corresponding spectral function).

The starting point of perturbative one-shot G_0W_0 calculations has a profound effect in accurate predictions of the quasiparticle energies and multiplet splittings. We performed G_0W_0 calculations with G and W computed with the same hybrid functional starting point containing varying amounts of exact exchange with those where G is still computed with a hybrid functional starting point but W is computed within PBE. The right panel of Fig. 2 shows the results using the second approach as a function of α, the exact exchange amount used in the calculation of G, for the first 5 peaks measured in the photoelectron spectrum of the NO_2 molecule. At $\alpha \sim 0.4$, the agreement with experiment is excellent. We also showed that it is possible to achieve excellent agreement with experiment using the first approach, but the amount of α needed for quantitative accuracy is lower, at $\alpha \sim 0.2$. We are currently working on extending this method to other open-shell molecules and single atoms.

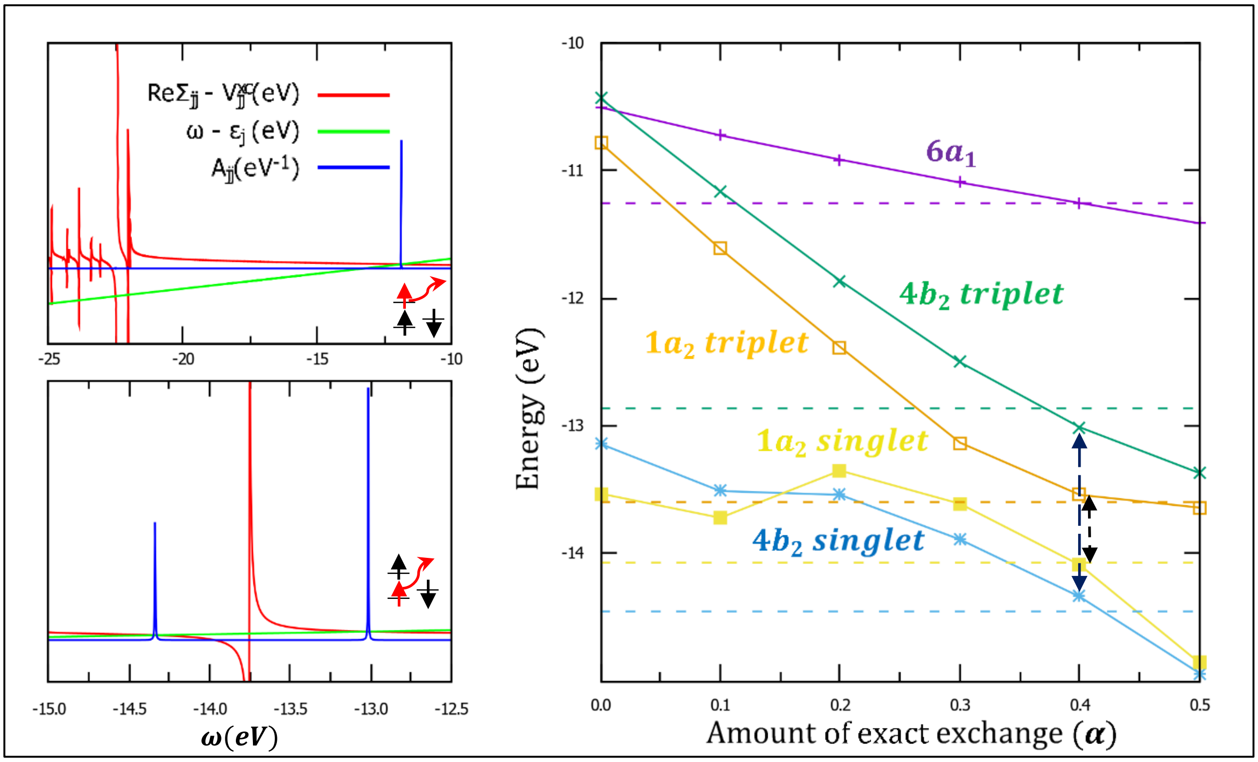


Fig. 2: (Left panel) Examples of graphical solutions of the quasiparticle equation and the corresponding spectral function A_{jj} for cases corresponding to the removal of an electron from HOMO (upper panel) that leads to a singlet solution, and from majority-spin channel of HOMO-1 (lower panel), that leads to both singlet and triplet solutions. (Right panel) Computed quasiparticle energies as a function of the exact exchange amount used in the computation of the Green's function G (W is computed within PBE) for the outermost 5 orbitals of the NO_2 molecule. The dashed horizontal lines represent experimental data. Note the excellent agreement with experiment for $\alpha \sim 0.4$ for the $4b_2$ and $1a_2$ singlet-triplet splitting as well as the absolute values of the obtained binding energies.

Software Development

For our work, we have been using the MOLGW code, which is an open-source project published under the GPL license and initially developed by F. Bruneval (CEA, France). We have been collaborating with F. Bruneval to improve the capabilities of MOLGW. My postdoc, Young-Moo Byun, supported under this grant, is listed as one of the contributors to MOLGW (http://www.molgw.org/contributors.html). MOLGW was initially parallelized using only MPI, but the NERSC supercomputers, which we have been using for our research, are designed for multi-threaded codes using shared memory. To fully utilize the NERSC computing resources, we parallelized MOLGW using OpenMP, reducing the high computational cost of 4-center Coulomb repulsion integrals that appear in SCF cycles and evaluation of the *GW* self-energy. Furthermore, we optimized our OpenMP implementation using thread affinity to enhance the memory bandwidth and reduce the memory latency. This optimization will enable us to fully utilize the AMD-powered next-generation NERSC supercomputer, Perlmutter, because AMD CPUs, which are based on a multi-chip module architecture, are strongly affected by memory bandwidth and latency. Our OpenMP implementation and optimization in MOLGW 1.F have recently been merged into a new version, MOLGW 2.A.

FUTURE WORK

Currently, we are testing the performances of COHSEX (a lower, but cheaper level of theory than G_0W_0 and ev*GW*), G_0W_0@COHSEX, and quasi-particle-self-consistent *GW* (a higher and less starting-point-dependent, but more expensive level of theory) for TMO anions. We have also started a new project on the performance of *GW* methods for transition-metal-dioxide (TMO_2) anion clusters.

PUBLICATIONS ACKNOWLEDGING THIS GRANT

1) L. Hung, L, F. H. da Jornada, J. Souto-Caseras, J. R. Chelikowsky, S. G. Louie, and S. Ogut, “Excitation spectra of aromatic molecules within a real-space *GW*-BSE formalism: Role of self-consistency and vertex corrections”, Phys. Rev. B **94**, 085125 (2016).
2) L. Hung, F. Bruneval, K. Baishya, and S. Ogut, “Benchmarking the *GW* approximation and Bethe-Salpeter Equation for Groups IB and IIB Atoms and Monoxides”, J. Chem. Theory Comput. **13**, 2135 (2017).
3) L. Hung, F. Bruneval, K. Baishya, S. Ogut, “Correction to Benchmarking the *GW* approximation and Bethe-Salpeter Equation for Groups IB and IIB Atoms and Monoxides”, J. Chem. Theory Comput. **13**, 5820 (2017).
4) L. Hung and S. Ogut, “Modeling Excited States of Confined Systems” in *Handbook of Materials Modeling. Volume I: Theory and Modeling*, W. Andreoni and S. Yip (eds) Springer, Cham (2018).
5) W. Gao, L. Hung, S. Ogut, and J. R. Chelikowsky, “The stability, Electronic Structure, and Optical Absorption of Boron-Nitride Diamondoids from First-Principles Calculations”, Phys. Chem. Chem. Phys. **20**, 19188 (2018).
6) B. Shi, S. Weissman, F. Bruneval, L. Kronik, and S. Ogut, “Photoelectron Spectra of Copper Oxide Cluster Anions from First Principles Methods”, J. Chem. Phys. **149**, 064306 (2018).

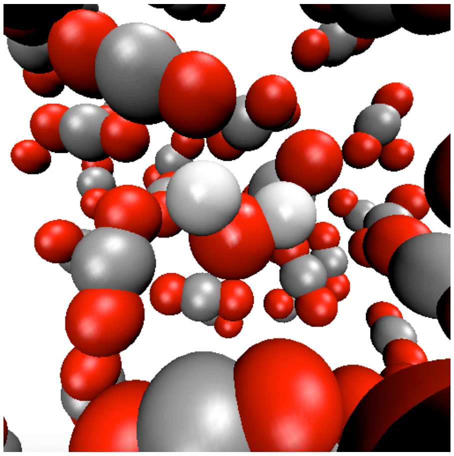
Francesco Paesani

Towards Realistic Simulations of Fluid Mixtures Through Many-Body Representations

Marc Riera, Eleftherios Lambros, Kartik Rallapalli, PI Francesco Paesani
Department of Chemistry and Biochemistry, Materials Science and Engineering, and San Diego Supercomputer Center, University of California San Diego, La Jolla, CA 92093

Abstract

The main objective of this project is the development and application of a new quantum mechanics/molecular mechanics (QM/MM) method to model chemical transformations and electronic excitations in fluid mixtures across different phases. The proposed method combines our many-body (MB) representations of molecular interactions with adaptive schemes for modeling chemical reactions in solution. The combination of these two components will result in an adaptive quantum mechanics/many-body (adQM/MB) method that will largely suppress discontinuities between QM and MM regions and will thus provide an accurate representation of both quantum mechanical and environmental effects through a rigorous description of mutual polarization between QM and MM regions.



MB-MD simulations of H_2O in CO_2

As discussed in "The Water–Energy Nexus: Challenges and Opportunities", to advance energy–water systems several challenges must be addressed, including the characterization of complex fluid behavior, the control of chemical reactions, both in bulk solutions and at interfaces, and the ability to make predictions about physicochemical transformations that span several orders of magnitude in length scale, from hydrogen bond rearrangements at the molecular scale to fluid flows at the macroscopic scale. In particular, many aspects of energy–water systems involve the interactions of multicomponent aqueous solutions and other complex fluids. The ability to reliably predict and control the emergence of structures and phases in these fluids requires fundamental knowledge of the underlying physical mechanisms which, in turn, demands a molecular-level understanding of the interactions between different molecular components. The extension of our MB representations to generic molecular species along with the development of the adQM/MB method will provide an integrated theoretical/computational infrastructure for molecular modeling of complex fluid mixtures under different thermodynamic conditions and in different environments.

Our initial efforts have focused on developing an accurate and efficient theoretical/computational framework 1) to model fluid mixtures from the gas to the condensed phase through many-body molecular dynamics (MB-MD) simulations, and 2) to investigate the relationship between individual many-body effects and the local structure of liquids. We will present our results for the properties of CO_2/H_2O mixtures and a systematic analysis of many-body effects in liquid water. In the case of the CO_2/H_2O mixtures, our studies demonstrate that our MB representations enable MB-MD simulations with chemical accuracy from small clusters in the gas phase to fluid mixtures at different temperatures and pressures. In the case of liquid water, our MB-MD simulations indicate that the local hydration structure is primarily determined by the delicate interplay between two-body and three-body interactions, which are further modulated by higher-body interactions and nuclear quantum effects. These results suggest that a correct representation of two-body and three-body interactions may require sub-chemical accuracy, which can be achieved by MB representations rigorously derived from the many-body expansion of the total energy where the individual terms are obtained at the CCSD(T) level of theory in the complete basis set limit.

Our future work will focus on combining our MB representations with electronic structure methods within the proposed adQM/MB scheme to characterize chemical transformations in complex fluid mixtures.

DE-SC0019490: Grant Titles Chemical Reactivity and Spectroscopy Through Adaptive Quantum Mechanics / Many-Body Representations: Theoretical Development, Software Implementation, and Applications

Student(s): Marc Riera, Eleftherios Lambros, Kartik Rallapalli

Publications

M. Riera. E. Lambros, T.T. Nguyen, A.W. Gotz, F. Paesani, “Low-order many-body interactions determine the local structure of liquid water”, submitted.

"Tight-binding Analysis of the Electronic Structure of Noble-Metal Compounds"

S. Silayi, P.-H. Chang, and D. A. Papaconstantopoulos

Department of Computational & Data Sciences, George Mason University, Fairfax, VA

ABSTRACT

We used the NRL-TB method with TB parameters determined from a fit that reproduces the electronic structure and total energy versus volume values of first-principles calculations to study the Cu-Ag noble metal binary system. The TB parameters were fit to the structures B1(CuAg), B2(CuAg), L12 (Cu3Ag and Ag3Cu) in addition to the FCC Cu and Ag. The method reproduced the first-principles ordering of these structures, and verified the ground state structure of the system to be the L12. As an output of this approach the following quantities were predicted correctly: elastic constants, phonon spectra, densities of electronic states as well as the total energies of additional crystal structures that were not included in the original first-principles database.

We also used this TB parametrization to perform molecular dynamics simulations and determined the energies for vacancy formation, temperature dependence of the coefficient of thermal expansion and the mean squared displacement. In addition, we have shown than these TB parameters work for determining binding energies and bond lengths of Cu-Ag fcc-like clusters.

We are now pursuing additional calculations on Cu-Au and Ag-Au compounds.

We have under development a website with instructions of the use of these tight-binding codes.

Kyungwha Park

kyungwha@vt.edu

Predicting magnetic properties of single-molecule magnets from self-interaction-free density-functional theory

Kyungwha Park

850 West Campus Drive, Department of Physics, Virginia Tech, Blacksburg, VA 24061

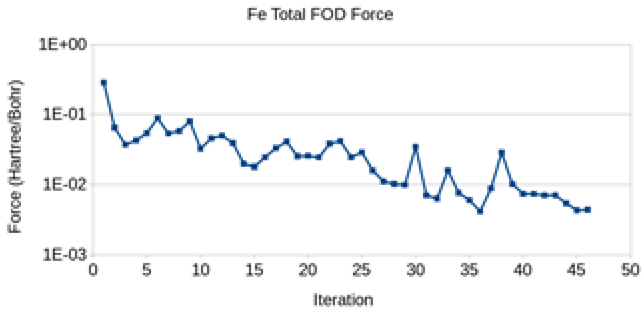
Over the past two decades, the research in nanoscale magnetic molecules or single-molecule magnets (SMMs) has been driven for their potential applications such as data storage, molecular spintronics, and quantum information science. Unique quantum properties of SMMs such as quantum tunneling of magnetization, quantum interference, strong spin-phonon coupling, and strong hyperfine Stark effect, allow such interesting applications based on molecules rather than more conventional silicon-based sold-state materials.

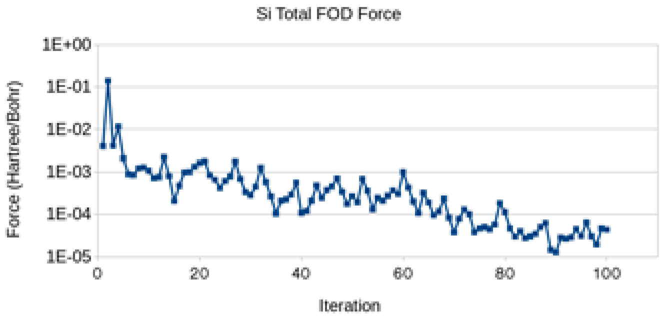
An individual SMM consists of one to several tens of transition metal or lanthanide elements coupled via anions through super-exchange interactions, and its trademark property is magnetic anisotropy induced by interplay between crystal fields (or ligand fields) and spin-orbit interaction, even in the absence of external magnetic field. The orbitals in the ground state of SMMs are often nearly degenerate and so multi-reference methods are desirable. However, for SMMs with multiple metal or lanthanide element sites, multi-reference methods are beyond current computational capabilities. In this case, we need to rely on low-level first-principles methods such as density-functional theory (DFT). For some SMMs, DFT including spin-orbit coupling produced reasonable magnetic anisotropy and other magnetic properties, while some other SMMs, DFT-based approach completely failed.

One of the reasons that DFT fails is due to self-interaction error (i.e. electrons interact with themselves) inherent in approximate exchange-correlation functionals. Recently, a new size-extensive self-interaction correction (SIC) method based on Fermi-Lowdin orbitals has been proposed and this method was successfully implemented into open-source FLOSIC code and applied to small magnetic molecules with improved magnetic properties, compared to DFT calculations without SIC. Our goal is to perform DFT+SIC calculations for a variety of SMMs in order to predict reliably their electronic, magnetic, and vibrational properties, in collaboration with the FLOSIC developers.

During the first year, a first-year graduate student, Anri Karanovich, joined the project. Karanovich participated in the first FLOSIC meeting held at Central Michigan University in September 2018 and in the 59th Sanibel Symposium held in St. Simons Island in February 2019. In these two meetings, he interacted with the FLOSIC developers and researchers and experts in SIC. He was trained for the basics of the recently proposed SIC method and the FLOSIC code. For this effort, we closely interacted with both the FLOSIC team at Central Michigan University led by Prof. K. A. Jackson and the FLOSIC team at University of Texas at El Paso led by Profs. T. Baruah and R. Zope. The success of the new SIC method heavily relies on efficient optimization of the Fermi orbital descriptors (FODs) for a given geometry. The following two figures show our initial results of the maximum FOD force on a single Fe and a single Si atom versus iteration number, where an initial guess of the FOD positions was obtained from the Monte

Carlo method developed by the FLOSIC team (Prof. K. A. Jackson) at Central Michigan University, using FLOSIC code version 0.2.





During the next year, we plan to use the following two approaches in order to optimize FODs for several small magnetic molecules, using FLOSIC code, in collaboration with the two FLOSIC teams: (i) starting with FODs optimized from individual atoms by Der-you Kao et al. and (ii) starting with FODs guessed by the Monte Carlo method developed by Prof. K. A. Jackson group (Central Michigan University). Then we will compute the magnetic properties of such magnetic molecules and compare with experimental data if available and with DFT calculations without SIC. The graduate student will present his work in the APS March meeting in 2020, and will write his first paper on this project.

Grant Number and Grant Title: DE-SC0019033. Predicting magnetic properties of single-molecule magnets from self-interaction-free density-functional theory

Student: Anri Karanovich

Electron and Electron-Nuclear Dynamics of Open Quantum Subsystems

Michele Pavanello[1]

[1]*Department of Chemistry, Rutgers University, Newark, NJ, U.S.A.*

Abstract

We develop methods for the simulation of the dynamics of excited electronic states in complex systems. That is, systems for which the typical quantum chemistry toolbox is simply not applicable due to the system size. Approximations are in order, however, our methods never shy away from the following important defining properties. They are: (1) all-electron, (2) mean field, (3) self-consistent.

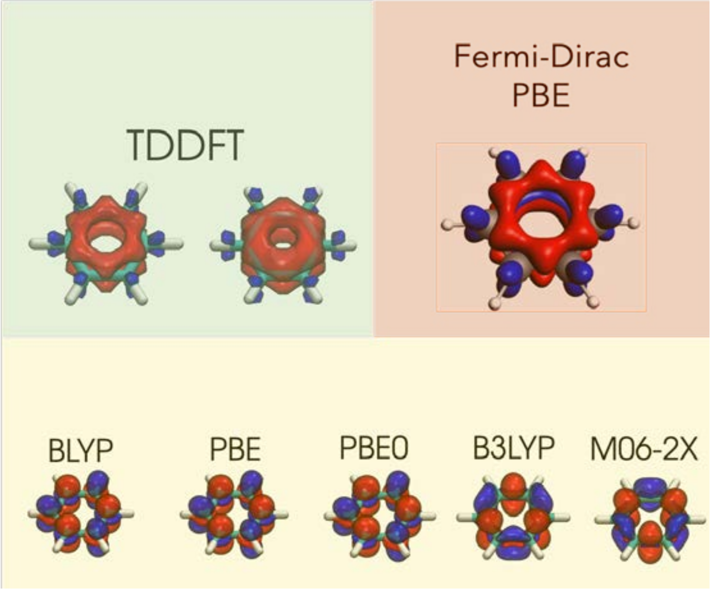


Figure 1: Density difference for the first excited state of benzene. XCDFT solved using Aufbau occupations (lower panel) delivers a mixed state, with an incorrect double excitation character and an incorrect density difference between ground and excited state. XCDFT solved with Fermi-Dirac occupations (upper rhs), delivers a state with no appreciable double excitation character that compares well with linear response TDDFT (upper lhs).

In the past year, we have focused on an approach for computing excited states that is as balanced as possible with ground state calculations and that can be seamlessly extended to a subsystem (embedding) formulation. Along this avenue, and exploiting the machinery of Constrained Density Functional Theory, we have recently proposed [2] a variational method for calculating low-lying excited states of molecular systems which we dub eXcited Constrained DFT (XCDFT). Excited states are obtained by self-consistently constraining a user-defined population of electrons, N_c, in the virtual space of a reference set of occupied orbitals. By imposing this population to be $N_c = 1$, we computed the first excited state of 15 molecules from a test set. Our results show that XCDFT achieves an accuracy in the predicted excitation energy only slightly worse than linear-response time-dependent DFT (TDDFT), but without incurring into problems of variational collapse typical of the more commonly adopted ΔSCF method. In addition, we selected a few challenging processes to test the limits of applicability of XCDFT. We find that in contrast to TDDFT, XCDFT is capable of reproducing energy surfaces featuring conical intersections (azobenzene and H_3) with correct topology and correct overall energetics also away from the intersection. Venturing to condensed-phase systems, XCDFT reproduces the TDDFT solvatochromic shift of benzaldehyde when it is embedded by a cluster of water molecules.

Problematic has been XCDFT's trend to introduce higher order excitation character in the computed excited states. This problem is shared with ΔSCF and is due to the restrictive character of the single Slater Determinant. We implemented an extension of XCDFT that solves the electronic structure with a "smeared" set of occupations. Fermi-Dirac distributions with very small broadening parameters (0.01 eV, typically) deliver excited states with much improved character compared to Aufbau XCDFT (see **Figure 1**).

In addition to our efforts developing XCDFT, leveraging an open-subsystem formulation of Density Functional Theory (DFT), we develop real-time subsystem TDDFT methods for simulating the electron dynamics of condensed-phase systems. In liquids and molecule-surface interfaces, we observe all the relevant regimes proper of non-Markovian open quantum system dynamics, such as electronic energy transfer, and screening. Metals and semiconductors typically have large polarizabilities, and even in a regime of low coupling their effect on impinging molecular species is significant – line broadening, peak shift, and intensity borrowing are observed, characterized, and explained in terms of inter-subsystem dynamical interactions and a many-body decomposition of the system's density-density response function in a way that transcends the canons of Fermi Golden Rule.

Future developments will involve implementation of nonadiabatic dynamics based on a subsystem real-time TDDFT approach as well as ibased on XCDFT. Codes are currently being developed by the PI and by students and postdocs supported by this grant. Additionally, we plan to explore alternative and nonstandard ways of coupling molecular systems with metals, i.e., employing time-dependent Thomas-Fermi theory for metal surfaces. We expect the latter to yield fast and still accurate models of the dynamics of molecule-metal interfaces which is still largely uncharted due to the large computational cost of modeling the metallic system.

Grant Number: DE-SC0018343.

Students: Alina Umerbekova (graduate student)

Postdoc: Dr. Pablo Ramos

Publications Acknowledging the Grant

1. Sudheer Kumar P. and Alessandro Genova and Michele Pavanello
   Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water
   J. Phys. Chem. Lett., **8**, 5077 (2017)

2. Pablo Ramos and Michele Pavanello
   Low-lying Excited States by Constrained DFT
   J. Chem. Phys., **148**, 144103 (2018)

3. Alina Umerbekova, Shou-Feng Zhang, Sudheer Kumar P. and Michele Pavanello
   Dissecting Energy Level Renormalization and Polarizability Enhancement of Molecules at Surfaces with Subsystem TDDFT
   Eur. Phys. J. B, **91**, 214, (2018) [Special Issue: Hardy Gross]

4. Pablo Ramos, Mark Mankarious, Michele Pavanello and Damien Riedel
   Probing charge transfer dynamics in a single iron tetraphenylporphyrin dyad adsorbed on an insulating surface
   Nanoscale, **10**, 17603 (2018) [Selected as "hot" article]

5. Johannes Tolle, Andre Gomes, Pablo Ramos and Michele Pavanello
   Charged-cell Periodic DFT Simulations Via an Impurity Model Based on Density Embedding: Application to the ionization potential of liquid water
   Int. J. Quantum Chem., **119**, e25801 , (2019) [Special Issue: Advances in Simulating Solvation]

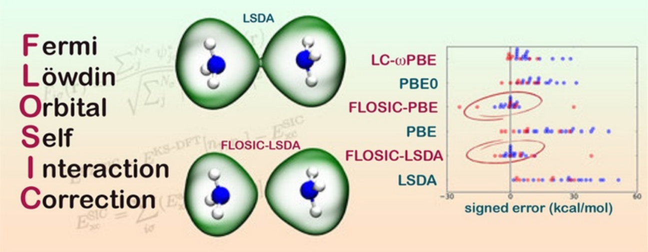
Improving Density Functional Theory Methods for Spin-Related Molecular Properties

Juan E. Peralta
Department of Physics, Central Michigan University, Mount Pleasant MI 49959,
juan.peralta@cmich.edu

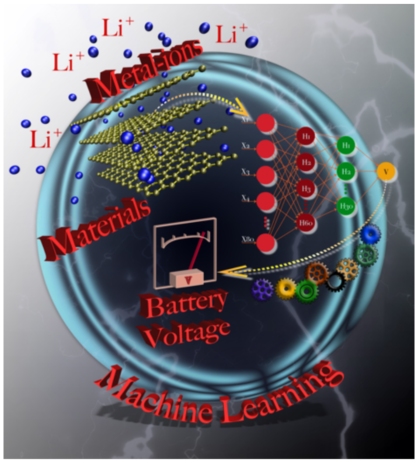
Abstract

Recent Progress:

(a) The effect of DFT self-interaction error (SIE) on calculated molecular and solid-state properties has been known for a long time. The most widely accepted framework for removing SIE in DFT is due to Perdew and Zunger (PZ) [Phys. Rev. B 23, 5048 (1981)]. However, due to the high computational cost associated with minimizing the PZ energy expression, the calculation of explicitly self-interaction free molecular properties remains elusive. Recently, an efficient implementation for SIE removal based on Fermi orbitals was proposed (FLOSIC) [JCP 140, 121103 (2014)]. This method explicitly avoids the unitary transformation from canonical to localized orbitals that is needed in standard PZ and replaces it by a Fermi-Löwdin transformation that depends only on one vector descriptor per orbital, or Fermi orbital descriptor (FOD). We have assessed the potential of this method for a number of molecular properties and the general conclusion is that it effectively eliminates the self-interaction error in a manner similar to traditional PZ.



(b) We are working on a new approach based on the direct propagation of the driven Liouville von Neumann (DLvN) equation for the simulation of many-electron (open) quantum systems out of equilibrium. This approach allows us to simulate the transient current and find stationary solutions of molecular complexes placed between explicit leads subject to an energy bias in a DFT framework. The code is very advanced but still needs adjustments. The idea is to be able to incorporate noncollinear magnetism and relativistic effects to model problems that involve electron spin transport with direct applications in spintronic devices.



(c) Some other projects involve the search for high magnetic anisotropy mononuclear Co(II) complexes inspired by recent experimental work where an anisotropy $D \sim -73\ cm^{-1}$ was observed. Also, we explored a machine learning method to estimate the voltage of electrode materials for batteries very efficiently, which is available as a web-accessible tool (http://se.cmich.edu/batteries).

Future Plans: At this point we expect FLOSIC improvement on two fronts: 1) Making the method more efficient. This can be achieved by accelerating the self-consistent procedure and also improving the energy minimization with respect to FOD positions; and 2) Improving the density functional realization that is combined with the explicit self-interaction free methodology. We also plan to finish the DLvN code.

† DE-SC0018331: FLO-SIC: Efficient Density Functional Theory Calculations without Self-Interaction

‡ DE-SC0005027: Computational Methods Based on Density Functional Theory for Reactions and Processes Involving Electronic Spin (currently on NCE).

Postdoc(s): Kamal Sharkas (supported from DE-SC0018331).

Student(s): R. P. Joshi (supported from DE-SC0005027).

10 Publications Acknowledging this DOE sponsored research (2015-2019)

‡ Machine Learning the Voltage of Electrode Materials in Metal-ion Batteries, R. Joshi, J. Eickholt, L. Li, M. Fornari, V. Barone, and J. E. Peralta, *ACS Appl. Mater. Interfaces*, accepted (**2019**).

‡ Magnetic Properties of Co(II) Complexes with Polyhedral Carborane Ligands, O. Oña, D. Alcoba, G. Massaccesi, A. Torre, L. Lain, J. I. Melo, J. Oliva-Enrich, and J. E. Peralta, *Inorg. Chem.* 58, 2550 (**2019**).

† Analytic Atomic Gradients in the Fermi-Lowdin Orbital Self-Interaction Correction, K. Trepte, S. Schwalbe, T. Hahn, J. Kortus, D-y. Kao; Y. Yamamoto, T. Baruah, R. Zope, K. Withanage, J. E. Peralta, and K. A. Jackson, *J. Comp. Chem.* 40, 820 (**2019**).

† Shrinking Self-Interaction Errors with the Fermi-Löwdin Orbital Self-Interaction Corrected Density Functional Approximation, K. Sharkas, L. Li, K. Trepte, K. Withanage, R. Joshi, R. Zope, T. Baruah, K. Johnson, A. Jackson, and J. E. Peralta, *J. Phys. Chem. A* 122, 9307 (**2018**).

† Fermi-Löwdin Orbital Self-interaction Correction to Magnetic Exchange Couplings, R. Joshi, K. Trepte, K. Withanage, K. Sharkas, Y. Yamamoto, L. Basurto, R. Zope, T. Baruah, A. Jackson, and J. E. Peralta. *J. Chem. Phys*. 149, 164101 (**2018**).

† On the Question of the Total Energy in the Fermi-Löwdin Orbital Self-interaction Correction Method, K. P. K. Withanage, K. Trepte, J. E. Peralta, T. Baruah, R. Zope, and K. A. Jackson, *J. Chem. Theory Comput.* 14, 4122 (**2018**).

‡ Magnetic Properties of Mononuclear Co(II) Complexes with Carborane Ligands, D. R. Alcoba, O. B. Oña, G. E. Massaccesi, A. Torre, L. Lain, J. I. Melo, J. E. Peralta, and J. M. Oliva-Enrich, *Inorg. Chem.* 57, 7763 (**2018**).

‡ Local Noncollinear Spin Analysis, B. A. Abate, R. P. Joshi, and J. E. Peralta, *J. Chem. Theory and Comput.* 13, 6101-6107 (**2017**).

‡ Magnetization Dynamics from Time-dependent Non-collinear Spin Density Functional Theory Calculations, J. E. Peralta, O. Hod, and G. E. Scuseria, *J. Chem. Theory and Comput.* 11, 3661–3668 (**2015**).

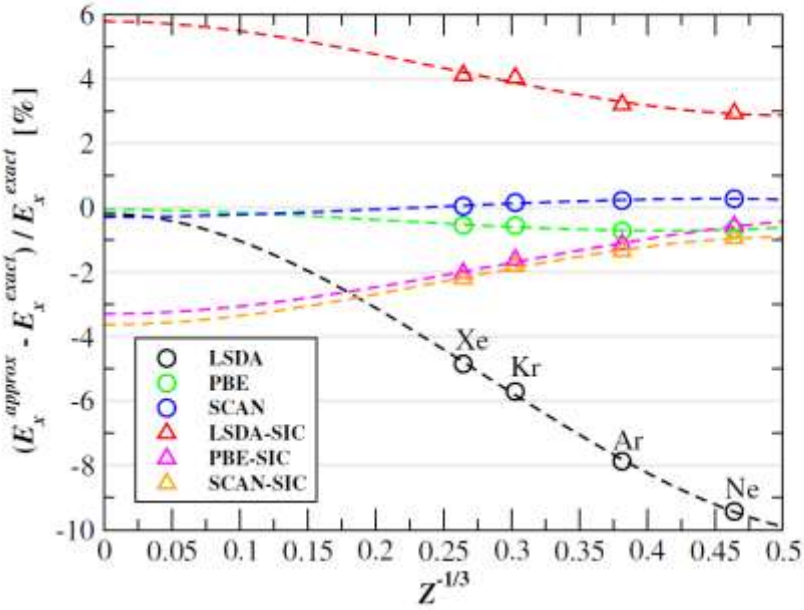
‡ Hexagonal BC_3: A Robust Electrode Material for Li, Na, and K Ion Batteries, R. P. Joshi, B. Ozdemir, V. Barone, and J. E. Peralta, *J. Chem. Phys. Lett.* 6, 2728-2732 (**2015**).

Perdew-Zunger Self-Interaction Correction: How Wrong for Uniform Densities and Large-Z Atoms?

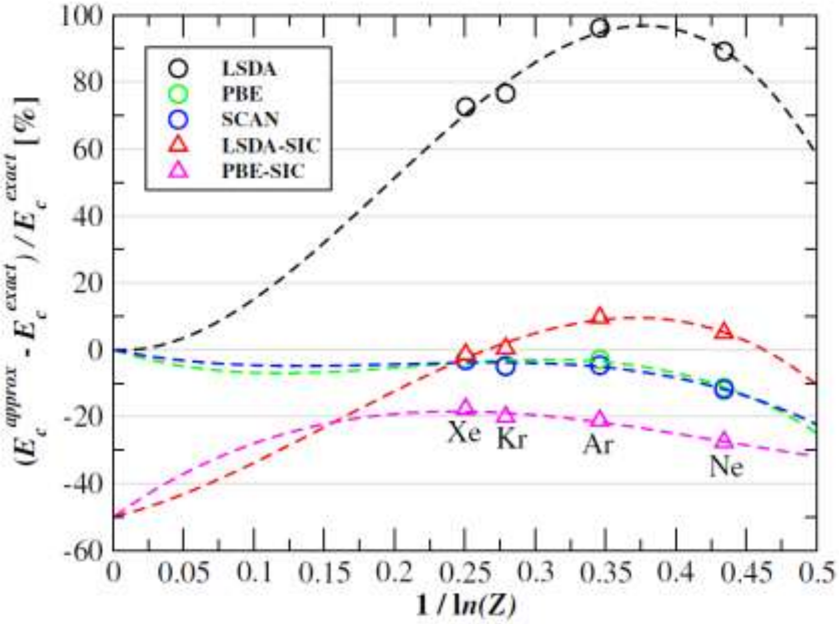
Biswajit Santra[1] and John P. Perdew[1]

[1]Department of Physics, Temple University, Philadelphia, PA 19122

Abstract



Semi-local density functionals for the exchange-correlation energy of a many-electron system cannot be exact for all possible one-electron densities. In 1981, Perdew and Zunger (PZ) subtracted the fully-nonlocal self-interaction error orbital-by-orbital, making the corrected functional exact for all collections of separated one-electron densities, and making no correction to the exact functional. Although the PZ self-interaction correction (SIC) eliminates many striking errors of semi-local functionals, it is often worse than the uncorrected functional for equilibrium properties of *sp*-bonded molecules and solids. Non-empirical semi-local functionals are usually designed to be exact for electron gases of uniform density, and thus also make 0% error for neutral atoms in the limit of large atomic number *Z*, but PZ SIC is not so designed. For localized SIC orbitals (either real or complex), we show analytically that the LSDA-SIC correlation energy per electron of the uniform gas in the high-density limit makes an error of -50% in the spin-unpolarized case, and -100% in the fully-spin-polarized case. Then we extrapolate from the Ne, Ar, Kr, and Xe atoms to estimate the relative errors of the PZ SIC exchange or exchange-correlation energies (with real localized SIC orbitals) in the limit of large atomic number: +5.5% for the local spin density approximation (LSDA-SIC), and -3.5% for nonempirical generalized gradient (PBE-SIC) and meta-generalized gradient (SCAN-SIC) approximations. The uncertainty from similar estimates for the semi-local functionals without SIC is+-0.5%. The SIC errors are considerably larger than those that have been estimated for LSDA-SIC by approximating the localized SIC orbitals for the uniform gas, and may explain the errors of PZ SIC for equilibrium properties, opening the door to a generalized SIC that is more widely accurate.



Grant Numbers and Grant Titles

DE-SC0018331

FLO-SIC: Efficient Density Functional Calculations without Self-Interaction

Lead PI: Koblar A. Jackson, Central Michigan University

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

[1] Perdew-Zunger Self-Interaction Correction: How Wrong for Uniform Densities and Large-Z Atoms?, B. Santra and J.P. Perdew, J. Chem. Phys., to appear, doi:10.1063/1.5090534.

[2] Stretched or Noded Orbital Densities and Self-Interaction Correction in Density Functional Theory, C. Shahi, P. Bhattarai, K. Wagle, B. Santra, S. Schwalbe, T. Hahn, J. Kortus, K.A. Jackson, J. Peralta,K. Trepte, S. Lehtola, N.K. Nepal, H. Myneni, B. Neupane, S. Adhikari, A. Ruzsinszky, Y. Yamamoto, T.Baruah, R. Zope, and J.P. Perdew, J. Chem. Phys., to appear, doi:10.1063/1.5087065

[3] Self-consistent self-interaction corrected density functional theory calculations for atoms using Fermi-Löwdin orbitals: Optimized Fermi-orbital descriptors for Li – Kr. D.-y. Kao, K. Withanage, T. Hahn, J. Batool, J. Kortus, and K. Jackson, J. Chem. Phys. **147**, 164107 (2017).

[4] The Effect of Topology in Lewis Pair Functionalized Metal Organic Frameworks on CO2 Adsorption and Hydrogenation, J. Ye, L. Li, and J. K. Johnson, Catal. Sci. & Tech. **8**, 4609 (2018) (Cover article)

[5] Shrinking Self-Interaction Errors with the Fermi-Löwdin Orbital Self-Interaction Corrected Density Functional Approximation. K. Sharkas, L. Li, K. Trepte, K. P. K. Withanage, R. P. Joshi, R. R. Zope, T. Baruah, J. K. Johnson, K. A. Jackson, and J. E. Peralta, J. Phys. Chem. A **122**, 9307-9315 (2018) DOI: 10.1021/acs.jpca.8b09940

[6] Fermi- Löwdin orbital self-interaction correction to magnetic exchange couplings. R. P. Joshi, K. Trepte, K. P. K. Withanage, K. Sharkas, Y. Yamamoto, L. Basurto, R. R. Zope, T. Baruah, K. A. Jackson, and J. E. Peralta, J. Chem. Phys. **149**, 164101 (2018). doi: 10.1063/1.5050809

[7] On the question of the total energy in the Fermi- Löwdin orbital self-interaction correction method. Kushantha P. K. Withanage, Kai Trepte, Juan E. Peralta, Tunna Baruah, Rajendra Zope, and Koblar A. Jackson, J. Chem. Theory Comput. **14**, 4122 (2018).

[8] Energy Efficient Formaldehyde Synthesis by Direct Hydrogenation of Carbon Monoxide in Functionalized Metal–Organic Frameworks, L. Li, S. Zhang, J. P. Ruffley, and J. K. Johnson, ACS Sustainable Chem. Eng. 7, 2508 (2019)

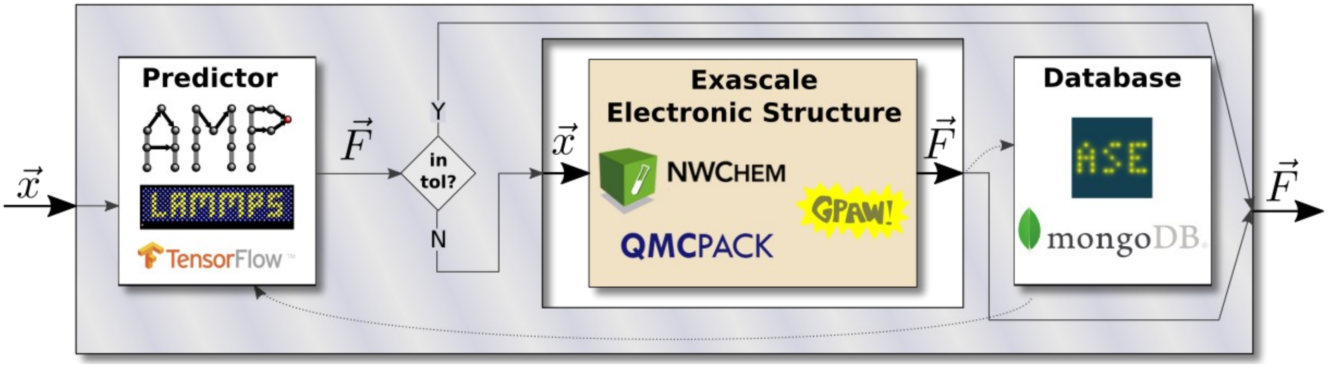
[9] Analytic Atomic Gradients in the Fermi- Löwdin orbital self-interaction correction. K. Trepte, S. Schwalbe, T. Hahn, J. Kortus, D-y. Kao, Y. Yamamoto, T. Baruah, R. R. Zope, K. P. K. Withanage, J. E. Peralta, and K. A. Jackson, J. Comp. Chem. **40**, 820-825 (2019). DOI**:**10.1002/jcc.25767

Bridging the time scale in exascale computing of chemical systems

C. Franklin Goldsmith[1], Andrew J. Medford[2], Brenda M. Rubenstein[3],
Zachary W. Ulissi[4], Adam P. Willard[5], Andrew A. Peterson[1,*]

[1]School of Engineering, Brown University
[2]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology
[3]Department of Chemistry, Brown University
[4]Department of Chemical Engineering, Carnegie Mellon University
[5]Department of Chemistry, Massachusetts Institute of Technology
[*]andrew_peterson@brown.edu

The broad aim of this project is to provide a generalized framework to accelerate the timescale of electronic structure calculations, particularly those of large atomic systems enabled by peta- and exascale computing infrastructures. Large atomic system sizes have complicated geometrical interactions, and even the simplest tasks, such as geometry optimization, are anticipated to take a very large number of ionic steps in standard routines. Of course, more complicated tasks such as saddle-point searches or molecular dynamics simulations require a very large number of time steps, and despite the rise of large computational facilities, many such calculations will remain out of reach using standard approaches. We are developing an approach that, if successful, will allow the seamless acceleration of large-scale electronic structure calculations in a framework shown in the image below. Briefly, when a user's routine (such as geometry optimization or molecular dynamics) requests a force call, the force call is first passed to *Amp* (our machine-learning code) rather than directly to the electronic structure calculator. *Amp* provides an estimate of the requested quantities, that is, the forces per atom, along with a quantification of the uncertainty of the estimate. If the uncertainty is within a user-specified tolerance, the forces are passed directly back to the user's routine, essentially instantaneously. If the uncertainty is high, an electronic structure calculation is triggered. At the conclusion of this electronic structure calculation, the result is passed to the user's routine, but is also included in the database of calculations, which in turn is used to re-train *Amp* to include this additional information. In this way, *Amp*'s representation of the potential-energy surface is self-improving, and the fraction of electronic structure calculations necessary should decrease as algorithms proceed. This allows an effective extension of the time scales achievable in exascale electronic structure calculations.



Here, we describe recent progress we have made in advancing our approach. Scaling atom-centered machine learning force fields to large datasets and on-line/iterative training is not currently possible with the current open-source *Amp* code. However, recent hardware and software platforms for machine learning are enabling us to implement scalable approaches. Nearly all deep learning (large artificial neural networks or similar) applications use GPUs or custom ASIC chips for hardware acceleration of the underlying code, and many large applications require many GPU nodes working in parallel to rapidly train and serve machine learning models. Our initial focus is on re-writing the core of the *Amp* machine learning model routines to use modern machine-learning (ML) packages that automatically provide these benefits. This will simultaneously make development easier, accelerate performance, increase accuracy with modern training methods, and enable uncertainty through more sophisticated neural networks. Examples of techniques that have considerably improved neural network training in the ML community but are not current available in *Amp* include batch normalization, regularization schemes, SGD/Adam optimizers, among many others. We now have an initial implementation of the Behler-Parinello model scheme using the open-source pyTorch package. We have implemented energy training and verified accuracy against the baseline *Amp* code, with training rates approximately twice as fast (before performance / GPU tuning). Force training is currently in progress and will be benchmarked against the *Amp* code. This is the first step to using/enabling more the testing of more modern neural network training methods and architectures and will be made available as an integral part of the *Amp* code for the community.

Quantum Monte Carlo (QMC) codes provide an attractive means to scalably calculate electronic structure with higher fidelity than methods such as density functional theory, and the machine-learning approaches in this project tie into QMC approaches well. First, for decades, the primary Achilles' heel of QMC methods has been their inability to efficiently produce forces. Although recent analytical advances in this direction have been made, many of the proposed algorithms remain computationally cumbersome. Here, we use artificial neural networks within *Amp* to learn the potential energy landscapes of and forces among water clusters provided energies of configuration produced using both Diffusion Monte Carlo and Auxiliary Field Quantum Monte Carlo. As a preliminary demonstration of our technique, we use the learned forces to relax the geometry of water from a stretched configuration to a "QMC" equilibrium geometry and compare the accuracy of the final structure and expense with previously proposed methods. Moving forward, we will employ the same techniques to repair *ab initio* DFT models of water and to accurately model the reactive dynamics of water at catalytic surfaces. Second, in order to avoid the infamous sign problem, most modern quantum Monte Carlo algorithms impose approximate, often uncontrolled constraints to prevent them from sampling negative probability distributions. These constraints are typically based upon trial wave functions produced using less accurate methodologies and are fixed at the start of each simulation. In this work, we exploit the many configurations generated during the course of a quantum Monte Carlo simulation to machine learn constraints that improve themselves, leading to virtually error-free constraints, while also accelerating expensive local energy calculations. We demonstrate these techniques within simulations of the correlated carbon dimer and aim to apply these techniques to simulations of transition metal and lanthanide molecular catalysts currently ongoing within the group.

The prediction of charged systems is crucial for many current atomistic applications, such as electrochemical systems of importance in catalysis and batteries, yet means of incorporating charge and potential into machine-learned potentials have not been demonstrated. Separately, we have developed a grand-canonical density functional theory technique known as the Solvated Jellium (SJ) method; this method allows us to control the potential by varying the number of electrons in the system while maintaining overall charge neutrality by means of a balancing jellium slab; the potential is thus referenced against a field-free region. We have developed preliminary means to predict the excess electrons required to maintain a specified potential in these SJ calculations by employing a modified fingerprint. Having demonstrated this portion of the problem, our intention is to employ a modified Goedecker scheme to predict the atomic energy and forces in a charge-electronegativity expansion.

Efforts are underway to construct a neural network force-field based on multiple levels of theory, ranging from molecular dynamics to quantum Monte Carlo (QMC). The initial target system is liquid water, which must be properly described in order to describe a reactive aqueous interface. The system is ideal because it is well-studied, but no single level of theory provides a fully accurate description. For example, classical force-fields reproduce statistical properties like density and pair-distribution functions, but cannot describe bond-breaking reactions. Contrarily, DFT methods like B3LYP can describe bond dissociation, but fail to reproduce statistical properties. This means that describing diffusion of protons or hydroxyl groups in water is currently extremely challenging, since both statistical and reactive properties must be properly described. Our strategy is to build on the current state-of-the-art "water-2017" reactive MD force-field, and use machine learning to augment it with data from higher levels of theory including B3LYP and QMC. This will be achieved by first generating a large amount of training data with water-2017 and training a neural network to reproduce it, and subsequently refining the network with data from higher levels of theory. Currently, we have developed machinery to generate training data and have validated diffusion constants and pair distribution functions for water-2017 based on existing literature. We have also developed a training pipeline capable of iterative training based on data from multiple sources. The pipeline has been tested on water-2017 data augmented with B3LYP, and generation of QMC training data is currently underway. The next step is to evaluate the performance of these refined force-fields for calculating proton/hydroxyl diffusion to ensure that the more accurate training data yields improvements in performance.

Associated Posters:
Zachary Ulissi, "Bringing State-of-the-Art Machine Learning Methods to *Amp*"

Brenda Rubenstein, "Quantum Monte Carlo Dynamics of Water Using Machine Learning"

Franklin Goldsmith, "Exascale molecular dynamics with machine learning & adsorbate partition functions under high-coverage conditions"

Andrew J. Medford, "Opportunities for coupling atomistic and electronic structure simulations with machine learning"

Adam P. Willard, "Capturing dynamics at the electrified solid-liquid interface"

Grant name: Bridging the time scale in exascale computing of chemical systems
Award number: DE-SC0019441

Graduate student participants (in bi-weekly conference calls):
Cheng Zeng (Brown), Xi Chen (Brown, Peterson Group), Per Lindgren (Brown), Xi Chen (Brown, Goldsmith Group), Benjamin Bodner (Brown), Cancan Huang (Brown), Ben Comer (Georgia Tech), Xiangyun Lei (Georgia Tech), Muhammed Shuaibi (CMU), Kevin Tran (CMU).

New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States

Piotr Piecuch
Department of Chemistry, Michigan State University, East Lansing, MI 48824
piecuch@chemistry.msu.edu

I. Program Scope

This research program focuses on the development, dissemination, and applications 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, systems involving substantial electronic quasi-degeneracies, and properties other than energy. The overall goal is to enable precise modeling of molecular processes and properties relevant to energy science, especially combustion, catalysis, energy storage, and photochemistry. The emphasis is on achieving 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 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, which can utilize modern computer architectures and which are well suited for automated implementations, are shared with the community through the GAMESS package and plugins to PSI4 in GitHub. Some of them can be found, in the original or modified form, in the NWChem, Q-Chem, and MRCC codes.

II. Recent Progress (2016 – 2018 and January 1 – April 15, 2019)

Our research in the reporting period has consisted of three distinct and yet closely related components, including **(1)** development of new generations of deterministic *ab initio* electronic structure approaches exploiting the exponential CC ansatz, **(2)** introduction of a new paradigm in the area of solving the electronic Schrödinger equation by combining stochastic Quantum Monte Carlo (QMC) propagations in the many-particle Hilbert space with deterministic CC-type computations, and **(3)** applications of new and existing quantum chemistry approaches to ground and excited-state potential energy surfaces, followed by time-dependent dynamics simulations, singlet-triplet and singlet-singlet gaps in biradical and prototype magnetic species, photoelectron spectra of transition metal nanoparticles, and structural, electronic, and spectroscopic properties of metal clusters. **(1)** and **(2)** have been accompanied by substantial mathematical and programming work and numerous benchmark calculations. Much of our recent method development work was enabled by our home-grown automated formula derivation and code implementation software, which produces efficient codes at the tiny fraction of the equivalent manual effort.

In the area of new deterministic *ab initio* methods, we have made significant progress in the development of biorthogonal moment energy expansions, which in the past resulted in the left-eigenstate completely renormalized (CR) CC and equation-of-motion (EOM) CC approaches, such as CR-CC(2,3) and CR-EOMCC(2,3) exploited, for example, in Refs. [3,4,6,7,9], by focusing on the CC(P;Q) formalism. The CC(P;Q) theory, which was originally proposed, as part of our earlier DOE funding, in 2012 [J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012); *J. Chem. Phys.* **136**, 144104 (2012); *J. Chem. Theory Comput.* **8**, 4968 (2012)], enables one to contemplate novel, computationally efficient, *ab initio* schemes for obtaining nearly exact ground- and excited-state potential energy surfaces along bond breaking coordinates within a single-reference framework. Among the most promising CC(P;Q) methods is the CC(t;3), CC(t,q;3), CC(t,q;3,4), and CC(q;4) hierarchy, in which energies obtained in the active-space CCSDt/EOMCCSDt, CCSDtq/EOMCCSDtq, and CCSDTq/EOMCCSDTq calculations are corrected for the subsets of triples, triples and quadruples, or quadruples missing in CCSDt, CCSDtq, and CCSDTq and their EOM extensions. In the reporting period, we extended the CC(t;3) approach, which provides molecular potential energy surfaces, reaction profiles involving biradicals, and singlet-triplet gaps in biradicals that agree with the parent full CCSDT data to within small fractions of a millihartree at a tiny fraction of the computational cost, to the CC(t,q;3), CC(t,q;3,4), and CC(q;4) models including connected quadruple excitations [3,7]. By examining the double dissociation of water, insertion of Be into H_2, and singlet-triplet gap in a prototype magnetic $(HFH)^-$ system, we demonstrated that the CC(t,q;3) and CC(t,q;3,4) approaches, especially the latter one, reproduce the exact, full configuration interaction (FCI), or virtually exact, CCSDTQ, total and relative energies to within small fractions of a millihartree at tiny fractions of the computational effort involved in the parent CCSDTQ calculations, even when electronic quasi-degeneracies are substantial [3]. Papers [7,9] extended these studies by examining the performance of CCSD, CCSD(T), CCSD$(2)_T$, CR-CC(2,3), CCSDt, CC(t;3), CCSDT, CCSD(TQ), CR-CC(2,4), CCSDtq, CC(t,q;3), CC(t,q;3,4), CCSDTq, CC(q;4), and CCSDTQ in describing the challenging potential energy curves and vibrational term values of the beryllium [7] and magnesium [9] dimers. We demonstrated that among the various non-iterative corrections to CCSD, our CR-CC(2,3) and CR-CC(2,4) approaches are most accurate. More importantly, we showed that the CC(P;Q)-based CC(t;3), CC(t,q;3), CC(t,q;3,4), and CC(q;4) methods, which correct the active-space CCSDt, CCSDtq, and CCSDTq energies, outperform the analogous approaches correcting CCSD in faithfully reproducing the respective parent CCSDT and CCSDTQ calculations. For example, it is hard to distinguish between the CC(t;3) and CCSDT or CC(q;4) and CCSDTQ potential energy curves and vibrational term values. In the case of Be_2 [7], we showed that the composite approach based on the all-electron CCSDT and valence CC(q;4) energetics, combined with the extrapolation to the complete basis set limit, reproduces the entire experimental vibrational spectrum, including states near the dissociation threshold, to within ~1 cm^{-1} (5 cm^{-1} at worst). In the case of Mg_2 [9], in addition to reproducing the experimentally determined part of the vibrational spectrum to within ~1 cm^{-1}, the analogous composite scheme combining the nearly all-electron CCSDT calculations with the valence CC(q;4) energetics predicts the existence of five extra vibrational levels, which were previously the subject of speculation, with the last, $\upsilon'' = 18$, state located only 0.2 cm^{-1} below the dissociation threshold. These findings are in perfect agreement with the calculations in which the valence CC(P;Q)-based CC(q;4) approach is replaced by a lot more expensive full CCSDTQ method. Encouraged by these successes, we used our most accurate representation of the ground-state $X\ {}^1\Sigma_g^+$ potential for Mg_2 and the similarly accurate excited-state $A\ {}^1\Sigma_u^+$ potential, along with the corresponding transition dipole moment function, to simulate the rovibrationally resolved photoemission spectrum of the magnesium dimer corresponding to the $A\ {}^1\Sigma_u^+ \rightarrow X\ {}^1\Sigma_g^+$ transition, obtaining perfect agreement with experiment and providing an accurate assignment of the rovibronic transitions that have not been previously resolved (manuscript in preparation). Other examples of successful exploitation of the CC(P;Q) methodology can be found in Refs. [4,6]. Paper [4] takes advantage of our CC(t;3) and CCSDT codes, which we incorporated in the reporting period (along with CCSDt) in GAMESS and, via the plugin deposited in GitHub, in PSI4, to examine the performance of a novel geminal-based approach, abbreviated as EERPA-GVB, in calculations of intermolecular potentials involving monomers with stretched intramonomer covalent bonds, where one has to capture weak long-range and strong non-dynamic correlations at the same time, as in the $NH_3\ldots F_2$ complex, in which we dissociated the F–F bond in F_2, and the strongly correlated $H_{12}\ldots H_{12}$ dimer, in which we stretched all H–H bonds in the linear H_{12} chains (as in models of metal-insulator transitions). Another work, where we benefited from the CC(t;3) methodology, was a collaboration with Professor Donald Truhlar, where we computed the equilibrium geometries, binding energies, adiabatic ionization potentials, and adiabatic electron affinities for $Mg_n^{0,\pm1}$ clusters with $n = 1 - 7$ using 39 exchange-correlation functionals in Kohn-Sham density functional theory (DFT) and several CC methods with singles, doubles, and triples, including CCSD(T), CCSD$(2)_T$, CR-CC(2,3), CCSDt, CC(t;3), and CCSDT [K. Duanmu *et al.*, *J. Phys. Chem. C* **120**, 13275 (2016)]. Consistent with Refs. [7,9], we demonstrated that the geometry and binding energy of Mg_2 requires a robust treatment of connected triple excitations, represented by CR-CC(2,3), CC(t;3), and CCSDT, which are substantially more accurate than the popular CCSD(T) approach, although CCSD(T) is sufficiently accurate for larger Mg clusters. We also showed that hybrid functionals are more accurate than the local ones. We completed the initial implementation of the excited-state CC(t;3) methodology, in which energies obtained in the active-space EOMCCSDt calculations are corrected for the subset of triples missing in EOMCCSDt (manuscript in preparation).

We also used the CC(P;Q) framework to propose a radically new way of obtaining accurate electronic energetics equivalent to high-level CC (CCSDT, CCSDTQ, etc.) calculations by merging the CC(P;Q) formalism with the stochastic CIQMC and CC Monte Carlo (MC) ideas [6]. According to one of the reviewers of Ref. [6], our fusion of the stochastic CIQMC and CCMC approaches with the deterministic CC(P;Q) methodology opens up a new paradigm in the area of solving the many-fermion Schrödinger equation. Indeed, there are two fundamentally different approaches in this area. One can use the deterministic *ab initio* wave function theories, where one ends up with highly complex systems of algebraic equations, whose solution may require enormous computer power, or turn to stochastic wave function sampling, as in QMC. In Ref. [6], we proposed a third-way, namely, use the stochastic methods, based on propagating the wave function in the many-fermion Hilbert space, to identify the leading wave function components, and the deterministic CC computations, combined with CC(P;Q) corrections, to provide the rest of the information. As shown in Ref. [6] and a longer paper presently in preparation, independent of the type of the MC sampling, the convergence toward target CC energetics (so far, we have tried full CCSDT and CCSDTQ) is rapid, already in the early stages of the MC wave function propagations, even when higher-order correlation effects and electronic quasi-degeneracies become substantial, accelerating high-level CC calculations by one or more orders of magnitude and freeing us from relying on user and system dependent concepts, such as active orbitals. In our most recent study [10], we extended the idea of identifying the leading higher–than–doubly excited determinants in the ground-state CC calculations via stochastic CIQMC propagations to excited electronic states by merging CIQMC with the deterministic EOMCC framework. By performing calculations aimed at recovering the EOMCCSDT energies of several excited states of CH^+ at the equilibrium and stretched geometries, in which the required lists of triples were extracted from FCIQMC propagations for the lowest-energy states in each symmetry category, we showed that one can accurately reproduce the EOMCCSDT results, including excited states having substantial multi-reference character, states of the same symmetry as the ground state, and states of other symmetries, out of the early stages of FCIQMC simulations [10]. We also proposed to accelerate convergence toward the exact, FCI, energetics by using the CC approach, in which singly and doubly excited clusters, needed to determine the energy, are iterated in the presence of their three- and four-body counterparts extracted from FCIQMC propagations, showing (using the water molecule at the equilibrium and stretched geometries) that one can extrapolate the FCI energetics based on short FCIQMC runs [8].

Other significant advances in the area of new CC and EOMCC methods in the reporting period were presented in Refs. [2,5], where we continued our previous work on extending the active-space EOMCC theories to the doubly electron-attached (DEA) formalism applicable to open-shell species with two electrons outside the closed-shell cores, especially the electronic spectra of biradicals and single bond breaking, without invoking complicated steps of multi-reference CC theories. Encouraged by our 2013 and 2014 studies [J. Shen and P. Piecuch, *J. Chem. Phys.* **138**, 194102 (2013); *Mol. Phys.* **112**, 868 (2014)], we demonstrated that the nearly exact DEA-EOMCC approach with up to 4-particle–2-hole (4*p*-2*h*) excitations can be extended to a much less expensive model, in which both 3*p*-1*h* and 4*p*-2*h* terms are selected using active orbitals [2]. By examining the low-lying singlet and triplet states of the methylene, $(HFH)^-$, trimethylenemethane, cyclobutadiene, and cyclopentadienyl cation biradicals and bond breaking in F_2, we showed that the DEA-EOMCC methods with an active-space treatment of 3*p*-1*h* or 3*p*-1*h* and 4*p*-2*h* excitations reproduce the results of the analogous parent calculations, in which these excitations are treated fully, at the small fractions of the computational effort and with virtually no loss in accuracy. We also demonstrated that the DEA-EOMCC methods with the active-space treatment of 3*p*-1*h* and 4*p*-2*h* or only 4*p*-2*h* excitations considerably improve the DEA-EOMCC theories truncated at 3*p*-1*h* excitations, while making the results almost insensitive to the type of molecular orbitals (MOs) used in the calculations [2]. The latter observation should be contrasted with the DEA/DIP-EOMCC methods truncated at 3*p*-1*h*/3*h*-1*p* excitations, which can be sensitive to the choice of MO basis. We also published a paper in collaboration with Professors Laura Gagliardi and Donald Truhlar, in which our converged DEA-EOMCC values of the singlet-triplet gaps in a series of antiaromatic molecules, including cyclobutadiene and its derivatives and cyclopentadienyl cation, provided definitive information for benchmarking CASPT2 and RASPT2 [5]. We continued working on the previously developed ionized (IP) EOMCC methodologies. For example, we used the scalar relativistic IP-EOMCC approaches to provide an accurate and complete assignment of peaks and other key features in the experimental photoelectron spectra of Ag_3^- nanoparticle, including electron binding energies as high as about 6.5 eV, for the first time [N.P. Bauman, J.A. Hansen, and P. Piecuch, *J. Chem. Phys.* **145**, 084306 (2016)]. In analogy to our 2014 study of the photoelectron spectrum of Au_3^-, we demonstrated that one has to correlate semi-core electrons, in addition to the valence ones, use larger basis sets, and include the high-order 3*h*-2*p* effects to obtain meaningful results. We also showed that geometry relaxation during electron ejection from Ag_3^- contributes to the peak widths, in addition to multiple electronic states behind a given spectral feature.

Other examples of successful application work in the reporting period include our collaboration with Professor Weston Thatcher Borden, where we performed the unprecedented CR-CC(2,3), active-space CCSDt, EOMCCSD, and multi-reference CI computations for the low-lying singlet and triplet states of the challenging organic biradical, 1,2,3,4-cyclobutanetetraone, which present major problems to the existing single- and multi-reference wave function and DFT approaches [J.A. Hansen *et al.*, *Mol. Phys.* **114**, 695 (2016)]. We provided a definitive state ordering and obtained a very good agreement with the negative ion photoelectron spectroscopy measurements of the tiny singlet-triplet gap. Finally, in collaboration with Professor Marcos Dantus, we revisited the classic problem of the femtosecond transition-state spectroscopy of sodium iodide, taking advantage of modern lasers, pulse-shaping, *ab initio* multi-reference CI calculations including spin-orbit coupling, and time-dependent wave packet dynamics simulations to map the low-lying electronic states forming predissociative wells through curve crossings [1].

III. Future Plans

Our future method development will focus on **(i)** extension of the merger of the deterministic CC(*P*;*Q*) methodology with the stochastic CIQMC and CCMC approaches to excited electronic states and exploration of the analogous ideas combining the CC(*P*;*Q*) and adaptive CI algorithms, **(ii)** development of novel classes of nearly exact or exact methods for strongly correlated systems by combining the ideas of approximate coupled-pair theories with the active-space, stochastic CIQMC/CCMC, and adaptive CI methodologies, and **(iii)** continuation of our work on accelerating convergence of the stochastic FCIQMC approach by cluster analysis of the corresponding wave functions, with a focus on strongly correlated systems. We also hope to continue working on our local correlation CC codes, exploiting the cluster-in-molecule framework, and their multi-level extensions in GAMESS and our recently initiated effort toward extending the EA/IP and DEA/DIP EOMCC theories to the triply electron-attached and triply ionized cases, which can be useful in studies of triradicals and inorganic chromophores of interest in solar energy conversion schemes. As in the past, the proposed methodological advances will be shared with the community via open-source mechanisms and accompanied by a wide range of benchmark and realistic molecular computations relevant to energy science, especially strongly correlated systems and photochemistry.

IV. Ten Selected Publications Resulting from DOE Sponsored Research in the Past 3 Years

[1] G. Rasskazov, M. Nairat, I. Magoulas, V.V. Lozovoy, P. Piecuch, and M. Dantus, *Chem. Phys. Lett.* **683**, 121 (2017). DOI: 10.1016/j.cplett.2017.02.019

[2] A.O. Ajala, J. Shen, and P. Piecuch, *J. Phys. Chem. A* **121**, 3469 (2017). DOI: 10.1021/acs.jpca.6b11393

[3] N.P. Bauman, J. Shen, and P. Piecuch, *Mol. Phys.* **115**, 2860 (2017). DOI: 10.1080/00268976.2017.1350291

[4] E. Pastorczak, J. Shen, M. Hapka, P. Piecuch, and K. Pernal, *J. Chem. Theory Comput.* **13**, 5404 (2017). DOI: 10.1021/acs.jctc.7b00797

[5] S.J. Stoneburner, J. Shen, A.O. Ajala, P. Piecuch, D.G. Truhlar, and L. Gagliardi, *J. Chem. Phys.* **147**, 164120 (2017). DOI: 10.1063/1.4998256

[6] J.E. Deustua, J. Shen, and P. Piecuch, *Phys. Rev. Lett.* **119**, 223003 (2017). DOI: 10.1103/PhysRevLett.119.223003

[7] I. Magoulas, N.P. Bauman, J. Shen, and P. Piecuch, *J. Phys. Chem. A* **122**, 1350 (2018). DOI: 10.1021/acs.jpca.7b10892

[8] J.E. Deustua, I. Magoulas, J. Shen, and P. Piecuch, *J. Chem. Phys.* **149**, 151101 (2018). DOI: 10.1063/1.5055769

[9] S.H. Yuwono, I. Magoulas, J. Shen, and P. Piecuch, *Mol. Phys.*, published online: 8 January, 2019. DOI: 10.1080/00268976.2018.1564847

[10] J.E. Deustua, S.H. Yuwono, J. Shen, and P. Piecuch, *J. Chem. Phys.* **150**, 111101 (2019). DOI: 10.1063/1.5090346

Modeling Heterogeneous Electrocatalysis on Realistic Surfaces from First-Principles, Thermodynamics, and Machine Learning

Andrew M. Rappe

Theoretical and computational approaches have made important contributions to heterogeneous electrocatalysis. Such approaches, however, assume that the catalytically-active surface for a particular class of materials is the same. We have discovered that the electrocatalytic activity of nickel phosphides and CaMnO3 toward the H2 and O2 evolution reactions, are governed by aqueous surface equilibria, i.e. the most catalytically-active surfaces are aqueous surface reconstructions. In addition to the determination of realistic surfaces for computational studies of heterogeneous electrocatalysis, we are also developing combined first-principles and machine learning techniques for the automated discovery of catalytic descriptors. Using these techniques, we discovered that the Ni-Ni bond length is an excellent descriptor for the hydrogen evolving activity of Ni2P and that it can be modulated via nonmetal surface doping, which induces a chemical pressure effect.

For decades, ab initio thermodynamics has been the method of choice for computationally determining the surface phase diagram of a material under different conditions. The surfaces considered for these studies, however, are often human-selected and too few in number, leading both to insufficient exploration of all possible surfaces and to biases toward portions of thecomposition-structure phase space that often do not encompass the most stable surfaces. To overcome these limitations and automate the discovery of realistic surfaces, we combine density functional theory and grand canonical Monte Carlo (GCMC) into "ab initioGCMC." We demonstrate ab initio GCMC for the study of oxide overlayers on Ag(111), which, for many years, mystified experts. Ab initio GCMC rediscovers the surface phase diagram of Ag(111) with no preconceived notions about the system. Using nonlinear,random forest regression, we discover that Ag coordination number with O and the surface O-Ag-O bond angles are good descriptors of the surface energy. Additionally, using the composition-structure evolution histories produced by ab initio GCMC, we deduce a mechanism for the formation of oxide overlayers based on the Ag3O4 pyramid motif that is common to many reconstructions of Ag(111). Ab initio GCMC is a promising tool for the discovery of realistic surfaces that can then be used to study phenomena oncomplex surfaces such as heterogeneous catalysis and materials growth, enabling reliable and insightful interpretations ofexperiments.

Henry F. Schaefer

Theoretical and Experimental Studies of Elementary Hydrocarbon Species and their Reactions

Henry F. Schaefer

Center for Computational Quantum Chemistry
University of Georgia
Athens, GA 30602
ccq@uga.edu

Abstract

Multi-Fidelity Gaussian Process Modeling for Chemical Potential Energy Surfaces

Reliable modeling of chemical phenomena often requires the availability of an accurate potential energy surface. Since computing points on a high level quantum mechanical energy surface is expensive, it is often cost-prohibitive to obtain these point values exclusively from *ab initio* data. Instead, some points may be inferred using a surrogate model, *i.e.* a method for predicting the outcome of an expensive process based on a limited set of sample calculations. Historically, surrogate models in quantum chemistry have relied on either interpolation or least-squares fitting techniques. However, in the past decade there has been increasing interest in surrogate models based on modern machine learning. Much of this research has centered around feedforward neural networks, which have proven useful in the technology sector. Neural network methods are best suited to the "big data" regime, as they require a large number of training points to achieve an accurate fit.

Gaussian process (GP) regression is an alternative machine learning technique which is optimal for small- and medium-sized data sets. Having been widely used for decades in statistics and geostatistics applications, GP regression began to receive more widespread attention in the early 2000s for other applications in engineering. In the recent years, GP methods have been increasingly used for quantum chemical applications, including energy surface regression.

Another quickly developing research area in the machine learning community is *transfer learning*, which can also enhance learning efficiency when training data is expensive. Transfer learning uses knowledge gained from a relevant auxiliary task to facilitate the learning of a target task. The most common approach to transfer learning is multi-task learning, which trains multiple related tasks in parallel, using extra tasks as an inductive bias to inform predictions of the target. Multi-fidelity modeling is a subset of multi-task transfer learning that exploits correlations between low- and high-accuracy data to enhance learning efficiency. This concept has also recently received some attention in the physical chemistry community.

In our research, we seek to draw attention to a multi-fidelity GP technique known as autoregressive Gaussian process (ARGP) modeling, which uses transfer learning to achieve further improvements over ordinary GP regression. This method is not original to us, but to our knowledge it has never been applied to the modeling of high-accuracy chemical energy surfaces. We point out that it seems particularly well-suited to electronic structure theory, where energy points are expensive but a large variety of approximations is available. ARGP regression was recently developed in a general, nonlinear form to study mixed convection flows in fluid dynamics. We demonstrate the utility of this method by presenting sample calculations for the N_2 dissociation curve and a near-equilibrium potential energy surface for H_2O. Our preliminary benchmarks suggest that it can yield substantial gains in learning efficiency. The methodological details of our methods may be found in Chem. Phys. Lett. X (doi.org/10.1016/j.cpletx.2019.100022).

Our figure compares three Gaussian process (GP) regression schemes using an MRCISD+Q/aug-cc-pCV5Z potential curve for N_2 as a benchmark. The results are plotted and compared quantitatively via their root-mean-square errors (RMSEs) relative to the test set. RMSEs relative to the training set, introduced by noise in the model, are also reported.

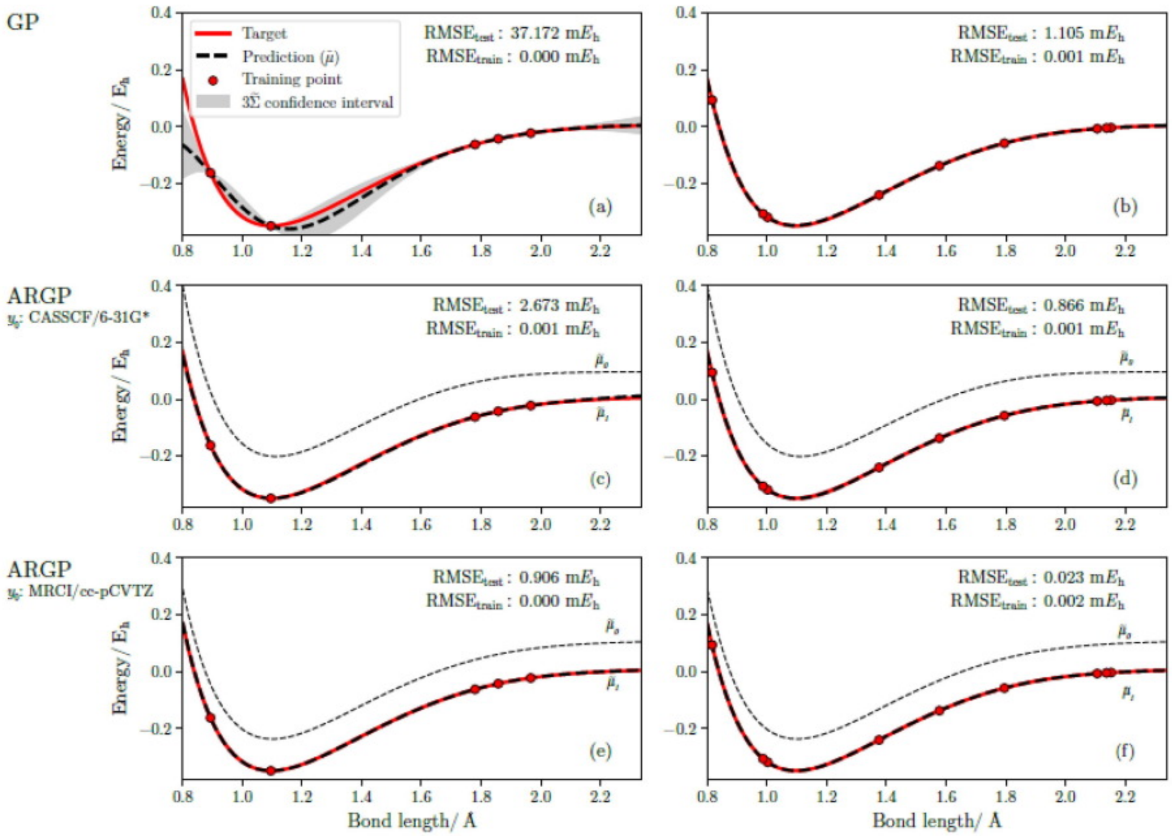
Plots (a) and (b) show ordinary GP regressions with five and ten training points, respectively. With five training points, the usual GP approach fails to capture the correct bonding curve within a 3σ (99.7%) confidence interval. In this case, the training data does not span the range of energy values on the curve. The MLE procedure therefore yields a misinformed prior distribution, resulting in an underestimated confidence interval and a large root-mean-square error of 37.2 mEh from the target surface. With ten training points, ordinary GP regression yields a qualitatively accurate result with an error of 1.1 mEh.

Plots (c) and (d) show the results of ARGP regression predicting the MRCISD+Q/aug-cc-pCV5Z target surface with CASSCF/6-31G* as the base model. With five training points, ARGP regression correctly captures the target potential curve within a 3σ confidence interval and achieves chemical accuracy with a prediction RMSE of 2.7 mEh. It is remarkable that such a cheap and highly approximate level of theory as CASSCF with a small basis set is able to improve the prediction of the target by an order of magnitude relative to ordinary GP, and at almost neglible additional cost. With ten training points, however, the same ARGP method yields an 0.87 mEh prediction error, only a marginal improvement over ordinary GP.

The nonlinear ARGP regression scheme reported here is able to improve the prediction error of the MRCISD+Q/aug-cc-pCV5Z dissociation curve of N_2 by more than a factor of 40 with five randomly selected training points. For the three-dimensional potential energy surface of H_2O, ARGP regression comfortably achieves sub-chemical accuracy with 25 training points on the target *ab initio* surface. These initial benchmarks suggest that using ARGP regression to leverage the relationships between different levels of theory may substantially improve learning efficiency in chemical energy surface regression. Furthermore, this approach is especially well-suited to high-accuracy quantum chemistry, where the cost differential between the desired level of theory and its nearest approximations can be very large. For example, the time it takes to solve the widely-used CCSD(T) approximation scales with the fourth power of basis set size for a given molecular system, which in turn scales quadratically with basis set cardinality.

Additional benchmark studies of polyatomic chemical systems will be necessary to further quantify the improvements in learning efficiency that autoregressive GP regression might yield over ordinary GP regression. Optimal sampling algorithms for this method will also need to be considered. Finally, an effective multi-fidelity model will take advantage of convergent hierarchies in basis set and level of theory to determine the best series of approximations. These are avenues that we hope to explore in future research.

Figure: Comparison of Gaussian Process and nonlinear Autoregressive Gaussian Process (ARGP) models for N_2 dissociation at the Davidson-corrected multireference configuration interaction singles and doubles (MRCISD+Q) level of theory with the aug-cc-pCV5Z basis set. Plots (c) and (d) employed complete active space self-consistent field theory (CASSCF) with the 6-31G*basis set as the base model for ARGP regression. Plots (e) and (f) employed MRCISD+Q/cc-pCVTZ as a base model. The ARGP base models were trained using ordinary GP regression on 30 points from the approximate surface; the energy curves illustrating the base models have been shifted upwards for clarity. Prediction errors for are reported as root-mean-square errors (RMSEs) from the training and test sets, *i.e.* all the points on the curve not used for training.



Grant No.: DE-SC0018412
Theoretical and Experimental Studies of Elementary Hydrocarbon Species and Their Reactions

Students: Marcus Bartlett, Sarah N. Elliott, Marissa L. Estep, Whitney J. Morgan, Jared Weidman

Ten Recent DOE Sponsored Publications, 2018- 2019

1. W. J. Morgan, D. A. Matthews, M. Ringholm, J. Agarwal, J. Z. Gong, K. Ruud, W. D. Allen, J. F. Stanton, and H. F. Schaefer, "Geometric Energy Derivatives at the Complete Basis Set Limit: Application to the Equilibrium Structure and Molecular Force Field of Formaldehyde," *J. Chem. Theory Comput.* **14**, 1333 (2018).

2. M. A. Bartlett, T. Liang, L. Pu, H. F. Schaefer, and W. D. Allen, "The Multichannel n-Propyl + O_2 Reaction Surface: Definitive Theory on a Model Hydrocarbon Oxidation Mechanism," *J. Chem. Phys.* **148**, 094303 (2018).

3. B. Zhang, J. E. Vandezande, R. D. Reynolds, and H. F. Schaefer, "Spin-Orbit Coupling via Four-Component Methods: Benchmarking and Recommendations," *J. Chem. Theory Comput.* **14**, 1235 (2018).

4. J. P. Misiewicz, S. N. Elliott, K. B. Moore, and H. F. Schaefer, "Re-Examining Ammonia Addition to the Criegee Intermediate: Converging to Chemical Accuracy," *Phys. Chem. Chem. Phys.* **20**, 7479 (2018).

5. J. D. Weidman, R. T. Allen, K. B. Moore, and H. F. Schaefer, "High-Level Theoretical Characterization of the Vinoxy Radical ($^{\bullet}CH_2CHO$) + O_2 Reaction," *J. Chem. Phys.* **148**, 184308 (2018).

6. P. R. Hoobler, J. M. Turney, and H. F. Schaefer, "Fundamental Vibrational Analysis of the HCN Monomer, Dimer, and Associated Isotopologues," *ChemPhysChem.* **19**, 3257 (2018).

7. M. C. Bowman, A. D. Burke, J. M. Turney, and H. F. Schaefer, "Mechanisms of the Ethynyl Radical Reaction with Molecular Oxygen," *J. Phys. Chem. A* **122** 9498 (2018).

8. W. J. Morgan, R. C. Fortenberry, H. F. Schaefer, and T. J. Lee, "Vibrational Analysis of the Ubiquitous Interstellar Molecule Cyclopropenylidene (*c*-C_3H_2): The Importance of Numerical Stability," *Molecular Physics* (doi.org/10.1080/00268976.2019.1589007).

9. A. E. Wiens, A. V. Copan, and H. F. Schaefer, "Multi-Fidelity Gaussian Process Modeling for Potential Energy Surfaces," *Chem. Phys. Lett.* (doi.org/10.1016/j.cpletx.2019.100022).

10. P. R. Franke, J. T. Brice, C. P. Moradi, H. F. Schaefer, and G. E. Douberly, "Ethyl + O_2 in Helium Nanodroplets: Infrared Spectroscopy of the Ethylperoxy Radical," *J. Phys. Chem. A* (doi/10.1021/acs.jpca.9b01867).

Surface Plasmon Enhanced Chemistry

George C. Schatz and Mark A. Ratner
Department of Chemistry, Northwestern University Evanston, IL 60208-3113
g-schatz@northwestern.edu, m-ratner@northwestern.edu

Program Scope: This project is concerned with the development of computational methods and new theory that enable the description of 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 are being used to model experiments being done by a number of collaborators.

Recent Progress:

An important result in the period since June, 2018 has been the completion of a project in which we have studied plasmon driven hot electron photodissociation of H_2 on a gold nanoparticle based on real-time TDDFT calculations in combination with nonadiabatic molecular dynamics [1]. In addition, we have developed a new electronic structure approach, denoted locally coupled open subsystems (LCOS) that enables proper dissociation of molecules into either neutral or charged fragments, while allowing for a density functional theory description.[2,3] Other projects include: (1) a determination of the importance of triplet states in electron transport for an irradiated molecular transistor[4]; (2) The successful testing of our INDO-based methods for calculating electrochemical formal potentials while at the same time determining plasmonic properties [5]; (3) collaboration with Mirkin group concerned the coupling of plasmon excitation in layered materials, where we discovered a new approach to the development of plasmonic/photonic crystals with high reflectivity[6]; (4) Study of plasmonic array properties (with Teri Odom) leading to the development of an aluminum-based plasmonic laser[7]; (5) collaboration with Christy Haynes concerning the Raman spectra of analytes.[8]

Real-time TDDFT study of plasmon driven H_2 photodissociation

Recent experiments in the Halas group at Rice have suggested that hot carriers produced in the photolysis of gold nanoparticles at visible wavelengths can cause the photodissociation of adsorbed H_2 that leads to isotope exchange in the presence of D_2. Carter and coworkers have studied this experiment using an embedded wavefunction approach, and were able to provide qualitative insight into the mechanism of this process, but there have not been dynamics studies that have coupled plasmon excitation to dissociation. However we have recently used real-time TDDFT combined with Ehrenfest nonadiabatic molecular dynamics to model this process[1] based a jellium description of a 2 nm gold nanoparticle that shows plasmonic excited states and a local density (LDA) approximation of the H_2. Using the OCTOPUS code, we demonstrated how the excitation of plasmon modes of the cluster leads to electron transfer to an antibonding state of H_2 resulting in dissociation of the molecule. Dissociation was found to be of high probability as long as the frequency of light was in the range 2-3 eV where plasmonic states can be excited. An analysis of orbital populations indicated that the antibonding state of H_2 transiently receives substantial occupation after photoexcitation. We also found that when H_2 is located at the hot-spot of a dimer of gold particles, electron transfer from one particle to H_2 is immediately followed by a second electron transfer to the other particle, and dissociation is suppressed.

Locally coupled open subsystem method for electronic structure calculations

Our first papers on this topic were recently published.[2,3] These develop the LCOS theory for systems that can be decomposed into two fragments A + B, where A could be a metal cluster and B a molecule, and where we want to describe both the neutral (A + B) and charge transfer states (let's say $A^+ + B^-$) of the system going all the way from separated fragments to the combined adduct. We start by writing down a trial wavefunction:

$$|\bar{\Psi}\rangle = C_N |A\rangle |B\rangle + C_{CT} |A^+\rangle |B^-\rangle \qquad (1)$$

where we assume that only the ground state neutral and one choice of the charge transfer states of the relevant species are of interest. More generally we can write the wavefunction in terms of a sum of many terms (but not too many), and each term is taken to involve an antisymmetrized tensor product of spin-orbitals. The theory has been developed both for the case where the orbitals are Kohn-Sham orbitals, or are based on a wavefunction method. Note that the A and B subspaces are taken to be separable. Also, $\bar{\Psi}$ is an auxiliary wavefunction that will eventually be used to define a density as part of a density functional-based formalism that will be used to determine the overall energy E. $\bar{\Psi}$ is determined based on a model Hamiltonian that we choose to be:

$$\hat{\mathcal{H}} = \hat{H}_A + \hat{H}_B + \int d^3r\ \theta(r)[\hat{\rho}(r) + \hat{\zeta}(r)] \qquad (2)$$

where $\hat{H}_Y$ is the Hamiltonian of subsystem Y (Y=A or B), so that Eq. (2) involves the sum of subsystems plus a coupling. In the latter, $\hat{\rho}(r)$ is the additive density operator of the system ($\hat{\rho}(r) = \hat{\rho}_A(r) + \hat{\rho}_B(r)$) and $\hat{\rho}_Y(r) = \hat{\psi}_Y^\dagger(r)\hat{\psi}_Y(r)$ where $\hat{\psi}_Y^\dagger(r)$ and $\hat{\psi}_Y(r)$ are the appropriate field creation and destruction operators). $\hat{\zeta}(r)$ is a Hermitian operator that allows electrons to be transferred between the A + B and $A^+ + B^-$ systems. Further details of the theory as well as applications to simple diatomic molecules are provided in the cited papers.

Importance of triplet states in electron transport of irradiated molecular junction

An important issue in single-molecule molecular electronics concerns the role of triplet states of the molecule in photoinduced electron transport. Fig. 1 (top) shows a schematic of the transistor structure we have studied[4], where there is a phthalocyanine at the junction that can be photoexcited (perhaps plasmon enhanced) and also serves as the active medium for electron transport. Fig. 1 (bottom) shows the energy levels we considered, including a singlet excited state S_1 and triplets T_1. In addition, there are states $\pm 1, D_o^\sigma$ associated with transfer of an electron to or from the molecule. The current is described using a master-equation formalism, and from this the steady-state current/voltage behavior is determined. The results show that the triplet state plays a significant role in the current/voltage results, independent of whether spin-orbit coupling is included in defining the states, due to direct coupling between the triplet and cation/anion states as mediated by electron transfer to/from the source/drain. The singlet state is similarly coupled to $\pm1,D_o^\sigma$ (Fig. 1), leading to singlet and triplet states whose populations are comparable. This treatment is based on an incoherent master equation approach, so an important step beyond what we have done involves including for quantum coherences in the interacting quantum states.

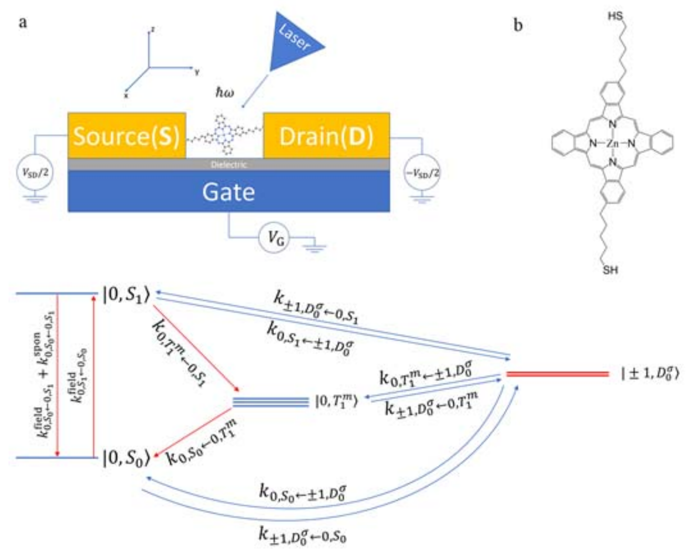


Fig. 1. (top) Schematic of the three terminal molecular transistor with zinc phthalocyanine (pictured right) as the active molecule. (bottom) Energy level scheme and transition rates assumed in the molecule.

INDO-based methods for plasmonics

In earlier work for this grant, we revised the INDO/S semiempirical method so that it could describe plasmonic clusters consisting of up to about 100 silver atoms. This approach has the advantage over TDDFT in that it can describe charge-transfer states accurately, so with this capability we have provided the first accurate determination of the charge-transfer contribution to SERS enhancement factors. A further development of this approach has been the ability to describe electrochemistry, which is an important capability for combining SERS measurements with electrochemistry, as this enables the study of single molecule electrochemistry, which is a big objective of that fields. In work completed this year we have provided a detailed calibration of the INDO method for determining electrochemical formal potentials[5], showing that our method gives results comparable to density functional theory, but with the added advantages of INDO concerning the description of plasmonic properties.

Collaborations with experimental groups:

We continue to collaborate with experimentalists on plasmonics problems as this provides an opportunity to test our understanding and identify new challenges. Some of these collaborations refer to SERS studies, where local fields and/or Raman spectra are calculated,[8] Another collaboration concerned the coupling of plasmon excitation with interference in layered materials, where we discovered a new approach to the development of plasmonic/photonic crystals with high reflectivity.[6] Finally, we have expanded our interest in studying lattice plasmon effects that are associated with arrays of Ag, Au and Al particles.[7] The most recent work has led to development of new classes of lasers that use Al nanoparticles on polymer substrates, with the ability to dynamically switch laser frequencies by stretching the polymer.

Future Plans: Our renewal proposal has described additional work with modeling hot-electron chemistry using nonadiabatic molecular dynamics. In addition, we will further develop the LCOS method, with our goal being to apply it to problems where molecules interact with plasmonic nanoparticles, as this will enable a more realistic description of the coupling between plasmons and charge-transfer states, which is an important issue both to the description of SERS and to plasmon chemistry. Another important direction concerns studies of plasmonic arrays, where we have discovered that by varying array topology, we can access lattice plasmon states with unusual optical properties (such as having forbidden transitions for plane wave excitation, but which can emit light with great efficiency).

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: Charles Cherqui (12), Rebecca L. M. Gieseking (1p), Martin Mosquera (1p), Dhara Trivedi (4p)
2. Students: Marc Bourgeois (12)

Up to Ten Publications Acknowledging the Grant

[1]Zhang, Y.; Nelson, T.; Tretiak, S.; Guo, H.; Schatz, G. C., Plasmonic Hot-Carrier-Mediated Tunable Photochemical Reactions. ACS Nano 12, 8415-22 (2018). DOI: 10.1021/acsnano.8b03830

[2]Mosquera, M. A.; Ratner, M. A.; Schatz, G. C., Locally coupled open subsystems: A formalism for affordable electronic structure calculations featuring fractional charges and size consistency. J. Chem. Phys. 149, 034105 (2018) DOI: 10.1063/1.5038557

[3]Mosquera, M. A.; Jones, L.; Ratner, M. A.; Schatz, G. C., Formalism based on locally coupled open subsystems for calculations in molecular electronic structure and dynamics. Phys. Rev. A 98, 062505 /1-20 (2018) DOI: 10.1103/PhysRevA.98.062505

[4]Fu, B.; Mosquera, M. A.; Schatz, G. C.; Ratner, M. A.; Hsu, L.-Y., Photoinduced Anomalous Coulomb Blockade and the Role of Triplet States in Electron Transport through an Irradiated Molecular Transistor. Nano Lett, 18, 5015-23 (2018). DOI: 10.1021/acs.nanolett.8b01838

[5]Gieseking, R. L. M.; Ratner, M. A.; Schatz, G. C., Benchmarking Semiempirical Methods to Compute Electrochemical Formal Potentials. J. Phys. Chem. A, 122, 6809-18 (2018). DOI: 10.1021/acs.jpca.8b05143

[6]Sun, L.; Lin, H.; Kohlstedt, K. L.; Schatz, G. C.; Mirkin, C. A., Design principles for photonic crystals based on plasmonic nanoparticle superlattices. PNAS 115 (28) 7242-7247 (2018). DOI: 10.1073/pnas.1800106115

[7]Wang, D.; Bourgeois, M. R.; Lee, W.-K.; Li, R.; Trivedi, D.; Knudson, M. P.; Wang, W.; Schatz, G. C.; Odom, T. W., Stretchable Nanolasing from Hybrid Quadrupole Plasmons. Nano Lett. 18, 4549-4555 (2018) DOI:10.1021/acs.nanolett.8b01774

[8]Szlag, V. M.; Jung, S.; Rodriguez, R. S.; Bourgeois, M. R.; Bryson, S.; Schatz, G. C.; Reineke, T. M.; Haynes, C. L., Isothermal Titration Calorimetry for the Screening of Aflatoxin B1 Surface-Enhanced Raman Scattering Sensor Affinity Agents. Anal. Chem. 90, 13409-18 (2018). DOI:10.1021/acs.analchem.8b03221

Gregory K. Schenter

Molecular Theory and Modeling

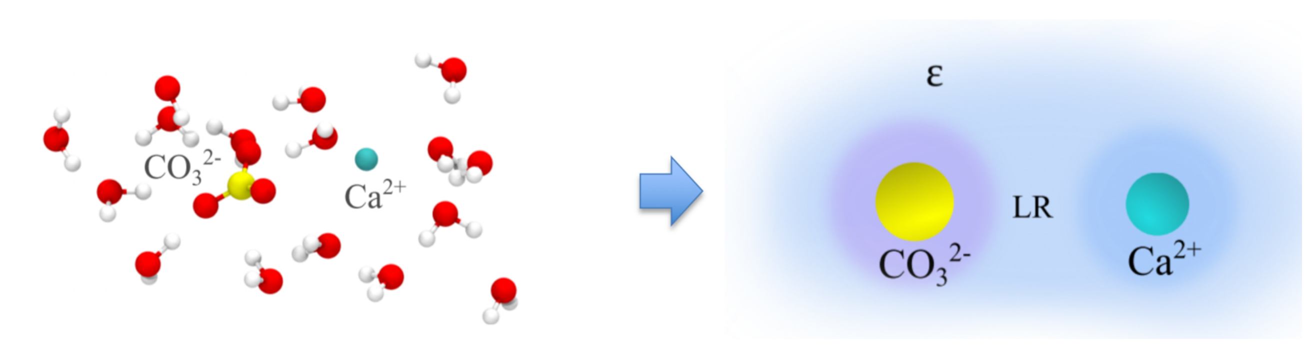
Gregory K. Schenter, Liem X. Dang, Shawn M. Kathmann, Chris J. Mundy, Sotiris S. Xantheas, and Marat Valiev

Pacific Northwest National Laboratory
PO Box 999

Richland WA 99352

Abstract

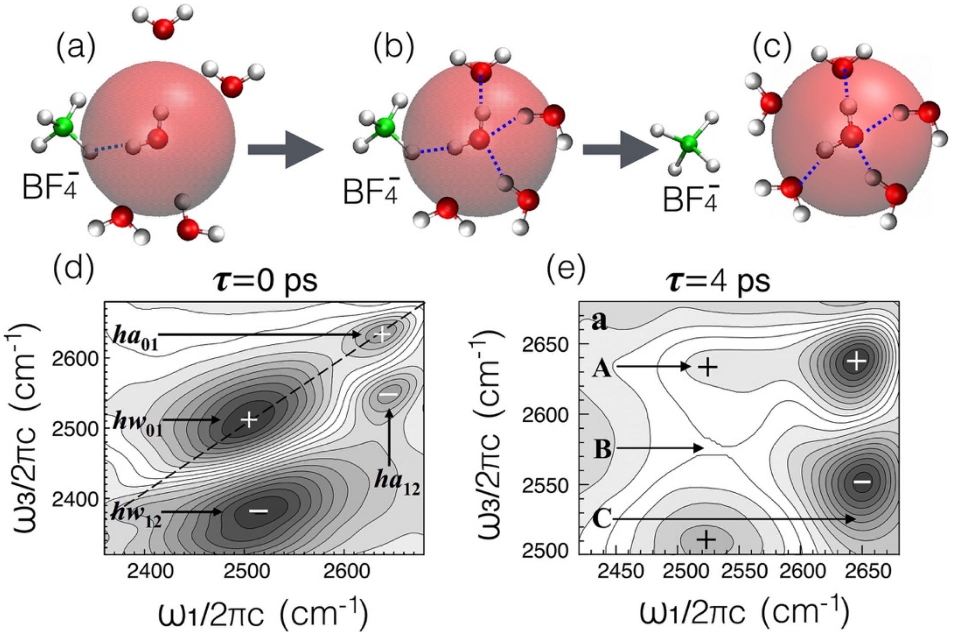
The overarching goals of the Molecular Theory & Modeling Program are: 1) development of a fundamental comprehension of the driving forces, processes and phenomena, such as solvation, nucleation, assembly, transport, and reaction, in complex condensed-phase, heterogeneous and interfacial molecular environments, and 2) development of theoretical and computational methods required to accelerate scientific advances in condensed-phase and interfacial molecular science.



We are examining the relation between continuum and molecular descriptions of electrolytes, extending what we have learned to concentrated electrolytes and solid/electrolyte interfaces.

In current efforts, we focus on the balance between descriptions of molecular interaction and statistical mechanical sampling. We find that the water exchange process can control chemical reaction and transport phenomena. It is necessary to find the proper balance between the ion-water and water-water interaction. 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 are still assessing the most effective representation of molecular interaction. In our studies we consider both descriptions that rely on a systematic many-body expansion [1] as well as direct Density Functional Theory simulations using the recent meta-GGA SCAN functional of Perdew. ("Hydration Structure of Sodium and Potassium Ions with DFT-MD," Timothy Duignan, Gregory K. Schenter, Mirza Galib, Marcel D. Baer, Jan Wilhelm, Jürg Hutter, Mauro Del Ben, Xiu Song Zhao, and Christopher J. Mundy, doi.org/10.26434/chemrxiv.7466426.v1) In both studies, we take ensembles generated by models of molecular interaction, predict an EXAFS spectrum and compare to measured signals. We are learning that simpler models are not robust enough to recover the balance between ion-water distances and the stiffness of the interaction in the condensed phase. (Debye-Waller factor or effective vibrational frequency) We continue to identify the distinguishing features of the disruption of the water network in response to the presence of ions, exploring the robustness of some empirical potentials and density functional theory for describing this interaction. [4][8][9][10]

We are also interested in characterizing the driving forces of collective phenomena. A critical task is to identify and characterize collective coordinates and effective reaction coordinates. We characterize the mean field thermodynamic landscape, the potential of mean force, as well as dynamical corrections to motion, the effective friction. In doing so, we are moving beyond geometrical order parameters, such as interatomic distance, and are exploring such collective descriptions such as coordination, electric fields, and local vibrational frequencies. Throughout, we construct effective Hamiltonian and General Langevin Equation descriptions of motion and find consistency with Transition State Theory characterization of rare event processes. This approach has been applied to ion-pairing at interfaces [2], solvent exchange and the associated spectroscopic signatures [3], as well as a Marcus-like description of ion-pairing.[6]



Proposed mechanism for ultrafast water exchange around BF_4^- ion [3]: Coordination number of an ion-bound water (a) has to increase to form an activated complex (b) that leads to the solvent-bound state (c). In the ion-bound state weak hydrogen bonds between the ion and water hydrogens result in a high frequency peak (ha_{01}), whereas in the water-bound state strong hydrogen bonds among water molecules result in a low frequency peak (hw_{01}) in the OD stretch 2DIR spectrum of isotope-diluted water (HOD in H_2O) at zero waiting time; ha_{01} and hw_{01} indicate the transitions between the vibrational ground (0) and singly excited states (1), while the transitions between the singly (1) and doubly (2) excited states are represented by ha_{12} and hw_{12} (d). At an increased waiting time, the cross peak A arises due to the transitions between the water-bound and ion-bound states of water hydrogens, describing the water exchange phenomenon around the ion (e). 2DIR spectra from PNAS January 13, 2009 106 (2) 375-380.

Molecular Theory and Modeling FWP 16249

Postdoc(s): Tim Duignan, Mirza Galib, and Santanu Roy

The Molecular Theory and Modeling FWP 16249 is co-managed by CTC and CPIMS programs of the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

.

Publications Acknowledging this Grant

1 Debbie Zhuang, Marc Riera, Gregory K. Schenter, John L. Fulton and Francesco Paesani, "Many-Body Effects Determine the Local Hydration Structure of Cs+ in Solution," Journal of Physical Chemistry Letters 10(3): 406-412 (2019).

2 Liem Dang and Gregory K. Schenter, "Rate theory of ion pairing at the water liquid-vapor interface: A case of sodium iodide," Journal of Chemical Physics 148(22): 7, (2018).

3 Santanu Roy, Mirza Galib, Gregory K. Schenter, and Christopher J. Mundy, "On the relation between Marcus theory and ultrafast spectroscopy of solvation kinetics," Chemical Physics Letters 692, 407-415 (2018).

4 Richard C. Remsing, Timothy T. Duignan, Marcel D. Baer, Gregory K. Schenter, Christopher J. Mundy, and John D. Weeks, "Water Lone Pair Delocalization in Classical and Quantum Descriptions of the Hydration of Model Ions," The journal of physical chemistry. B 122 (13), 3519-3527 (2018).

5 Katja Henzler, Evgenii O. Fetisov, Mirza Galib, Marcel D. Baer, Benjamin A. Legg, Camelia Borca, Jacinta M. Xto, Sonia Pin, John L. Fulton, Gregory K. Schenter, Niranjan Govind, J. Ilja Siepmann, Christopher J. Mundy, Thomas Huthwelker, and James J. De Yoreo, "Supersaturated calcium carbonate solutions are classical," Science Advances 4 (1) (2018).

6 Santanu Roy, Marcel D. Baer, Christopher J. Mundy, and Gregory K. Schenter, "Marcus Theory of Ion-Pairing," Journal of Chemical Theory and Computation 13 (8), 3470-3477 (2017).

7 Mirza Galib, Timothy T. Duignan, Yannick Misteli, Marcel D. Baer, Gregory K. Schenter, Jurg Hutter, and Christopher J. Mundy, "Mass density fluctuations in quantum and classical descriptions of liquid water," Journal of Chemical Physics 146 (24) (2017).

8 Mirza Galib, Marcel D. Baer, Lawrie B. Skinner, Chris J. Mundy, Thomas Huthwelker, Gregory K. Schenter, Chris J. Benmore, Niri Govind, and John L. Fulton, "Revisiting the hydration structure of aqueous Na+," Journal of Chemical Physics 146 (8) (2017).

9 Timothy T. Duignan, Marcel D. Baer, Gregory K. Schenter, and Christopher J. Mundy, "Real single ion solvation free energies with quantum mechanical simulation," Chemical Science 8 (9), 6131-6140 (2017).

10 Timothy T. Duignan, Marcel D. Baer, Gregory K. Schenter, and Christopher J. Mundy, "Electrostatic solvation free energies of charged hard spheres using molecular dynamics with density functional theory interactions," Journal of Chemical Physics 147 (16) (2017).

Crystal growth and nucleation at metal-organic framework / solution interfaces

Mary Van Vleet, Tingting Weng, Xinyi Li, Kai Cui, J.R. Schmidt

Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison,
1101 University Ave, Madison, WI 53706

Abstract

Metal-organic frameworks (MOFs) represent an incredibly diverse class of materials with equally diverse applications in catalysis, separations, and gas storage. Despite the prevalence of MOF structures in the literature, in many cases the synthesis of pure, crystalline MOF materials remains a significant challenge, with failed syntheses often yielding mixed crystalline or non-porous amorphous products. Our recent work aims to enable targeted MOF synthesis by developing a comprehensive and predictive model of the fundamental processes occurring at the MOF-solution interface under synthetically-relevant conditions. Our recent accomplishments include: (i) development and implementation of a GPU-accelerated approach to simulation the nucleation of weak electrolytes; and (ii) development of highly transferable zeolitic imidazolate framework (ZIF) force fields for various crystalline phases, and application to ZIF amorphization; and (iii) studies of the structure of ZIF interfaces under conditions relevant to crystal growth.

Nucleation of weak electrolytes. Predictive modeling of the nucleation of weak electrolytes presents fundamental challenges of widespread relevance in many domains (e.g. CaCO$_3$/biomineralization, oxalates/kidney stones, MOF growth). We recently developed a rigorous GPU-accelerated Grand Canonical Monte Carlo (GCMC)-based methodology that allows us to model the nucleation of low-solubility crystals in explicit solvent that are otherwise completely inaccessible to traditional molecular dynamics simulation. Our approach allows us to calculate the thermodynamic barriers governing the growth of small nucleates in solution, without relying on ad hoc "grafting" methods.

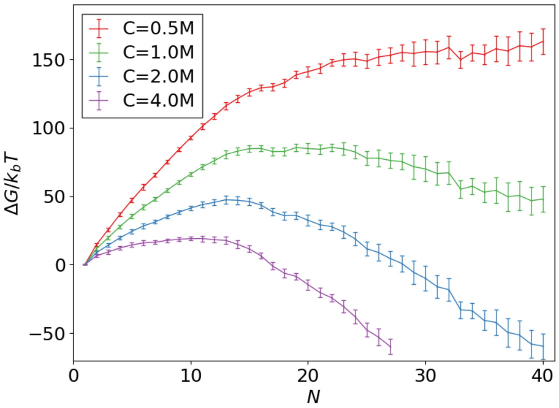


Figure 1. Free energy of salt cluster vs. size for various concentrations.

We have completed a draft manuscript that documents this new approach and demonstrates an application to the nucleation and growth of model (sparingly soluble) salt structure. This example was chosen because the solubility of this salt makes it amenable to both our GCMC method as well as brute-force molecular dynamics nucleation studies, providing elegant validation. The free energy of the growing salt cluster vs. # of ion pairs is shown for a variety of concentrations in Figure 1. Impressively, we can combine these results for the nucleation free energy barrier with an analytic Zeldovich pre-factor to predict an absolute nucleation rate of about $7\text{x}10^{-4}$ / ns (for a box of our simulation size). This result agrees to within a factor of two (!) with complementary rate calculations via extensive brute force molecular dynamics simulations; in contrast, it is not uncommon for conventional absolute nucleation rate predictions to be in error by *many* orders of magnitude! We are also able to extrapolate our results to dramatically lower supersaturations, where we find that our predicted nucleation rates are also in reasonable accord with the experimentally-observed "maximum" supersaturations that can be achieved for NaCl (where careful experimental have been done).

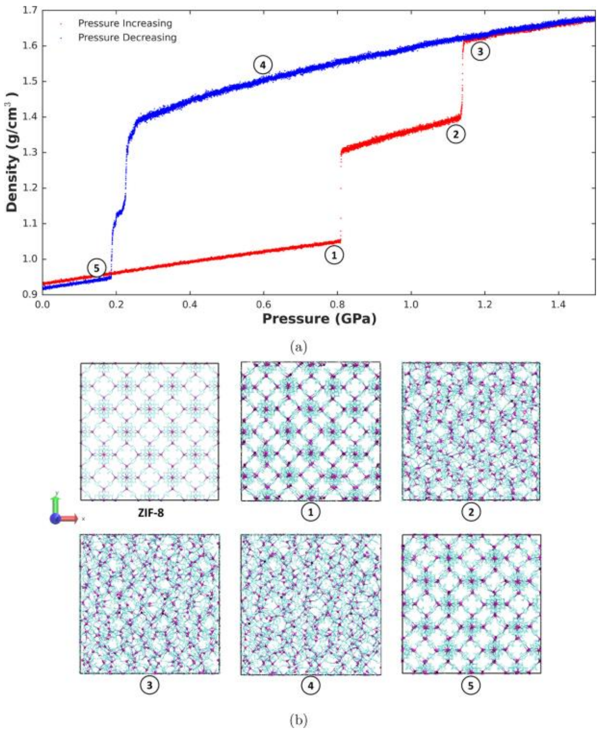


Figure 2. Density of ZIF-8 as a function of pressure during pressure-induced amorphization, modeled using ZIF-FF. The top panel shows density change with pressure, while the bottom panel shows representative structures at the marked time points.

Structure of ZIF-solution interfaces and ZIF growth. We recently published a manuscript documenting a highly transferable set of intra-molecular force fields for ZIFs. The resulting force fields can describe a huge number of different ZIF topologies using a single set of parameters. Crucially, the force fields reproduce the relative stability of these ZIF phases (as calculated form DFT) and thus are amenable for use in simulations of ZIF nucleation and growth. A fascinating application of these force fields to the pressure-induced amorphization of ZIF-8 is shown in Figure 2. Within the simulation, we observe a pressure-induced amorphization that exhibits hysteresis (due to a pressure ramp that is rapid on the experimental time scale), with the experimental amorphization pressure (~0.3 GPa) lying within the hysteresis "loop". The predicted amorphous structure is also in excellent agreement with the experimentally observed structure factor (not shown). This result is particularly impressive in that the force fields were not parameterized for the amorphous.

More recently, we utilized these force fields, in conjunction with plane-wave DFT calculations, to predict the structure and surface termination of ZIF interfaces under both gas-phase and solution-phase conditions. In contrast to nearly all prior work, our calculations properly account for the thermodynamic conditions (imidazole concentrations, solvent partial pressures…) and solvation effects that ultimately control the structure of a ZIF surface. We have constructed a ZIF "surface phase diagram" under conditions relevant to ZIF crystal growth (or, alternatively, ZIFs in the gas-phase subsequent to crystallization). Figure 3 shows predictions for the surface termination of a ZIF [110] interface in an aqueous imidazole solution of varying concentration. These results indicate that a fully imidazole terminated surface is favored at high imidazole concentrations, but also show a transition to a partially water-terminated surface at more modest (~mM) concentrations. Currently we are generalizing these results to other common ZIF synthetic conditions / solvents (MeOH, DMF).

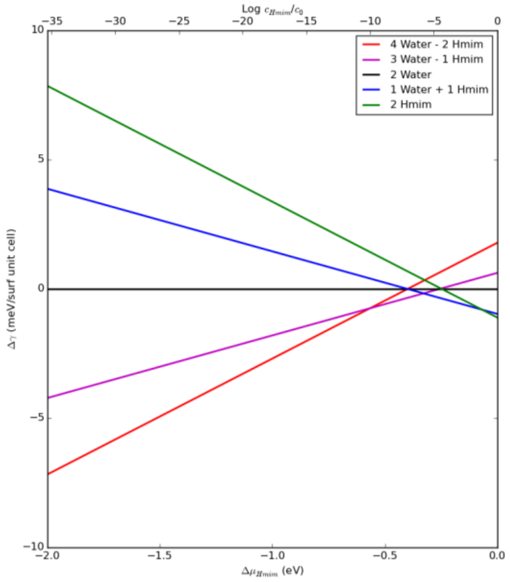


Figure 3. ZIF-8 surface phase diagram at 298K in aqueous solution. Relative surface energy vs. imidazolate concentration.

Grant Numbers and Grant Titles

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

Student(s): Tingting Weng; Kai Cui

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

1. Weng, T.; Schmidt, J. R., A Flexible and Transferable Ab-initio Force Field for Zeolitic Imidazolate Frameworks: ZIF-FF. *J. Phys. Chem. A* **2019,** 13,3000-3012 (invited manuscript) .
2. Vleet, M. J. V.; Misquitta, A. J.; Schmidt, J. R., New angles on standard force fields: towards a general approach for incorporating atomic-level anisotropy. *J. Chem. Theory Comput.* **2018,** 14, 739–758.
3. Van Vleet, M. J.; Weng, T.; Li, X.; Schmidt, J. R., In Situ, Time-Resolved, and Mechanistic Studies of Metal–Organic Framework Nucleation and Growth. *Chemical Reviews* **2018,** 2018, 3681–3721.
4. Van Vleet, M. J.; Misquitta, A. J.; Stone, A. J.; Schmidt, J. R., Beyond Born–Mayer: Improved Models for Short-Range Repulsion in ab Initio Force Fields. *J. Chem. Theory Comput.* **2016,** 12, 3851-3870.
5. McDaniel, J. G.; Schmidt, J. R., Next-Generation Force Fields from Symmetry-Adapted Perturbation Theory. *Annu. Rev. Phys. Chem.* **2016,** 67, 467-88.
6. McDaniel, J. G.; Choi, E.; Son, C.-Y.; Schmidt, J. R.; Yethiraj, A., Conformational and Dynamic Properties of Poly(ethylene oxide) in an Ionic Liquid: Development and Implementation of a First-Principles Force Field. *J. Phys. Chem. B* **2016,** 120, 231-243.
7. McDaniel, J. G.; Choi, E.; Son, C. Y.; Schmidt, J. R.; Yethiraj, A., Ab Initio Force Fields for Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2016,** 120, 7024-7036.

Aromaticity of Unsaturated BEC_4 Heterocycles (E = N, P, As, Sb, O, S, Se, Te)

Paul A. Brown, Caleb D. Martin, Kevin L. Shuford

Department of Chemistry, Baylor University, One Bear Place #97348, Waco, TX 76798

Abstract

A compendium of pnictogen and chalcogen substituted boron heterocycles were assessed for their aromatic character by first principles density functional theory. Group-15 and Group-16 elements were placed at the ortho-, meta-, and para-positions of six-membered rings relative to boron to assess their impact on the aromaticity of the unsaturated heterocycles. Aromaticity was analyzed by a multidimensional approach using nuclear independent chemical shifts, gauge-including magnetically induced current, as well as natural bond orbital and natural resonance theory analyses. Based on these methods, we observe a general decline of aromaticity in heavier pnictaborines while the chalcogen analogues maintain relatively strong aromatic character. These general trends result from complementary π-π* natural bond order interactions that sustain resonance within the ring of each heterocycle establishing a pattern of cyclic delocalization. Consequently, natural resonance theory displays strong resonance, which is corroborated with the signed modulus of ring current, toroidal vortices of current maps, and elevated average induced current throughout the ring. The 1,3-configurations for pnictaborines and chalcogenaborines are generally more aromatic compared to the 1,2- and 1,4-isomers, which contain π-holes that limit diatropism within the heterocycles. However, an

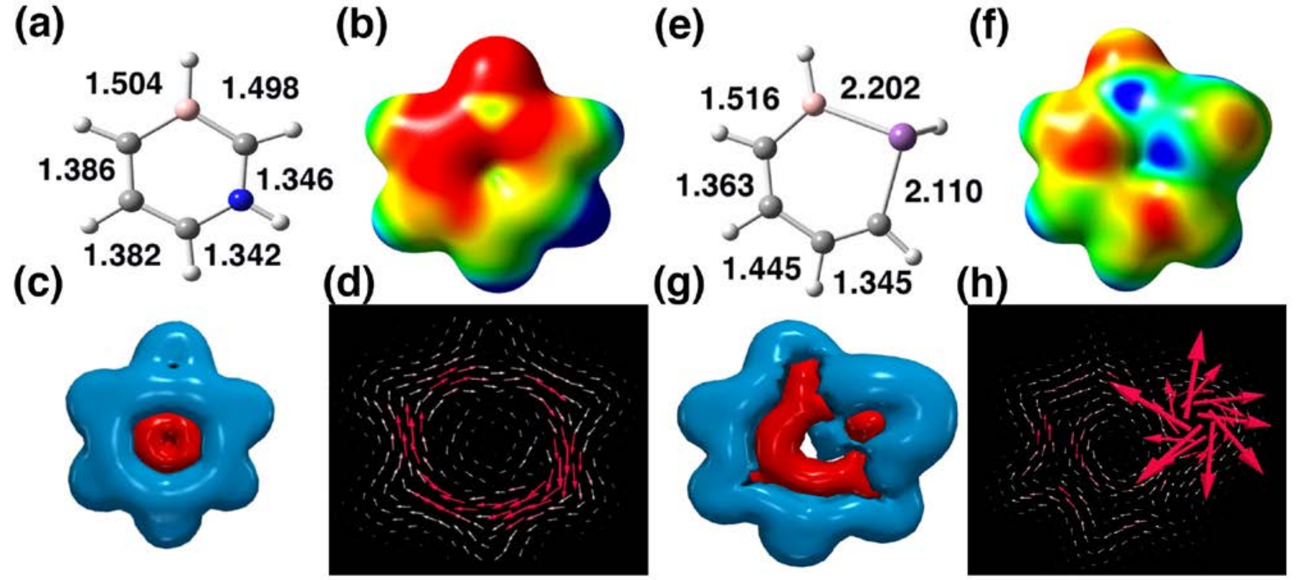


Figure 1: Optimized pnictaborines and aromaticity metrics for (a)-(d) 1,3-azaborine (most aromatic) and (e)-(h) 1,2-stibaborine (least aromatic). (a)/(e) optimized ground state geometry and equilibrium bond lengths (Ang.), (b)/(f) electrostatic potential maps, (c)/(g) signed modulus of the current density displaying the location of diatropic (blue) and paratropic (red) current, and (d)/(h) current maps 1 Angstrom above the molecular plane. The electrostatic potentials are projected onto the ground state electron density to identify regions of charge inhomogeneity. Isosurface values range from $-1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ a.u. (blue to red). The signed modulus of the current is given in ±0.01 nAT^{-1}.

energetic trend favors the 1,2-heterocycles in both groups, with a few exceptions driven in large-part by π-donation of the lone pair on the heteroatom to the p_z orbital on the adjacent boron resulting in stabilization. The importance of planarity for high aromaticity is demonstrated, especially in the pnictaborine isomers where pyramidalization at the pnictogen is favored, while bond regularity seems a less important criterion.

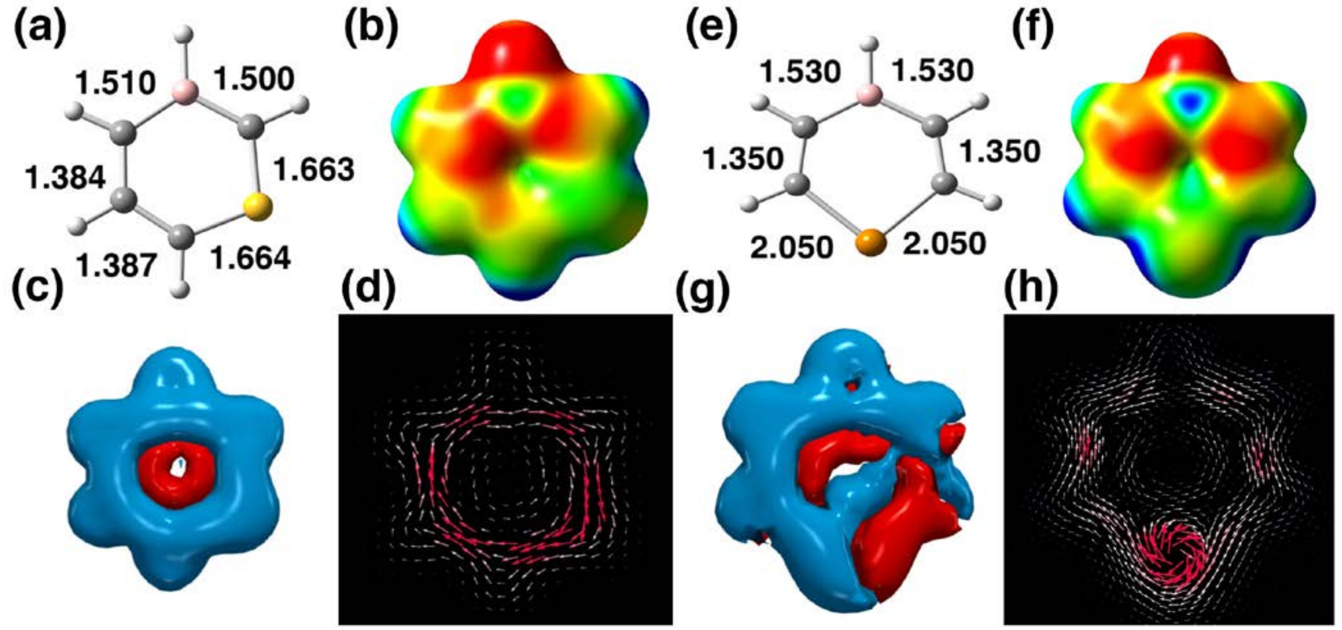


Figure 2: Optimized chalcogenaborines and aromaticity metrics for (a)-(d) 1,3-thiaborine (most aromatic) and (e)-(h) 1,4-telluraborine (least aromatic). (a)/(e) optimized ground state geometry and equilibrium bond lengths (Ang.), (b)/(f) electrostatic potential maps, (c)/(g) signed modulus of the current density displaying the location of diatropic (blue) and paratropic (red) current, and (d)/(h) current maps 1 Angstrom above the molecular plane. The electrostatic potentials are projected onto the ground state electron density to identify regions of charge inhomogeneity. Isosurface values range from $-1.0 \times 10^{-4} - 1.0 \times 10^{-1}$ a.u. (blue to red). The signed modulus of the current is given in ±0.01 nAT^{-1}.

Development of Metal-Free Photocatalysts (Grant Number DE-SC0019327)

Kevin L. Shuford
Department of Chemistry, Baylor University, One Bear Place #97348, Waco, TX 76798
(254) 710-2576, kevin_shuford@baylor.edu

Postdoc(s): Thomas Ellington

Student(s): Olatunde Olademehin, Emvia Calixte, Paul Brown

Program Scope

Solar fuels show great promise as clean, sustainable energy sources; however, established technologies are still plagued by high price, toxicity concerns, or low efficiencies. There is a critical need for inexpensive, benign materials that can effectively harness the sun’s energy. The overarching objective of this project is to evaluate the compatibility of novel material combinations for use as metal-free, heterojunction photocatalysts. Our central hypothesis is that by tuning the electronic structure of individual components in hybrid composites, via selective chemical modifications and physical stimuli to the interface, we can improve the photocatalytic properties of the overall assembly. We will determine factors that affect energy band gaps and band edge positions in isolated photocatalyst systems as well as explore routes to modulate heterojunction band alignments in composite assemblies. Our results will predict accessible pathways for charge carriers in new composite photocatalysts, facilitating access to more of the solar spectrum via inexpensive, environmentally-friendly material combinations.

Future Plans

Our recent work demonstrates how chemical dopants, surface adsorbates, and mechanical strain can create and modulate band gaps. By controlling these surface perturbations, the electronic properties of the material can be tuned with selectivity. One can imagine extrapolating these concepts to controlling both energetics in individual materials and band alignments in assemblies to enhance relevant photocatalytic processes that occur at material interfaces. We will use a combination of molecular quantum chemistry and periodic system approaches to determine the fundamental chemical and photophysical properties of emerging photocatalytic materials. Our near-term plans are to focus on the 2D material graphitic carbon nitride. Specifically, we will determine the effects of chemical doping and size-dependent quantum confinement on the electronic structure and optical properties of graphitic carbon nitride. Elemental dopants will be added to graphitic carbon nitride via lattice substitutions and interstitial sites to ascertain changes to electronic structure. Quantum confinement effects in these systems will be gauged by examining absorption properties of zero-dimensional quantum dots up to the bulk material. Later studies will combine graphitic carbon nitride with other materials to form metal-free composites for photocatalysis.

Publications Acknowledging this Grant (start date September 2018)

1. Paul A. Brown, Caleb D. Martin, and Kevin L. Shuford, "Aromaticity of Unsaturated BEC_4 Heterocycles (E = N, P, As, Sb, O, S, Se, Te)," Submitted.
2. O. Tara Liyanage, Matthew R. Brantley, Emvia I. Calixte, Touradj Solouki, Kevin L. Shuford, and Elyssia Gallagher, "Characterization of Electrospray Ionization (ESI) Parameters for In-ESI Hydrogen/Deuterium Exchange of Carbohydrate-Metal Ion Adducts," J. Amer. Soc. Mass Spectrom. **30**, 235-247 (2019).

Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

J. Ilja Siepmann, Nandini Ananth,[2] Alan Aspuru-Guzik,[3] Coray M. Colina,[4] Christopher J. Cramer,[1] Omar K. Farha,[5] Laura Gagliardi,[1] Jason D. Goodpaster,[1] Maciej Haranczyk,[6] Joseph T. Hupp,[5] Jeffrey R. Long,[7] Smaranda Marinescu,[8] David S. Sholl,[9] Randall Q. Snurr,[5] Donald G. Truhlar,[1] and Michael Tsapatsis[1]

[1]U Minnesota, [2]Cornell U, [3]U Toronto, [4]U Florida, [5]Northwestern U, [6]Lawrence Berkeley National Laboratory, [7]U California–Berkeley, [8]U Southern California, [9]Georgia Institute of Technology

Lead institution address: Chemistry, Univ. of Minnesota, Minneapolis, MN 55455-0431
Director e-mail address: siepmann@umn.edu

Abstract

The Nanoporous Materials Genome Center (NMGC) will develop computational/theoretical chemistry methods and data-driven science approaches with the aims of (i) de-novo design of novel functional nanoporous materials, (ii) discovery and selection of the most promising functional nanoporous materials from databases of synthesized and hypothetical framework structures, and (iii) microscopic-level understanding of the fundamental interactions underlying the function of nanoporous materials. A pivotal part of NMGC's success is a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups that allows for iterative feedback.

Building upon prior NMGC research focused mostly on gas capture, separation and catalysis in crystalline nanoporous materials, the team will work on the development and application of a predictive hierarchical chemical modeling toolbox that can tackle increasingly complex chemical separations and transformations in complex nanoporous materials, including metal-organic frameworks, zeolites, and polymers with intrinsic microporosity. Research will be directed toward liquid-phase adsorption and catalysis in multi-component mixtures. The nanoporous materials will include hierarchical architectures, responsive frameworks that may undergo phase transitions or post-synthetic modifications, and may contain defects, partial disorder, interfaces or be a composite material. Tunable electronic properties of nanoporous materials, including luminescence and magnetic coupling and anisotropy, will be addressed Another major aspect of the proposed research is the development and application of data-driven science approaches that will lead to advances in machine learning for the discovery of optimally-performing materials, in genetic algorithms for the tailored design of nanoporous materials, and in computational methods to systematically identify and to characterize metal-organic frameworks and other nanoporous materials. The team will also work on the development of data repositories for nanoporous materials that add value by providing structures optimized via electronic structure calculations, along with their energetics for solvent removal, pore characteristics, and their adsorption and transport properties. Data management and computing will primarily use current petascale and future exascale capabilities at the Argonne Leadership Computing Facility, as well as NERSC.

The collaborative NMGC activities will also contribute to the training of graduate students and postdoctoral researchers with broad expertise in data-driven science approaches and computational chemistry methods, in addition to the skills to thrive in an integrated experimental and computational research environment.

This talk will highlight recent developments enabling first principles Monte Carlo (FPMC) simulations for which the potential energy is calculated on-the-fly using Kohn-Sham density functional theory. Applications of FPMC to the prediction of (a) unary and binary adsorption isotherms for gas molecules in metal-organic frameworks with under-coordinated metal nodes and (b) reaction equilibria in cation-exchanged zeolites (see **Figure 1**). Emphasis will be given to simulation methodologies and microscopic-level origins of the observed thermodynamic behavior.

Over the next year, the NMGC team will continue its collaborative endeavors to discover functional nanoporous materials and to use an integrated computational/data science/experimental approach for unraveling structure/chemistry/function relationships.

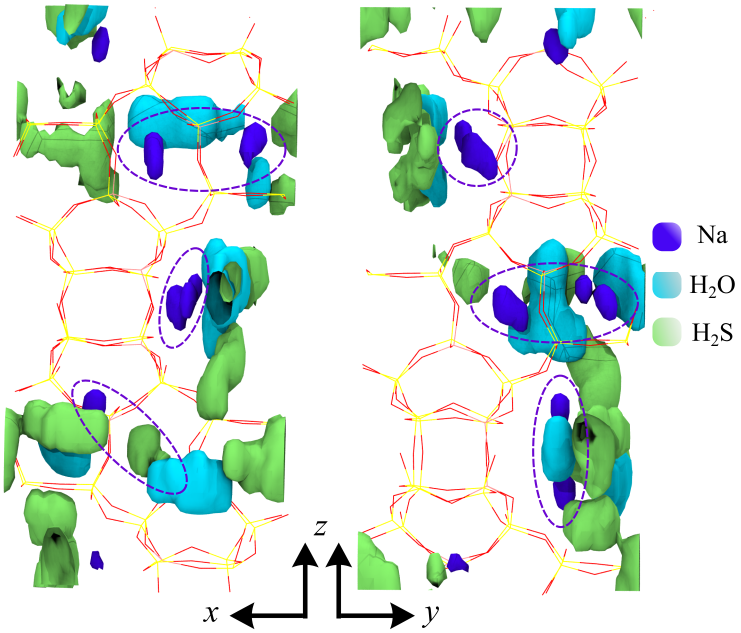


Figure 1: Spatial Distribution Spatial distributions of sodium cations, H_2O and H_2S molecules in Na-BEA. The isosurfaces indicate regions with densities larger than twice the corresponding average densities in the micropore. The dashed ellipses highlight the locations of Na+ pairs.

Grant Number and Grant Title

DE-FG02-17ER16362
Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

Postdoc(s): Peng Bai (UMN), S. Bobbitt (NU), Dhabib Chulhai (UMN), Hakan Demir (UMN), Subhadip Goswami (NU), Wooseok Jeong (UMN), Britta Johnson (Cornell), Ping Lin (UF), Andreas Mavrantonakis (UMN), Mohammad Momeni (UMN), Manuel Ortuno (UMN), David Presti (UMN), Saied Pratik (UMN), Dai Tang (GA Tech), Raghuram Thyagarajan (UMN), Pragya Verma (UMN), Jenny Vitillo (UMN), Xinping Wu (UMN), Zhenpeng Yao (UT), Mike Ziebel (UCB)

Student(s): B. Bucior (NU), Courtney Downes (USC), Sina Chiniforoush (UMN), Ricki Drout (NU), Yuexing Cui, Lucy Darago, Evgenii Fetisov (UMN), Daniel Graham (UMN), Soumen Ghosh (UMN), Eric Johnson (USC), Grit Kupgan (UF), Roshan Patel (UMN), Damir Popov (USC), Mansi Shah (UMN), Samuel Stoneburner (UMN), Yangzeshang Sun (UMN).

Publications Acknowledging this Grant

P. Verma, Z. Varga, and **D. G. Truhlar**, "Hyper Open-Shell Excited Spin States of Transition-Metal Compounds: FeF_2, $FeF_2\cdots$ethane, and $FeF_2\cdots$ethylene," *J. Phys. Chem. A* **122**, 2563-2579 (2018).

D. V. Chulhai and **J. D. Goodpaster**, "Projection-Based Correlated Wave Function in Density Functional Theory Embedding for Periodic Systems," *J. Chem. Theory Comput.* **14**, 1928-1942 (2018).

E. O. Fetisov, M. S. Shah, C. Knight, **M. Tsapatsis**, and **J. I. Siepmann**, "Understanding the Reactive Adsorption of H_2S and CO_2 in Sodium-Exchanged Zeolites," *ChemPhysChem* **19**, 512-518 (2018).

S. Hwang, A. Gopalan, M. Hovestadt, F. Piepenbreier, C. Chmelik, M. Hartmann, **R. Q. Snurr**, and J. Kärger, "Anomaly in the Chain Length Dependence of n-Alkane Diffusion in ZIF-4 Metal-Organic Frameworks," *Molecules* **23**, art. no. 668/16 pages (2018).

M. S. Shah, E. O. Fetisov, **M. Tsapatsis**, and **J. I. Siepmann**, "C2 adsorption in zeolites: In silico screening and sensitivity to molecular models," *Mol. Syst. Des. Eng.* **3**, ASAP article. DOI: 10.1039/C8ME00004B

H. Q. Pham, V. Bernales, and **L. Gagliardi**, "Can Density Matrix Embedding Theory with the Complete Activate Space Self-Consistent Field Solver Describe Single and Double Bond Breaking in Molecular Systems?" *J. Chem. Theory Comp.* **14**, 1960-1968(2018).

T. Islamoglu, M. A. Ortuño, E. Proussaloglou, A. J. Howarth, N. A. Vermeulen, A. Atilgan, **C. J. Cramer**, and **O. K. Farha**, "Presence versus Proximity: The Role of Pendant Amines in the Catalytic Hydrolysis of a Nerve Agent Simulant," *Angew. Chem. Int. Ed.* **57**, 1949-1953 (2018).

C. A. Downes and **S. C. Marinescu**, "Electrocatalytic Metal-Organic Frameworks for Energy Applications," *ChemSusChem **10***, 4374-4392 (2017).

Y.-L. Wu, N. S. Bobbitt, J. L. Logsdon, N. Powers-Riggs, J. N. Nelson, X. Liu, T. C. Wang, **R. Q. Snurr**, **J. T. Hupp**, **O. K. Farha**, M. C. Hersam, and M. R. Wasielewski, "Tunable Crystallinity and Charge Transfer in Two-Dimensional G-Quadruplex Organic Frameworks," *Angew. Chem. Intl. Ed.* **57**, 3985-3989 (2018).

M. E. Ziebel, L. E. Darago, and **J. R. Long**, "Control of Electronic Structure and Conductivity in Two-Dimensional Metal–Semiquinoid Frameworks of Titanium, Vanadium, and Chromium," *J. Am. Chem. Soc.* **140***,* 3040–3051 (2018).

Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: (i) Role of Nuclear Quantum Effects in Zeolite Selectivity, (ii) Molecular Simulations of Amorphous Materials, (iii) Data Science and Machine Learning

Nandini Ananth,[2] **Coray M. Colina**,[4] **J. Ilja Siepmann**,[1] Alan Aspuru-Guzik,[3] Christopher J. Cramer,[1]
Omar K. Farha,[5] Laura Gagliardi,[1] Jason D. Goodpaster,[1] Maciej Haranczyk,[6] Joseph T. Hupp,[5]
Jeffrey R. Long,[7] Smaranda Marinescu,[8] David S. Sholl,[9] Randall Q. Snurr,[5] Donald G. Truhlar,[1]
and Michael Tsapatsis[1]

[1]U Minnesota, [2]Cornell U, [3]U Toronto, [4]U Florida, [5]Northwestern U, [6]Lawrence Berkeley National Laboratory, [7]U California–Berkeley, [8]U Southern California, [9]Georgia Institute of Technology

Lead institution address: Chemistry, Univ. of Minnesota, Minneapolis, MN 55455-0431
Director e-mail address: siepmann@umn.edu

Abstract

The Nanoporous Materials Genome Center (NMGC) develops computational/theoretical chemistry methods and data-driven science approaches with the aims of (i) de-novo design of novel functional nanoporous materials, (ii) discovery and selection of the most promising functional nanoporous materials from databases of synthesized and hypothetical framework structures, and (iii) microscopic-level understanding of the fundamental interactions underlying the function of nanoporous materials. A pivotal part of NMGC's success is a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups that allows for iterative feedback.

Building upon prior NMGC research focused mostly on gas capture, separation and catalysis in crystalline nanoporous materials, the team is now working on the development and application of a predictive hierarchical chemical modeling toolbox that can tackle increasingly complex chemical separations and transformations in complex nanoporous materials, including metal-organic frameworks (MOFs), zeolites, and polymers with intrinsic microporosity. Research is directed toward liquid-phase adsorption and catalysis in multi-component mixtures. The nanoporous materials will include hierarchical architectures, responsive frameworks that may undergo phase transitions or post-synthetic modifications, and may contain defects, partial disorder, interfaces or be a composite material. Tunable electronic properties of nanoporous materials, including luminescence and magnetic coupling and anisotropy, will be addressed. Another major aspect is the development and application of data-driven science approaches that will lead to advances in machine learning for the discovery of optimally-performing materials, in genetic algorithms for the tailored design of nanoporous materials, and in computational methods to systematically identify and to characterize MOFs and other nanoporous materials. The team is also working on the development of data repositories for nanoporous materials that add value by providing structures optimized via electronic structure calculations, along with their energetics for solvent removal, pore characteristics, and their adsorption and transport properties. Demanding computational tasks will primarily use current petascale and future exascale capabilities at the Argonne Leadership Computing Facility, as well as NERSC.

The collaborative NMGC activities also contribute to the training of graduate students and postdoctoral researchers with broad expertise in data-driven science approaches and computational chemistry methods, in addition to the skills to thrive in an integrated experimental and computational research environment.

Nandini Ananth's talk will focus on the development and implementation of path-integral based techniques to investigate the role of nuclear quantum effects in nanoporous materials (see **Figure 1**). Specifically, zeolites and MOFs exhibit selective adsorption and diffusion of small molecule gases, and this selectivity is not captured by classical molecular dynamics simulations. Path integrals methods offer an efficient and accurate approach to incorporating quantum effects in computing various molecule-porous material interactions including insertion barriers, adsorption free energies, and diffusion rates. Here, we present path integral molecular dynamics (PIMD) simulations implemented in **CP2K**, an open source software platform, that compare free energy barriers for H_2/D_2 entering into the RHO zeolite. We also describe our work towards implementing ring polymer molecular dynamics (RPMD) simulations to calculate diffusion rates. Finally, using force fields developed by our NMGC collaborators we undertake a systematic investigation into energy-efficient routes to separate ethylene from ethane and other lighter hydrocarbons using zeolites.

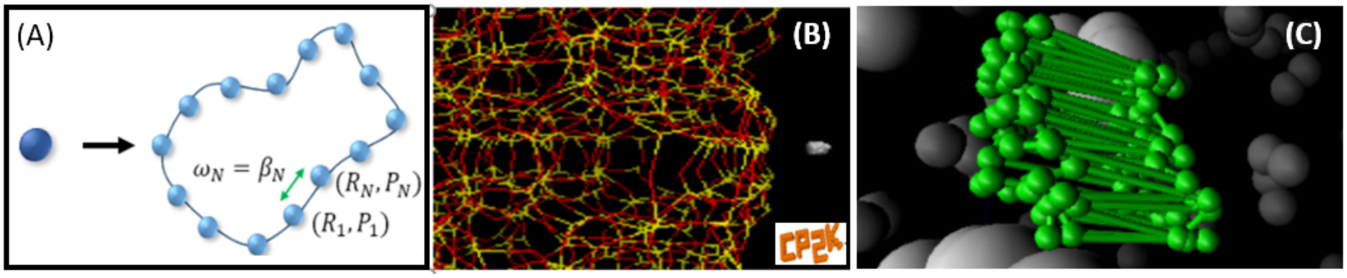


Figure 1: Path integral methods employ classical isomorphic representations of quantum systems that allow us to capture quantum effects using only classical molecular dynamics trajectories. (a) Cartoon depicting the exact mapping of a quantum particle at thermal equilibrium to a classical 'ring polymer'. (b) Computing insertion barriers for small molecules into the RHO zeolite. Here, we show a snapshot from our PIMD simulation with the quantized H_2 molecule in white. (c) RPMD simulations can be used to simulate real-time dynamic events, such as diffusion.

Coray Colina's talk will highlight recent developments on atomistic-level simulations of amorphous materials (polymers of intrinsic microporosity, hyper-crosslinked polymers) and mixed matrices that include organic molecules of intrinsic microporosity as nanoparticles. Applications to the prediction of (a) structure and thermodynamic properties of the materials, and (b) unary and binary adsorption isotherms for gas molecules in these amorphous systems will be provided [28; number reflects the reference list] (see **Figure 2**). Emphasis will be given to simulation methodologies, comparisons with order structures, generation of the data needed for further machine learning applications, and microscopic level origins of the observed thermodynamic behavior.

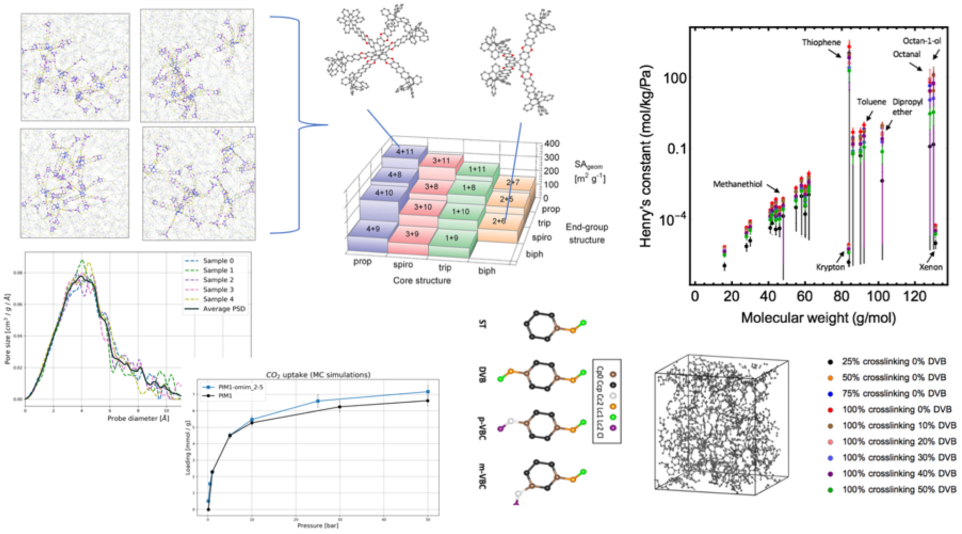


Figure 2 (top to bottom counter clock-wise): Mixed matrices of PIM-1/OMIMs membranes (MMM). Characterization (pore size distributions, gas loading) of the MMM. Hyper-crosslinked polymer (HCP) membranes at several cross-linker densities. Henry's constant for 27 molecules, as a function of their molecular weight, in HCPs.

Ilja Siepmann's poster will provide an NMGC overview and highlight four data science and machine learning activities: (i) Using a data-driven approach to accelerate materials screening and learn structure-property relationships, we report new descriptors for gas adsorption in MOFs derived from the energetics of MOF-guest interactions. Using the bins of an energy histogram as features, we trained a sparse regression model to predict hydrogen and identified a promising candidate for hydrogen storage that was validated experimentally [34]. (ii) A deep neural network, called *SorbNet*, is developed that can predict multi-component adsorption isotherms over a wide range of temperatures and pressures and allows for finding optimal conditions for challenging separations. Big data from high-throughput simulations and *SorbNet* are utilized to find desorptive drying condition that enable the separation of valuable alkane diols (produced from renewable feedstocks) from water with 99.9% purity and > 99% recovery [42]. (iii) A major update to the Computation-Ready, Experimental (CoRE) MOF Database includes about 15,000 and 10,000 porous structures with all or only free solvent molecules removed, respectively. CoRE MOF 2019 also provides additional pore analytics including open metal site detection. (iv) We propose a systematic, machine-readable identification scheme for MOFs. The format, which we call MOFid, includes the MOF topology and SMILES strings for the building blocks. We anticipate that MOFid will be of considerable value for various analyses of MOFs, and we provide a few preliminary examples.

Over the next year, the NMGC team will continue its collaborative endeavors to discover functional nano-porous materials and to use an integrated computational/data science/experimental approach for unraveling structure/chemistry/function relationships.

Grant Number and Grant Title

DE-FG02-17ER16362

Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

Postdoc(s): Peng Bai (UMN), Scotty Bobbitt (NU), Haoyuan Chen (NU), Indrani Choudhuri (UMN), Dhabib Chulhai (UMN), Hakan Demir (UMN), Farhad Gharagheizi (GAT), Subhadip Goswami (NU), Timur Islamoglu (NU), Wooseok Jeong (UMN), Britta Johnson (Cornell), Tyler Josephson (UMN), Ping Lin (UF), Lian Liu (NU), Andreas Mavrantonakis (UMN), Mohammad Momenitaheri (UMN), Manuel Ortuno (UMN), Damir Popov (USC), David Presti (UMN), Saied Pratik (UMN), Ravithree Senanayake (UMN), Saurabh Singh (UMN), Dai Tang (GA Tech), Raghuram Thyagarajan (UMN), Pragya Verma (UMN), Jenny Vitillo (UMN), Xin-Ping Wu (UMN), Jing Xie (UMN), Zhenpeng Yao (UT), Xuan Zhang (NU), Mike Ziebel (UCB).

Student(s): Dylan Anstine (UF), Benjamin Bucior (NU), Sina Chiniforoush (UMN), Brianna Collins (UMN), Robert DeJaco (UMN), Alexander Demidov (UF), Courtney Downes (USC), Ricki Drout (NU), Yuexing Cui (NU), Lucy Darago (UCB), Evgenii Fetisov (UMN), Soumen Ghosh (UMN), Arun Gopalan (NU), Daniel Graham (UMN), Shalini Jayaraman (UF), Eric Johnson (USC), Grit Kupgan (UF), Nathan London (Cornell), Ryan Murphy (UCB), Roshan Patel (UMN), Damir Popov (USC), Mansi Shah (UMN), Samuel Stoneburner (UMN), Yangzesheng Sun (UMN).

Ten Selected Publications Acknowledging this Grant

[42] Y. Sun, R. F. DeJaco, and **J. I. Siepmann**, “Deep Neural Network Learning of Complex Binary Sorption Equilibria from Molecular Simulation Data,” *Chem. Sci.* **10**, 4377-4388 (2019). DOI: 10.1039/C8SC05340E

[41] M. L. Aubrey, M. T. Kapelewski, J. F. Melville, J. Oktawiec, D. Presti, **L. Gagliardi**, and **J. R. Long**, “Chemiresistive Detection of Gaseous Hydrocarbons and Interrogation of Charge Transport in Cu[Ni(2,3-pyrazinedithiolate)2] by Gas Adsorption,” *J. Am. Chem. Soc.* **141**, 5005–5013 (2019) DOI: 10.1021/jacs.9b00654

[36] S. Kato, K.-i. Otake, H. Chen, I. Akpinar, C. T. Buru, T. Islamoglu, **R. Q. Snurr**, and **O. K. Farha**, “Zirconium-Based Metal–Organic Frameworks for the Removal of Protein-Bound Uremic Toxin from Human Serum Albumin,” *J. Am. Chem. Soc.* **141**, 2568–2576 (2019) DOI: 10.1021/jacs.8b12525

[35] M. R. Hermes and **L. Gagliardi**, “Multiconfigurational Self-Consistent Field Theory with Density Matrix Embedding: The Localized Active Space Self-Consistent Field Method,” *J. Chem. Theory Comput.* **15**, 972–986 (2019) DOI: 10.1021/acs.jctc.8b01009

[34] B. J. Bucior, N. S. Bobbitt, T. Islamoglu, S. Goswami, A. Gopalan, T. Yildirim, **O. K. Farha**, N. Bagheri, and **R. Q. Snurr**, “Energy-based descriptors to rapidly predict hydrogen storage in metal–organic frameworks,” *Mol. Syst. Des. Eng.* **4**, 162-174 (2019) DOI: 10.1039/C8ME00050F

[28] G. Kupgan, A. G. Demidov, **C. M. Colina**, “Plasticization behavior in polymers of intrinsic microporosity (PIM-1): A simulation study from combined Monte Carlo and molecular dynamics,” *J. Membr. Sci.* **565**, 95-103 (2018) DOI: 10.1016/j.memsci.2018.08.004

[24] E. O. Fetisov, M. Shah, **J. R. Long**, **M. Tsapatsis**, and **J. I. Siepmann**, “First principles Monte Carlo simulations of unary and binary adsorption: CO_2, N_2, and H_2O in Mg-MOF-74,” *Chem. Commun.* **54**, 10816-108192 (2018) DOI: 10.1039/C8CC06178E

[15] S. Goswami, D. Ray, K.-I. Kung, S. Garibay, T. Islamoglu, A. Atilgan, Y. Cui, **C. J. Cramer**, **O. K. Farha**, **J. T. Hupp**, “A porous, electrically conductive hexa-zirconium(IV) metal-organic framework,” *Chem. Sci.* **9**, 4477-4482 (2018) DOI: 10.1039/C8SC00961A

[14] D. Tang, Y. Wu, R. J. Verploegh, and **D. S. Sholl**, “Efficiently Exploring Adsorption Space to Identify Privileged Adsorbents for Chemical Separations of a Diverse Set of Molecules,” *ChemSusChem* **11**, 1567-1575 (2018) DOI: 10.1002/cssc.201702289

[4] C. A. Downes and **S. C. Marinescu**, “Electrocatalytic Metal-Organic Frameworks for Energy Applications,” *ChemSusChem* **10**, 4374-4392 (2017) DOI: 10.1002/cssc.201701420

Center for Scalable Predictive methods for Excitations and Correlated Phenomena (SPEC)

Edoardo Aprà,[a] Anne Chaka,[a] Wibe de Jong,[b] Thom H. Dunning, Jr.,[c] Niranjan Govind,[a] So Hirata,[d]
Karol Kowalski,[a] Sriram Krishnamoorthy,[a] Xiaosong Li,[c] Christopher J. Mundy,[a] John J. Rehr,[c]
Chao Yang,[b] Dominika Zgid,[e] Sotiris S. Xantheas[a]

[a] Pacific Northwest National Laboratory, Richland, WA 99352
[b] Lawrence Berkeley National Laboratory, Berkeley, CA 94720
[c] Department of Chemistry, University of Washington, Seattle, WA 98195
[d] Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801
[e] Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

Abstract

The Center for Scalable Predictive methods for Excitations and Correlated Phenomena (SPEC) aims at capitalizing on DOE's investments in experimental light source facilities (APS, ALS, LCLS, and NSLS) and national leadership computing facilities. The scientific vision of SPEC is to

- develop state-of-the-art, many-body electronic structure methodologies for excited state complex systems,
- implement these methods on leadership class computer architectures,
- deliver scalable, open-source electronic structure software libraries that are interoperable with community electronic structure software,
- address challenges in excited-state and correlated phenomena in complex chemical systems.

SPEC is comprised of team members with expertise in the domain science, computer science and applied mathematics fields (Figure 1). The goal is to deliver scalable software that is appropriate to make efficient use of DOE's leadership class computer architectures in support of the mission of DOE's Office of Basic Energy Sciences (BES). The currently existing knowledge and capability gaps in the area of highly-accurate, exited-state electronic structure methods, and their efficient implementation on leadership class computer architectures, define scientific and methodological challenges to address in order to advance our ability to model, understand, predict, control and design the properties of complex molecules and molecular assemblies. This will be achieved via the following 3 research goals (G1 – G3):

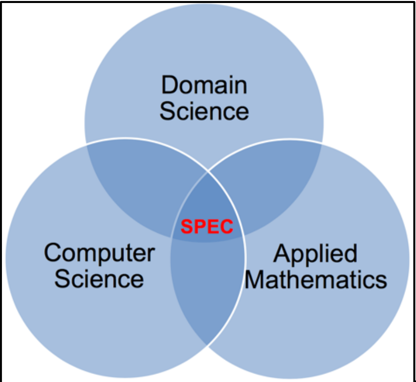


Figure 1. SPEC includes expertise from Domain Science, Computer Science & Applied Mathematics.

G1. ***Develop theoretical approaches that provide an accurate description of valence- and core level excited states of molecules in their local environment.***

The proposed methods consist of:

(*i*) Equation-Of-Motion Coupled Cluster (EOMCC) based on standard excited-state extension of the ground-state CC formalism that includes a hierarchical structure of approximations (singles, doubles, triples, …) and includes relativistic EOMCC formulations.

(*ii*) Multi-Reference (MR) Methods, which include Multi-Reference Coupled Cluster (MRCC), novel selected Configuration Interaction (CI) in Complete Active Space SCF (CASSCF), heat-bath and Adapted Sampling CI (ASCI) integrated with CASSCF, core-hole and excited states as well as spin-orbit coupling.

(*iii*) Hierarchical Green's Function (GF) Methods including Green's Function Bethe Salpeter Equation (GW-BSE), Cumulant expansions, GF2 (second order self-energy), Green's function Perturbation Theory (GFPT), Green's function Coupled Cluster (GFCC) and relativistic formulations.

G2. ***Develop methodologies to model excited state potential energy surfaces with an accuracy and consistency well beyond that provided by standard DFT-based methods.***

The goal is to develop robust, first principles-based protocols that are able to model excited state processes in realistic systems (i.e. systems beyond simple models), which will include the effect of the system's environment. This will be achieved via the coupling of the developed hierarchical methods (higher level) with the Self-Energy Embedding Theory (SEET, lower level) that allows the quantitative account for the system's environment. In addition, EOMCC excited state gradients will offer the capability to obtain geometries, transition states and the location of conical intersections on excited state potential energy surfaces.

G3. ***Develop scalable implementations that take full advantage of leadership class petascale computing facilities and establish a path towards future exascale computers.***

The goal is to reduce the computational cost of calculations and deliver sustainable performance that exceeds current levels by at least an order of magnitude to enable calculations to be extended to real systems. This will be achieved by the development of Tensor Algebra library for Many-body Methods (TAMM) targeting the efficient implementation of EOMCC, GFCC, Many Body Perturbation Theory (MBPT) and Many Body Green's Function (MBGF), and MRCC methods, the use of Model Order Reduction (MOR) method for core excitations with Green's Function approaches and the development of efficient and robust optimization algorithms for Multi Configurational SCF (MCSCF) iterations.

The research strategy for fulfilling the above research goals consists of the breakdown of the effort into 6 Tasks (T1 – T6), shown in Figure 2.

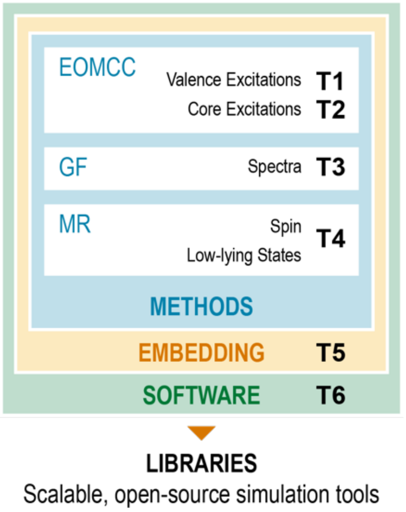


Figure 2. An integrated approach combining method development, computer tools and optimization (T1–T6) that will deliver scalable open-source libraries.

T1 Accurate Equation-of-Motion Coupled Cluster Formalisms for Valence Excited States (G1, G2)
T2 Accurate Equation-of-Motion Coupled Cluster Formalisms for Core Excited States (G1)
T3 Hierarchical Green's Function Formulations (G1, G2)
T4 Scalable Multi-Configurational and Multi-Reference Methods for Quasi-Degenerate Molecular Systems (G1, G2)
T5 Self-Energy Embedding Approaches (G1, G2)
T6 Programming Models, Computer Science Tools, and Optimization for Many-Body Methods (G3)

Grant Numbers and Grant Titles

This work was supported as part of the Computational Chemical Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division in the Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC) at Pacific Northwest National Laboratory.

Publications in the last year (2018)

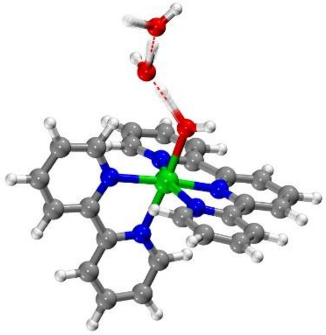
1. Bo Peng, Karol Kowalski, “Green’s function coupled-cluster approach: simulating spectral functions for molecular systems,” *J. Chem. Theory Comput*. (submitted, 2018)
2. Karol Kowalski, “Properties of coupled-cluster equations originating in excitation sub-algebras,” *J. Chem. Phys*. **148**, 094104 (2018).

VIBRATIONAL SIGNATURES OF ELECTRONIC PROPERTIES IN RENEWABLE-ENERGY CATALYSIS

Elizabeth Christensen, Gabriel McDonald, Matthew Wilkinson, Justin J. Talbot, **Ryan P. Steele**

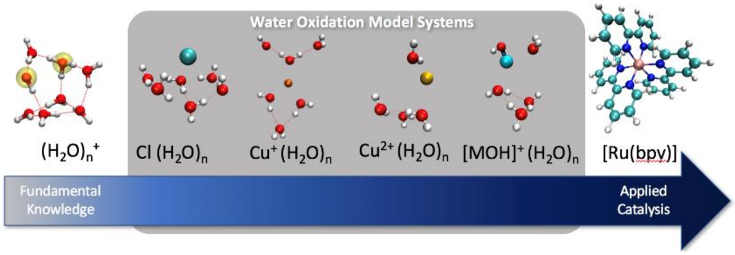
The University of Utah &
Henry Eyring Center for Theoretical Chemistry

Abstract



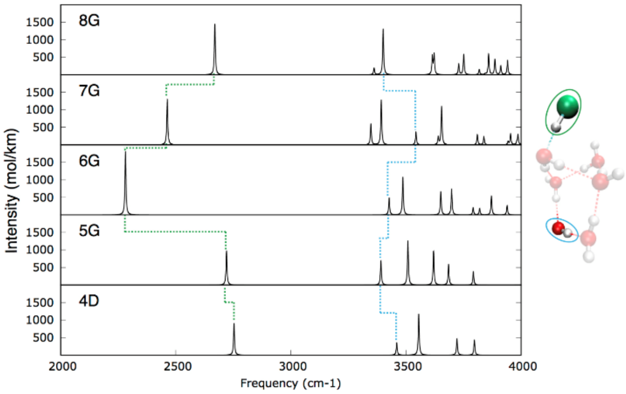
Background & Broad Goals: Nearly all of the catalytic transformations of modern energy interest involve a strong coupling of unique electronic structures—ions, radicals, and partially broken/formed chemical bonds—to the ensuing molecular motion. Water-splitting and carbon dioxide reduction chemistries, for example, both involve challenging redox transformations that are coupled to the activation of hydrogen-containing chemical bonds. Recent developments in vibrational spectroscopy techniques, including cold ion sources and mass spectrometry-based action spectroscopies, have provided unprecedented access to the inner-sphere mechanisms of these catalytic transformations. These experimental techniques allow the reactive centers to be "plucked out" of an otherwise-complex chemical environment and directly probed, rather than relying on indirect measures of outer-sphere effects and assumed reaction mechanisms. When coupled with modern electrochemical and spectroscopic probes of oxidation/spin states and kinetics, these methods begin to provide a cohesive view of redox mechanisms.

These same techniques are presently reliant on the admittedly sub-par tools provided by the computational community in order to *explain* the resulting spectra. Computed harmonic spectra, for example, are often qualitatively incorrect for these complexes, and anharmonic spectra for large, relevant complexes are often cost-prohibitive. The need for good underlying quantum chemistry methods—often beyond density functional theory—further widens this experiment-theory gap. Experimentalists, many of whom are funded by DOE, are now (publicly!) pleading for help from theorists and for better computational tools, and the methods developed in this program aim to address this continually growing need. Importantly, the developed methods will focus on a true quantum chemistry interface, which allows for a key connection between these *vibrational* signatures and the underlying *electronic* properties that dictate these motions.



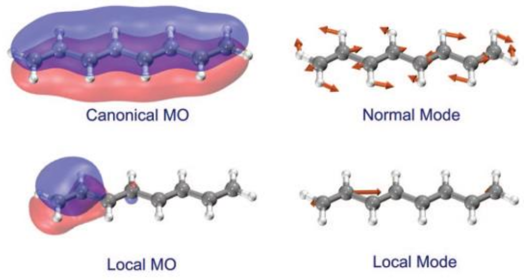
Applications: Vibrational spectra of catalytic water-splitting intermediates are a key focus of this research program. Close collaboration with experimental spectroscopists will steer many of these studies, and the guiding philosophy is to attempt to unify both the fundamental manner in which strong ions/radicals activate solvent, as well as vibrational signatures that highlight the mechanisms of real water-splitting catalysts.

Recent progress has included the study of the interaction between fundamental ions/radicals and water, including (a) the chlorine atom (radical) and (b) Cu^{II}/CuOH hydrated clusters.

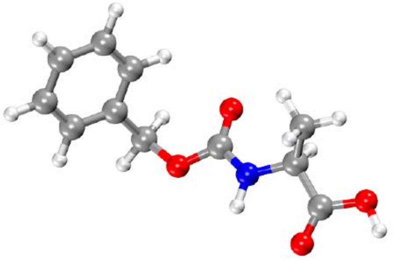


In the $Cl(H_2O)_n$ case, this d-orbital-free water-oxidation problem highlighted the transition from a hydrated radical to an activated-water complex. Size-dependent structural properties were closely correlated with spectroscopic trends that serve as key signatures of the charge-transfer process. The 'crossover' from hydrated radical to oxidized water occurred surprisingly late in the size progression ($n \approx 75$), and the underlying ion/radical hydration trends that explain this trend were determined. These computational predictions will soon be tested by experimental collaborators.

In the copper(II) and copper(II) hydroxide case, results to-date have shown several new insights. First, the electronic state dependence of these clusters has been explicitly determined, and somehow this aspect not been analyzed previously in the literature. With seven putative electronic states available, the independent properties of these states should be included in an analysis of $CuOH(H_2O)_n$ behavior. Second, the size-dependent energy/structure trends have helped explain the experimental transition from $CuOH(H_2O)_n$ to $Cu^{2+}(H_2O)_n$ in mass spectrometry studies. Importantly, computational studies can probe high-energy cluster morphologies that would not be present in these experiments, and trends in these 'dark' structures served as important guideposts in determining the experimentally observed trend.



Methodology: Continued development of local-mode anharmonic vibrational spectroscopy techniques has occurred. The central design challenge for new anharmonic computational spectroscopy methods involves the nominally non-local coupling of vibrational modes. Local-mode techniques, developed in our group, have recently shown promise in tackling this prohibitive computational scaling. Speedups of several orders of magnitude have already been demonstrated, and system-size scaling is dramatically more promising than in existing approaches.



Recent work has focused on the appropriateness of local-mode approaches for low-frequency motions. On one hand, terahertz-region transitions should be expected to be inherently non-local, collective motions. Yet our recently developed "version 2" local-mode approach allows for mixing of modes only within a well-defined frequency window, which provides the potential for an optimal degree of locality. Computations of the spectra of the Z-alanine peptide are currently underway, and comparison to molecular dynamics-based vibrational spectra will be made throughout.

Grant #DE-SC0019405
(“Vibrational Signatures of Electronic Properties in Renewable-Energy Catalysis”)

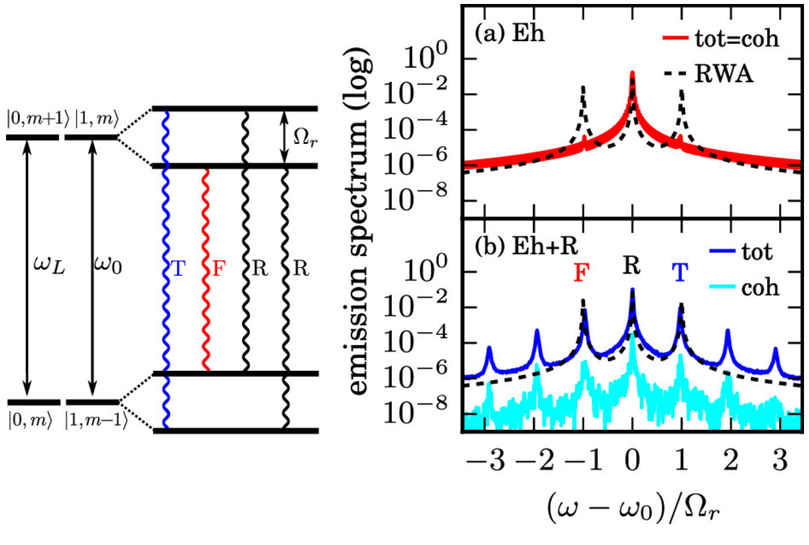
Postdoc(s): --

Student(s): Elizabeth Christensen, Gabriel McDonald, Matthew Wilkinson, Justin J. Talbot

Joseph Subotnik
University of Pennsylvania, Department or Chemistry
231 S. 34th Street
Philadelphia, PA 19104
subotnik@sas.upenn.edu

Program: There are today a large and growing number of experiments demonstrating strong light matter coupling, either in cavities or within plasmonic materials. As such, there is a growing need for an improved theoretical understanding of how exactly (for large realistic systems) photons interacts with electrons in a *quantum mechanical* sense. This program is designed to explore the applicability of *semiclassical* algorithms (as developed for nuclear-electronic dynamics) for modeling such electrodynamics with coupled photonic and electronic degrees of freedom.

Recent Progress: We have developed a preliminary improvement of standard Ehrenfest dynamics, labeled Ehrenfest+R dynamics. The basic idea is to force a random radiation field to emerge from an excitonic center so as to recapitulate fermi golden rule rate of spontaneous emission. We also enforce energy conservation in the spirit of surface hopping. We have already shown that the +R addendum leads to the correct Raman spectrum plus Mollow triplet phenomena, which is completely absent for the usual Ehrenfest picture of electrodynamics coupled to electronic motion.



Future Plans: There are many directions possible for this research, ranging from the theoretical justification of semiclassical dynamics to the application of semiclassical dynamics to large systems with strong light-matter coupling.

Grant Award Number: U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0019397.

Grant Title: Multilinear Spectroscopy, Semiclassical Electrodynamics, and Energy Transfer Under Strong Illumination
Postdoc(s): Chen, Hsing-Ta

Student(s): Li, Tao E.

References:

H-T. Chen and T. E. Li and A. Nitzan and and J. E. Subotnik. "Predictive Semiclassical Model for Coherent and IncoherentEmission in the Strong Field Regime: The Mollow Triplet Revisited"
J. Phys. Chem. Lett. 10 , 1331 - 1336 (2019)

T. E. Li, H-T Chen, and J. E. Subotnik "Comparison of Different Classical, Semiclassical, and Quantum Treatments of Light−Matter Interactions: Understanding Energy Conservation"
J. Chem. Theor. Comp. 15, 1957-1973 (2019)

H.-T. Chen, T. E. Li, M. Sukharev. A. Nitzan, J. E. Subotnik "Ehrenfest+R dynamics. II. A semiclassical QED framework for Raman scattering"
J. Chem. Phys. 150, 044103 (2019)

H.-T. Chen, T. E. Li, M. Sukharev. A. Nitzan, J. E. Subotnik "A mixed quantum–classical electrodynamics simulation of spontaneous emission"
J. Chem. Phys. 150, 044102 (2019)

T. E. Li, H-T Chen, A. Nitzan, M. Sukharev and J. E. Subotnik “A Necessary Trade-off for Semiclassical Electrodynamics: Accurate Short-Range Coulomb Interactions versus the Enforcement of Causality?”

Development of a local hybrid density functional to treat the self-interaction error and the non-local many-electron interaction

Jianwei Sun

Department of Physics and Engineering Physics, Tulane University
jsun@tulane.edu

Abstract

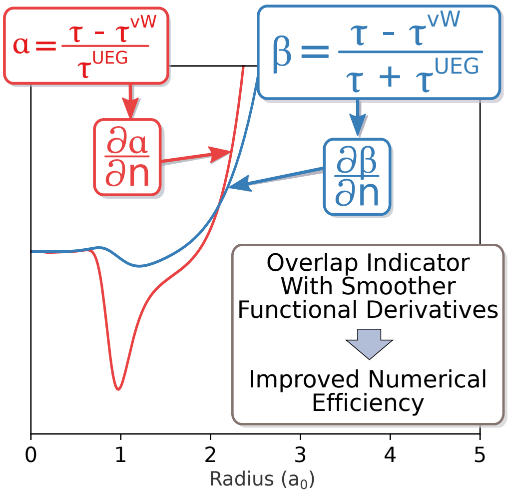
A high computational efficiency and impressive accuracy has resulted in density functional theory (DFT) becoming one of the most widely used electronic structure theories for energy studies, and it remains the only practical method for high-throughput computational discovery of novel materials for energy applications. A recently constructed non-empirical density functional, termed the strongly-constrained and appropriately-normed (SCAN) density functional, has greatly advanced the development of DFT methods, giving improved accuracy over conventional density functionals without sacrificing computational efficiency. Despite this success though, all conventional density functionals (including SCAN) suffer a number of deficiencies, the most serious two of which are the strong many-electron interaction (SMEI) originating from a degeneracy or near-degeneracy and the self-interaction error (SIE) due to the imperfect cancellation of the spurious classical Coulomb interaction between an electron and itself. These deficiencies prevent the DFT-based simulations from accurately describing key properties and systems important for energy applications, including band gaps, band alignments, stretched bonds, interactions with transition metal catalysts, charge transfer, reaction barriers and their spin-dependencies. The underutilized class of functionals termed local hybrids can provide a solution by incorporating the non-local information needed to correctly treat SIE and SMEI through a space dependent local admixture of the exact exchange energy density, which is non-local and computationally available even from a conventional DFT calculation. The goal of the proposed research is to develop a local hybrid density functional that can correctly treat SIE and SMEI simultaneously with a computational efficiency at the upper bound of popular conventional density functionals. The novel local hybrid density functional will build upon the core principles used in the construction of SCAN, largely solve the difficult properties and systems affected by SIE and SMEI while at least matching the popular conventional density functionals for other properties, and therefore has great potential to change the landscape for studies of molecules, nanoparticles, surfaces/interfaces, and solids. The new local hybrid functional will then be applied to study processes relevant to solar energy utilization.

In this progress report, we show that self-interaction error (SIE) remains the dominant cause of error for density functional studies of TiO_2. We detail progress towards developing a local hybrid functional to address SIE and report a novel iso-orbital indicator variable with appealing properties.

Advanced semi-local density functionals from the meta-generalized gradient (meta-GGA) class have made accurate low-cost computational studies of materials possible. Despite this success such functionals are necessarily limited by SIE and we show this to be the leading cause of error in energetic orderings for the structural phases of TiO_2. To improve on this limitation a local-hybrid functional that will be constructed and used for high accuracy studies of TiO_2 and related materials.

Titanium dioxide, TiO_2, has wide ranging applications in energy science, including in important dye-sensitized solar cells. TiO_2 predominantly exists in two competing structural phases, rutile and anatase. Predicting the relative stability of these has been a long-standing challenge and we show that such difficulties are largely the result of SIE. Previous work reports the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) and Heyd-Scuseria-Ernzerhof (HSE) range-separated hybrid functional significantly over-stabilize the anatase phase compared to benchmark data. We show that the SCAN meta-GGA functional largely corrects this over-stabilization. By investigating the energetic behavior of fractionally occupied isolated Ti atoms, and the effect of including Hubbard U correction we can understand this improvement as a reduction of SIE, though as SCAN is a semi-local functional some SIE necessarily remains. Inclusion of an empirical Hubbard U correction to SCAN can give transition free energies very close to those observed in experiment. Selection of the appropriate U parameter is non-predictive however, highlighting the need for non-empirical SIE schemes such as local hybrid functionals.

The success of the SCAN functional rests upon its use of the iso-orbital indicator variable $\alpha = (\tau - \tau^{\mathrm{vW}})/\tau^{\mathrm{UEG}}$ to recognize and appropriately handle differing chemical environments. Here, $\tau = \frac{1}{2}\sum_i^N |\nabla\varphi_i|^2$ is the kinetic energy density of the occupied Kohn-Sham orbitals, $\{\varphi_i\}$, $\tau^{\mathrm{vW}} = |\nabla n|^2/(8n)$ is the single orbital kinetic energy density of the electron density n, and $\tau^{\mathrm{UEG}} = (3/10)(3\pi^2)^{2/3}n^{5/3}$ is that of the uniform electron gas. Extensive use has revealed that SCAN, and other meta-GGA built around α, have poor numerical performance in real-space DFT grid integration. Conventionally this problematic behavior has been handled by employing large integration grids, significantly reducing computational efficiency.



We rationalize the numerical inefficiencies suffered by recent mGGA functionals as the result of sharp variations in the derivatives of the α iso-orbital indicator variable causing sharp oscillations in the exchange correlation potential. To address this, we propose an alternative iso-orbital indicator, $\beta = (\tau - \tau^{\mathrm{vW}})/(\tau + \tau^{\mathrm{UEG}})$, constructed from the same semi-local ingredients that identifies the same chemical environments. The β variable does not suffer the numerical inefficiencies of α and we show that with minimal adjustment simple substitution of α for 2β can produce related functionals with greatly improved performance on real-space numerical integration grids. Alongside this the good accuracy enabled by identification of distinct chemical environments was preserved. Hence, β is a desirable replacement for α in mGGA and higher-level, such as local-hybrid, functional development.

Alongside improved numerical efficiency, we show that β offers two further advantages. Previous iso-orbital indicators are unable to uniquely identify tail densities. In contrast, β in combination with the reduced density gradient, $s = |\nabla n|/(2(3\pi^2)^{1/3}n^{4/3}$, can. Unique identification of tail densities is impossible for α, even in combination with s, as it has two possible behaviors in this environment. In single orbital systems $\alpha = 0$ while s diverges, in many orbital systems both α and s diverge. In contrast, in all systems β decays towards zero while s diverges, uniquely characterizing all tail densities. Additionally, we show that the divergence of $d\alpha/d\tau$ in single orbital systems causes problematic divergences in exchange-correlation potential terms if the first exchange enhancement factor derivative $dF_{\mathrm{x}}/d\alpha \neq 0$. This is problematic for the SCAN functional and prevents straight-forward construction of pseudopotentials for SCAN. The β indicator does not suffer these limitations as the derivative divergences are properly controlled. Hence pseudopotential generation is possible regardless of functional form, freeing functional construction.

In light of these developments, particularly the identification of β, it has become apparent that a number of improvements can be made to the already enormously successful SCAN functional. This will form the first developments for the second year of the project and we expect this work to result in a SCANβ functional with improved numerical performance and accuracy for some systems that are pathological for SCAN. We expect the SCANβ functional to be immediately impactful for studies using conventional DFT functionals. Following its completion, we will take the new SCANβ as the semi-local core for the proposed local-hybrid.

One challenge identified in the early progress of this work is in how to handle the gauge freedoms in the non-local and semi-local exchange energy densities, termed the gauge problem. The gauge problem has conventionally been handled by including a correction 'calibration function' to bring the semi-local exchange into the conventional gauge of the non-local exact exchange. We have explored the reported calibration functions and find this solution to be non-ideal with existing constructions breaking exact constraints, being computationally cumbersome, or being numerically problematic. Appropriate resolution of the gauge problem is a key barrier for local hybrid development, and we will explore alternatives to calibration functions for solving the gauge problem.

Alongside this functional development we have been continuing to work on efficient implementation of local hybrid functionals. To date we have been using the 'resolution of the identity' scheme of Della-Salla to evaluate the non-local exchange energy density. We have found, as others have, that whilst simple to implement this technique is computationally inefficient and numerically problematic. We will therefore proceed using the alternative semi-numerical schemes that have been reported as highly efficient and stable schemes. We will initially seek to collaborate with authors of existing implementations in high-performance codes to avoid repeating the implementation work. However, if such collaboration proves impossible we will produce our own implementation.

Grant Numbers and Grant Titles

U.S. DOE, Office of Science, Basic Energy Sciences Grant No. DE-SC0019350 (core research)

Postdoc(s): James W. Furness

Publications Acknowledging this Grant in last year

[1] Y. Zhang, J. W. Furness, B. Xiao, and J. Sun, *Subtlety of TiO2 Phase Stability: Reliability of the Density Functional Theory Predictions and Persistence of the Self-Interaction Error,* J. Chem. Phys. **150**, 014105 (2019).

[2] J. W. Furness and J. Sun, *Enhancing the efficiency of density functionals with a novel iso-orbital indicator,* Phys. Rev. B **99**, 041119 (2019).

SPARC-X: Quantum simulations at extreme scale — reactive dynamics from first principles

Phanish Suryanarayana[1*], Andrew J. Medford[1], Edmond Chow[2], John E. Pask[3]

[1]*College of Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[2]*College of Computing, Georgia Institute of Technology, Atlanta, GA 30332, USA*
[3]*Physics Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA*
*phanish.suryanarayana@ce.gatech.edu

Abstract

The objective of this project is to develop SPARC-X: an open source computational framework for performing Kohn-Sham Density Functional Theory (DFT) calculations that scale linearly with system size, leveraging petascale/exascale parallel computers to study chemical phenomena at length and time scales previously accessible only by empirical approaches — e.g., 100,000 atoms for a few picoseconds using semilocal functionals or 1,000 atoms for a few nanoseconds using hybrid functionals. To do so, SPARC-X will exploit a recent breakthrough in electronic structure methodologies: systematically improvable, strictly local, orthonormal, discontinuous real-space bases that efficiently and systematically capture the local chemistry of the system [1–4]. With further adaptation using new machine-learning techniques [5] and the use of the massively parallel Spectral Quadrature (SQ) method, the algorithmic complexity and prefactor associated with DFT calculations involving semilocal as well as hybrid functionals will be dramatically reduced.

The capability provided by SPARC-X has applications in a wide variety of chemical sciences, including reactive interfaces where large length- and/or long time-scales are needed and traditional force fields fail. This is particularly important in dynamic catalysis, where bond breaking and formation must be understood in detail. This project will develop, test, and apply the SPARC-X framework to understand the photocatalytic properties of TiO_2 systems with and without Au co-catalysts for nitrogen transformations. This integrated development and application strategy will ensure that SPARC-X is a robust, efficient, and scalable software package for quantum simulations on current petascale and future exascale computing resources and enable fully ab initio investigation of key catalytic systems previously beyond reach.

In this presentation, we first discuss our recent progress in the development of SPARC-X. Then, we discuss future efforts related to SPARC-X development and its application to dynamic catalysis.

Building on the state-of-the-art parallel SPARC electronic structure code, our recent additions include: (i) notably higher efficiency achieved through reformulation of expressions for energy and atomic forces, highly optimized BLAS kernels, improved CPU vectorization of finite-difference stencil operations, threading for previously serial parts, and improved preconditioned mixing schemes; (ii) considerably improved parallel scaling (**Figure 1**) achieved through an additional level of parallelization over bands, efficient data transfer between different parallelization schemes, and implementation of a scalable linear solver; (iii) increased generality through additional features including the GGA semilocal exchange-correlation, various flavors of geometry optimization/molecular dynamics (MD) algorithms with restart capability, Gaussian smearing, and ability to study non-orthogonal systems; (iv) increased portability by limiting dependencies to industry-standard BLAS, LAPACK, ScaLAPACK, and MPI libraries; (v)

increased ease of use by minimizing the number of parameters that need to be input; and (vi) high-throughput testing framework (**Figure 1**) that integrates with modern data infrastructure such as MongoDB databases and Jupyter notebooks. With these and other advances, SPARC-X currently outperforms established planewave codes such as Quantum Espresso by more than an order of magnitude in terms of minimum wall time to solution (**Figure 1**), enabling long time scale quantum MD.

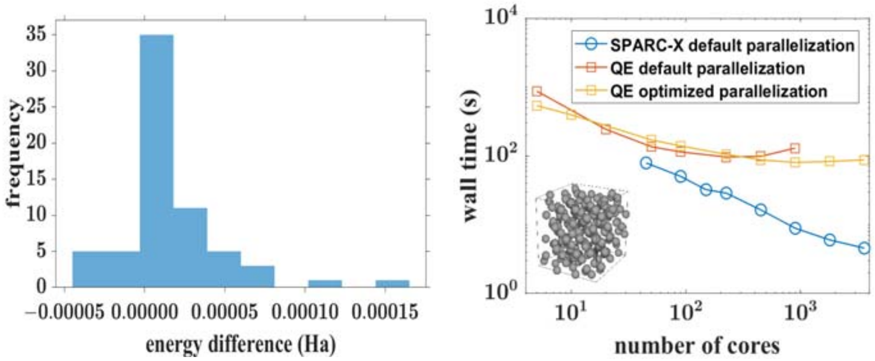


Figure 1: Left: Difference in formation energy computed by SPARC-X and Quantum Espresso (QE) for 120 small-molecule systems from the G2 database. Right: Strong scaling of SPARC-X and QE for a 216-carbon atom ground state calculation, with all parameters chosen to achieve the same accuracy in both codes. QE timings courtesy M. Bethkenhagen (U Rostock) and S.E. Weitzner (LLNL).

Other recent work includes OpenMP and GPU support for the most time-consuming SPARC-X kernels, i.e., stencil operations and unstructured matrix-vector multiplications. In addition, a machine-learning approach based on convolutional kernels and a neural network [5] has been developed for generating improved guesses in the self-consistent iteration. Preliminary results indicate that the machine learned guess can reduce the self-consistent error by 2-3 orders of magnitude.

Going forward, we plan to first implement the Complementary Subspace [3] approach to push back the cubic-scaling bottleneck, and then the DDBP method [4] to enable strong scaling of SPARC-X to still larger numbers of processors, bringing down time to solution still further. The DDBP method will also enable efficient DFT calculations with hybrid functionals and the linear scaling SQ method, which will be implemented subsequently. As done currently, parallelization will be achieved via MPI, OpenMP, and GPU. Machine learning techniques will also be leveraged to further increase the efficiency of the calculations. With these advances, initial applications will focus on screening a large number of possible active sites for both slab and nanoparticle models of TiO_2, assessing the solvation effects and the transfer of hydrogen to the nitrogen molecule.

Grant Numbers and Grant Titles

DE-SC0019410 (2018–present) SPARC-X: Quantum simulations at extreme scale — reactive dynamics from first principles

DOE SCW1357 (2012–2017) Discontinuous methods for accurate, massively parallel quantum molecular dynamics: Lithium ion interface dynamics from first principles

Students

Qimen Xu, Abhiraj Sharma, Benjamin Comer, Xiangyun Lei, Hua Huang

Selected Publications Acknowledging these Grants in the last 3-4 years

[1] A. Banerjee, L. Lin, W. Hu, C. Yang, and J.E. Pask, Chebyshev polynomial filtered subspace iteration in the Discontinuous Galerkin method for large-scale electronic structure calculations, *J. Chem. Phys.* **145**, 154101, 2016.

[2] G. Zhang, L. Lin, W. Hu, C. Yang, and J.E. Pask, Adaptive local basis set for Kohn-Sham density functional theory in a discontinuous Galerkin framework II: Force, vibration, and molecular dynamics calculations, *J. Comput. Phys*. **335**, 426, 2017.

[3] A.S. Banerjee, L. Lin, P. Suryanarayana, C. Yang, and J.E. Pask, Two-level Chebyshev filter based complementary subspace method: pushing the envelope of large-scale electronic structure calculations, *J. Chem. Theory Comput*. **14**, 2930–2946, 2018.

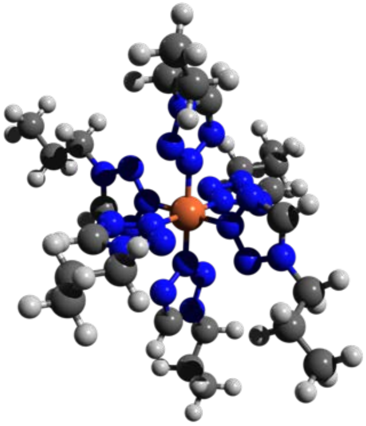
[4] Q. Xu, P. Suryanarayana, and J.E. Pask, Discrete discontinuous basis projection method for large-scale electronic structure calculations. *J. Chem. Phys.*, **149**, 094104, 2018.

[5] X. Lei, A.J. Medford, Design and analysis of machine learning exchange-correlation functionals via rotationally invariant convolutional descriptors, *arXiv preprint* ***arXiv:1901.10822***, 2019.

Light-Induced Spin Trapping in Transition Metal Compounds

Inga S. Ulusoy, Angela K. Wilson
Department of Chemistry, Michigan State University, 578 S Shaw Lane, East Lansing, MI 48824
wilson@chemistry.msu.edu

Spin-crossover (SCO) complexes can undergo a transition from a low-spin (LS) to a high-spin (HS) state and vice versa through irradiation with light, pressure or temperature changes. The most prominent SCO complexes contain Fe(II) metal ions connected to ligands through nitrogen atoms. LS and HS states of SCO compounds have strikingly different structural, magnetic, and electronic properties, and a controlled switching between these states is interesting for a multitude of applications in energy conversion, pressure-sensitive devices, data processing and information storage.



$[Fe^{II}(ptz)_6]^{2+}$ SCO complex

The theoretical study of SCO complexes has been hindered by the size and complexity of the compounds. Initial studies focused on density functional theory (DFT) as the only viable method, but with the development of more efficient algorithms in wavefunction based theories, and advances in computer architectures, SCO compounds can now also be studied using configuration interaction (CI) or complete active space (CAS) methodologies. Of all the different characteristics of SCO compounds, light-induced excited state spin trapping (LIESST) is of special interest due to its potential application in energy and information storage and conversion. In LIESST, a (typically octahedral) SCO compound is excited from the $^1A_1$ ground state into a metal to ligand charge transfer (MLCT) state by irradiation. From this state, the system can undergo intersystem crossing (ISC) to a triplet and through another ISC to the HS metastable $^5T_2$ state. The system is trapped in the HS state, since a direct conversion from HS to LS is only possible through tunneling; these metastable states can be very long-lived, with lifetimes of up to several days at low temperatures. Fe(II) compounds exhibiting LIESST are replacement candidates for the expensive Ru-based complexes in dye-sensitized solar cells.

In this project, advanced wave-function based methods such as CI are used to model several exemplary SCO compounds. CI methods are generally capable of a highly accurate description of SCO compounds, however the level of truncation, core-correlation effects and the quality of the electronic basis largely influence the level of accuracy. We have recently devised a routine by which the convergence of the CI wave function can be estimated, based on its representation in length and velocity gauge[1]. One advantage of CI methods is that they can be improved systematically, and that the inclusion of spin-orbit coupling (SOC) is fairly straightforward through the Breit-Pauli spin orbit coupling (SOC) Hamiltonian as in standard SO-CI (spin-orbit CI) implementations. So far, we have addressed the project from different angles. Several Fe(II) compounds have been optimized using DFT methods, to obtain a good structure for the subsequent SO-CI calculations. As starting point, $[Fe(CN)_6]^{4-}$, $[Fe(NH_3)_6]^{2+}$, $[Fe[bpy]_3]^{2+}$ (bpy – bipyridyl), and the largest compound, $[Fe(ptz)_6]^{2+}$ (ptz – propyl-tetrazol), have been selected, as these exhibit energetic differences of varying degree between LS and HS. The compounds have been optimized in the LS and HS spin states, using the TPSS functional and with basis sets up to the TZVP basis set. We have implemented the time-dependent SO-CI method (TD-SOCI) into our in-home time-dependent CI (TDCI) program. As test cases, we have selected several small molecules, such as LiH, CO^{2+}, and $Fe^{II}CO$ that exhibit varying strengths of SOC. For the implementation, modifications to the GAMESS-US program package were required to obtain not only the CI wave function and integrals, but also the SOC Hamiltonian. The TD-SOCI calculation is carried out in the spin-mixed SOC eigenfunctions, while a transformation to the spin-pure CI eigenstates is possible at all times. During the propagation, not only the population of SO-CI and CI states, but also of configuration state functions (CSFs) and molecular orbitals (MOs) are being monitored. With this information, (de-)excitation pathways upon irradiation with light are obtained, and electronic charge density and flux can be calculated at all time steps. We are currently connecting our TD-(SO)CI code to a program that generates such current maps (detCI/ORBKIT). Furthermore, we have nearly completed a manuscript in which the TD-SOCI method is described and applied[2].

Building upon our recent progress, we will apply the TD-SOCI to the larger Fe(II) compounds, and investigate how the spin trapping in these compounds is triggered. (De-)Excitation pathways, time-dependent populations of spin-mixed and spin-pure states, and lifetimes/transition rates will be obtained. We are extending the TD-SOCI methodology to a reduced density matrix representation, in which effects of the environment such as spontaneous emission, and the presence of a solvent or a metallic surface influence the electronic pathways. In the final phase, a set of design parameters is being developed which will aid the experimental design of promising SCO candidates.

[1] Inga S. Ulusoy, Zachary Stewart, Angela K. Wilson, “The Role of the CI Expansion Length in Time-Dependent Studies”, *J. Chem. Phys*. **148**, 014107 (2018)
[2] Inga S. Ulusoy, Angela K. Wilson, “Time-Dependent Configuration Interaction for Multiple Spin States”, *to be submitted*

DE-SC0017889, “Light-Induced Spin Trapping in Transition Metal Compounds”

Student: Zachary J. Stewart

Probing Large Complex Systems with DFTB: Parallelization Enhancements and Self-Interaction Corrections

Bryan M. Wong
Department of Chemical & Environmental Engineering, Materials Science & Engineering Program, and Department of Physics & Astronomy
University of California-Riverside, Riverside, CA 92521
E-mail: bryan.wong@ucr.edu, Web: http://www.bmwong-group.com

1. Abstract

This project is comprised of two complementary (but parallel) thrusts: (1) implementing massively-parallelized enhancements (with new computational hardware that may replace GPUs) for calculating the electron dynamics of large chemical systems, and (2) introducing self-interaction corrections for improving the accuracy of the density functional tight binding (DFTB) approach. While classical molecular dynamics can handle hundreds of thousands of atoms, it cannot provide a first-principles based description of mesoscale systems at the quantum level. At the other extreme, conventional Kohn-Sham DFT methods can probe the true quantum mechanical nature of chemical systems; however, these methods cannot tackle the large sizes relevant to mesoscale dynamics and length scales. The DFTB formalism utilized in this project provides a viable approach for probing these large systems at a quantum mechanical level of detail. However, to utilize the DFTB approach for accurate calculations of electronic properties, it is crucial to incorporate *quantum-based non-empirical corrections* in DFTB since exchange-correlation effects can still remain very strong in these large systems. At the same time, enhancing the computational efficiency of DFTB is also essential since optimal computational performance is required for addressing the large size scales associated with mesoscale systems. As such, the new non-empirical corrections and other hardware enhancements implemented in this project will enable accurate *and* computationally efficient approaches to directly probe quantum dynamics in these large, complex systems.

2. Recent Progress

The start date of this project was 08/15/2016, and during the past two and a half years we have devoted half of our initial efforts to massive parallelization (with additional chemical applications) of the electron dynamics code and the other half of our focus to an in-house (i.e., from scratch) implementation of self-interaction corrections (SICs). One of the chemical/material systems that we have applied our real-time, time-dependent DFTB (RT-TDDFTB) approach is large metallic nanocluster systems and arrays. Since our last progress update, Niranjan Ilawe (a graduate student funded by this DOE project) graduated with a Ph.D. and published his last paper on RT-TDDFTB simulations of a large plasmonic antenna, which will be presented as a poster at the CTC meeting.

One of the recurring issues with the practical application of these plasmonic ensembles is that the propagation distance of energy transfer remains too short. A possible solution for increasing this propagation distance in plasmonic chains is to (naturally) decrease the interparticle spacings, which results in stronger plasmon couplings. As the interparticle distance is decreased, however, various hybridized plasmon resonances emerge as a result of interactions between the individual plasmon resonances of the elementary nanoparticles. For example, the Bonding Dipole hybridized Plasmon (BDP) is characterized by in-phase charge oscillations in each of the nanoparticles.

Another hybridized plasmon mode, the Charge Transfer Plasmon (CTP), is observed in the structure when the nanoparticles touch each other or a conductive junction is established between them, allowing for a direct charge transfer from one nanoparticle to the other. The onset of these hybridized plasmon resonances drastically modify the near and far field properties of the systems, resulting in new mechanisms to modulate energy/charge transfer in these plasmonic ensembles.

To augment our previous studies, we have made new progress in investigating extremely *small inter-particle spacings*, where quantum effects play an essential role and are beyond the scope of classical finite-difference time domain (FDTD) methods. In addition, to make closer contact to relevant chemical systems of interest to experimentalists, we have moved beyond the simple sodium nanoparticles used in our previous report to large silver nanoparticle arrays. In these new studies, we first characterized the plasmon resonance energy of a single silver nanoparticle containing 55 atoms and having an icosahedral shape. As can be seen in **Fig. 1**, a prominent peak, corresponding to the plasmon resonance is observed around 3.23 eV, which is in good agreement with a time-dependent density functional theory (DFT) calculation of 3.6 eV and a recent experimental result of 3.8 eV for similar-sized Ag nanoparticles.

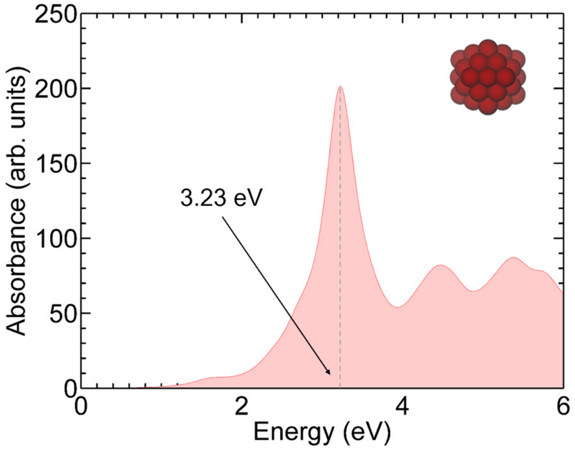


Figure 1. Absorption spectra of a 55-atom icosahedral silver nanoparticle obtained with RT-TDDFTB. A prominent plasmon resonance peak is observed around 3.23 eV.

With the energy of a single Ag nanoparticle (NP) characterized, we proceeded with an analysis of energy transfer in plasmonic NP assemblies, each containing 8 Ag NPs and with varying interparticle spacings (ranging from 5 to 0.5 Å). All of these chains are extremely large systems with each containing a total of 440 atoms, as shown in **Fig. 2**. To simulate energy transfer along the NP chains, we excite only the first Ag NP in the chain using a monochromatic laser with an energy equal to the plasmonic resonance energy of a single Ag NP (3.23 eV), and the entire system is allowed to evolve in time via the RT-TDDFTB propagation. To quantify the energy-transfer efficiency along the chain, we computed the electric field intensities, $I \propto |\mathbf{E}|^2$, where $\mathbf{E}$ is the total electric field between each of the NPs along the axial direction of the chain. We have chosen this metric of computing electric field intensities along the NP chain since this allows a direct comparison of energy transfer efficiencies that were used in previous studies. **Fig. 3** on the following page shows the trends in the intensities of the NP chains with interparticle distances ranging from 0 to 5 Å. From the trends in **Fig. 3**, we observed a monotonic

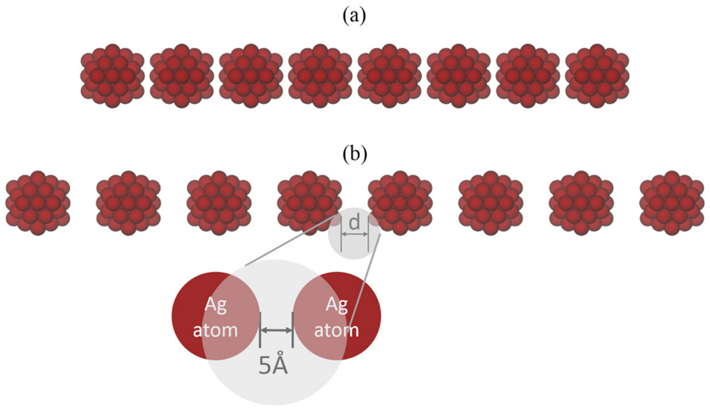


Figure 2. Pictorial representation of two of the nanoparticle chains with interparticle (edge-to-edge) distances equal to (a) 1 Å and (b) 5 Å.

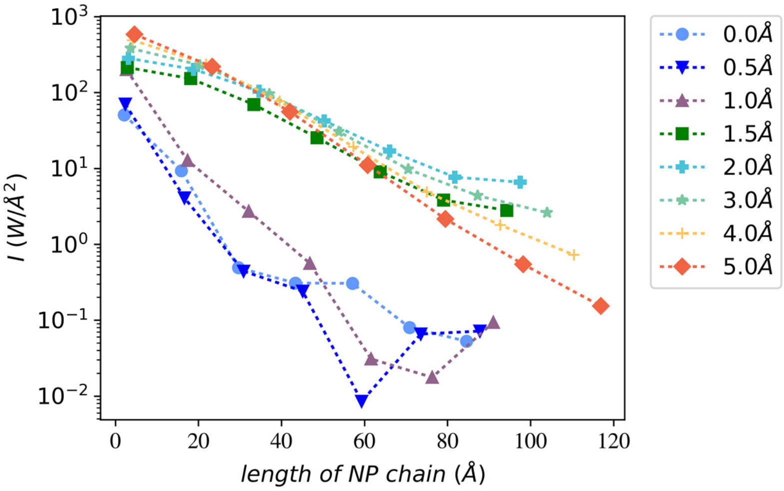
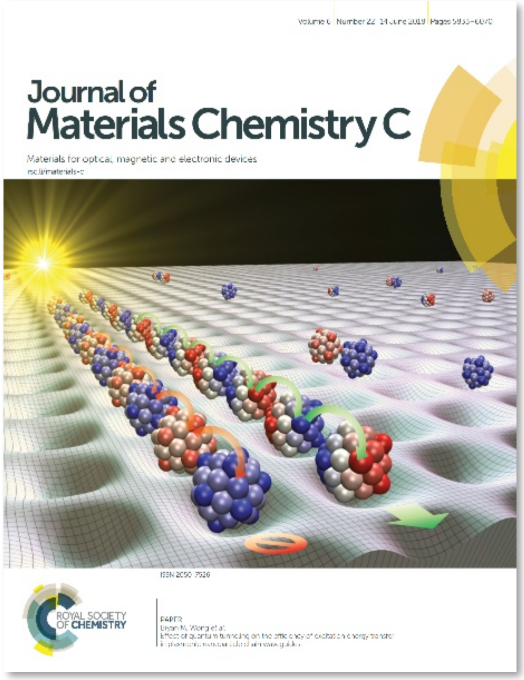


Figure 3. Field intensities along silver NP chains with varying interparticle distances. The first nanoparticle in each of the chains is excited at the plasmon resonance energy, and the intensity values are computed at the interparticle gaps of the NPs as shown in Figure 2. The excitation energy used in the simulation is equal to the plasmon resonance energy of the single Ag nanoparticle. A drastic drop in the field intensity is seen for Ag chains with interparticle spacings less than 2 Å.

increase in energy transfer efficiency (i.e. the slope of the intensity lines and transmission loss factor both decrease) as the interparticle distance is reduced from 5 Å to about 2 Å. This result is in qualitative agreement with results obtained by previous studies on similar systems using classical electrodynamic methods and can be attributed to an increase in capacitive coupling between the Ag NPs as the interparticle distance between them is reduced. This phenomenon is analogous to a charged capacitor, where the capacitance of a capacitor increases as the charged plates are brought closer together. However, as the interparticle distance is further reduced below 2 Å, we observed an opposite trend – a sudden drop in energy-transfer efficiency occurs for interparticle distances below 2 Å (i.e. the slope of the intensity line increase), which is qualitatively opposite to what has been predicted by previous computational studies. Specifically, previous studies have observed a decrease in energy transfer when the interparticle distance is reduced to a distance where the NPs directly touch each other. In contrast, we observe a decrease in energy-transfer efficiency even before the instance when the NPs touch each other. We attribute this decrease to competing mechanisms between a Bonding Dipole hybridized Plasmon (BDP) and another hybridized plasmon mode, the Charge Transfer Plasmon (CTP). In short, at subnanometer interparticle spacings, the hybridized BDP allows for a small charge transfer between NPs and, therefore, reduces the capacitive coupling between the NPs. Going back to the capacitor analogy used previously, this is analogous to a leaking capacitor which reduces the overall efficiency of the entire antenna (and, more importantly, cannot be predicted by classical approaches). Consequently, our study has two important ramifications on EET in plasmonic nanosystems: (1) while classical methods based on solving Maxwell's equations have long been used to analyze a variety of nanoantenna systems, our findings


Journal of
Materials Chemistry C
Materials for optical, magnetic and electronic devices
rsc.li/materials-c

ISSN 2050-7526

ROYAL SOCIETY OF CHEMISTRY

PAPER
Bryan M. Wong et al.

show that the inclusion of quantum effects has a nontrivial effect on EET dynamics, especially in plasmonic nanoantennas with subnanometer interparticle spacings, and (2) decreasing the interparticle spacing beyond a certain limit may not have the intended effect of increasing EET efficiency and, therefore, a more careful consideration of other strategies may be necessary in improving energy transfer in plasmonic devices fabricated with subnanometer dimensions. This work was prominently featured as a front cover of the *Journal of Materials Chemistry C*.

3. Future Plans

We intend to focus most of our attention to massive parallelization of our real-time approach (with new computational hardware that may replace GPUs) for calculating the electron structure and dynamics of large chemical systems. In addition, two manuscripts detailing our progress in (1) computational parallelism and (2) self-interaction corrections have already been submitted and are undergoing peer review. This DOE Grant has supported 2 Postdoctoral Associates, 3 PhD students, and 2 MS students.

Grant Number and Title: DE-SC0016269: **"***Non-Empirical and Self-Interaction Corrections for DFTB: Towards Accurate Quantum Simulations for Large Mesoscale Systems***"**

Postdoc: Dr. Fredy W. Aquino and Dr. Ravindra Shinde
Students: Mr. Jose Rodriguez Borbon, Ms. Lihua Xu, Mr. Niranjan Ilawe, Ms. Sangavi Pari, and Ms. Lindsey N. Anderson

Publications acknowledging DOE grant in the last 30 months:

1. A. A. Barragan, N. V. Ilawe, L. Zhong, B. M. Wong, and L. Mangolini, *"A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles."* *Journal of Physical Chemistry C*, **121**, 2316 (2017).
2. S. Pari, I. A. Wang, H. Liu, and B. M. Wong, *"Sulfate Radical Oxidation of Aromatic Contaminants: A Detailed Assessment of Density Functional Theory and High-Level Quantum Chemical Methods."* *Environmental Science: Processes & Impacts*, **19**, 395 (2017). **(Cover Article & Invited Paper)**
3. L. N. Anderson, M. B. Oviedo, and B. M. Wong, *"Accurate Electron Affinities and Orbital Energies of Anions from a Non-Empirically Tuned Range-Separated Density Functional Theory Approach."* *Journal of Chemical Theory and Computation*, **13**, 1656 (2017).
4. N. V. Ilawe, M. B. Oviedo, and B. M. Wong, *"Real-Time Quantum Dynamics of Long-Range Electronic Excitation Transfer in Plasmonic Nanoantennas."* *Journal of Chemical Theory and Computation*, **13**, 3442 (2017).
5. L. N. Anderson, F. W. Aquino, A. E. Raeber, X. Chen, and B. M. Wong, *"Halogen Bonding Interactions: Revised Benchmarks and a New Assessment of Exchange vs Dispersion."* *Journal of Chemical Theory and Computation*, **14**, 180 (2018).
6. N. V. Ilawe, M. B. Oviedo, and B. M. Wong, *"Effect of Quantum Tunneling on the Efficiency of Excitation Energy Transfer in Plasmonic Nanoparticle Chain Waveguides."* *Journal of Materials Chemistry C*, **6**, 5857 (2018). **(Cover Article)**
7. F. W. Aquino and B. M. Wong, *"Additional Insights between Fermi-Löwdin Orbital SIC and the Localization Equation Constraints in SIC-DFT"* *Journal of Physical Chemistry Letters*, **9**, 6456 (2018).
8. L. Xu, A. Kumar, and B. M. Wong, *"Linear Polarizabilities and Second Hyperpolarizabilities of Streptocyanines: Results from Broken-Symmetry DFT and New CCSD(T) Benchmarks"* *Journal of Computational Chemistry*, **39**, 2350 (2018). **(Cover Article)**
9. Z. A. Ali, F. W. Aquino, and B. M. Wong, *"The Diamine Cation is Not a Chemical Example where Density Functional Theory Fails"* *Nature Communications*, **9**, 4733 (2018).

Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC)

Sotiris S. Xantheas,[1] Edoardo Aprà,[1] Anne Chaka,[1] Wibe de Jong,[2] Thom H. Dunning, Jr.,[3]
Niranjan Govind,[1] So Hirata,[4] Sriram Krishnamoorthy,[1] Karol Kowalski,[1] Xiaosong Li,[3]
John J. Rehr,[3] Chao Yang,[2] Dominika Zgid[5]

[1] Pacific Northwest National Laboratory
[2] Lawrence Berkeley National Laboratory
[3] University of Washington
[4] University of Illinois at Urbana-Champaign
[5] University of Michigan

Abstract

The Center's **objectives** are (1) developing new approaches for describing the valence- and core-level excited states of complex molecular systems and their local environment based on accurate and scalable electronic structure methods for highly correlated systems; (2) delivering scalable, open-source libraries that are interoperable with other community electronic structure codes; (3) fully utilizing the unique computational resources at DOE's leadership class computing centers to advance scientific discovery at BES light sources; (4) engaging the basic energy sciences community to provide input on the development of open-source libraries and experimental data that can be used to validate them.

Accomplishments:

- **Coupled-Cluster Green's Function (GFCC):** We have developed iterative formulations for the cost-effective inclusion of triple excitations in GFCC. These new approximations can be categorized as GFCC-i(*n*, *m*) methods, where the excitation level of the inner auxiliary operators (*m*) used to describe the ionization potentials and electron affinities effects in the N−1 and N+1 particle spaces is higher than the excitation level (*n*) used to correlate the ground-state CC wave function for the N-electron system. Rigorous criteria, the so-called "*n*+1" conditions, were introduced to assure the size-extensivity of the corresponding GF. The GFCC-i(2,3) formalism was found to exhibit better agreement with the experimental and other theoretical results, particularly in terms of providing higher resolution of satellite peaks compared to the standard GFCC approximation with singles and doubles.
- **Model-Order-Reduction (MOR)** techniques were successfully implemented in the GFCC framework. For a frequency regime of interest, instead of solving the GFCC linear equations of full dimension for every single frequency point, an efficiently solvable linear system model of a reduced dimension may be built upon projecting the original GFCC linear system onto a subspace. From this a reasonable approximation to the full dimensional GFCC linear equations in both interpolative and extrapolative spectral regions was obtained. The subspace can be properly constructed from the auxiliary vectors of the GFCC equations at selected frequencies in the spectral region of interest.
- **Monte Carlo explicitly correlated second-order many-body Green's function method:** A highly scalable stochastic algorithm was proposed and implemented for computing the basis-set-incompleteness correction to the diagonal, frequency-independent self-energy of the second-order many-body Green's function (MC-GF2) theory within the explicitly correlated (F12) formalism. The 6-, 9-, 12-, and 15-dimensional integrals comprising the F12 correction are directly evaluated by the Monte Carlo method using appropriate weight functions for importance sampling. The method is easily parallelized, involves minimal memory space and no disk I/O, and can use virtually any mathematical form of a correlation factor. Its computational cost to correct all ionization energies increases as the fourth power of system size, as opposed to the fifth power of the deterministic counterpart.
- **Monte Carlo third-order many-body Green's function method:** We fully developed the MC-GF*n* methods with the following enhancements: (i) The perturbation order is raised from two (MC-GF2) to

three (MC-GF3) by automatic diagram generation, algebraic translation, and implementation into a CPU/GPU parallel code; (ii) The imaginary-time integrations are performed by a non-Metropolis Monte Carlo method with a speedup by a factor of 400 relative to the quadrature in previous implementations; (iii) The diagonal and frequency-independent approximations to the self-energy are lifted; (iv) The efficiency of the redundant-walker convergence acceleration is analyzed numerically, and the cost scaling with size of MC-GF3 is shown to be favorable as compared with the deterministic algorithms.

- **Grid-based diffusion Monte Carlo for fermions:** By confining the real-space electron walkers to evenly-spaced grid points and allowing positively- and negatively-valued walkers on these grid points to meet and annihilate one another, we lifted the fixed-node approximation in the diffusion Monte Carlo (DMC) method. An application of this method to the helium atom in the singlet and triplet ground states showed that the respective energy systematically approaches within 15 mE_h of the correct values as we make the grid spacing smaller and the imaginary-time interval shorter.
- **Finite-temperature many-body perturbation theory:** (i) We obtained the benchmark numerical data for the several lowest-order many-body perturbation corrections to the grand potential, internal energy, chemical potential, and entropy in the grand canonical ensemble for electrons that maintains the charge neutrality as a basic tenet of electronic thermodynamics. We showed that the textbook many-body perturbation theory gives results that deviate from these benchmark data and is incorrect. Punit Jha received an IBM-Löwdin Award from the 2019 Sanibel Symposium for this work. (ii) We derived analytical formulas for the first-order perturbation corrections in a time-independent and non-diagrammatic method which reproduce the benchmark data numerically exactly.
- **Gaussian basis set implementation of the GW formalism for molecular & nano-systems:** We have implemented a Gaussian basis set based resolution-of-identity (RI) GW (“one-shot” G0W0 and evGW) method in a standalone pilot code. We have successfully tested its validity against the MolGW and CP2K implementations for a series of small molecules for both core and valence states. Our algorithm utilizes the contour deformation technique to calculate the self-energy on a real frequency grid, alleviating the need to perform analytic continuation. The latter is crucial for accurate treatment of the core states within GW as analytic continuation methods fail to reproduce complicated structure of the self-energy in the core region. We have demonstrated that the multi-solution behavior of the inverse Dyson equation for core states can be tackled by searching for the quasiparticle energies corresponding to the largest pole strengths.
- **1-particle Green's function from Coupled Cluster (CC)** was developed based on the non-hermitian Lanczos algorithm. In this method, the scaling does not depend on the number of frequency points and no divergences near the poles appear. We have tested the applicability of the CCSD Green's function in the weak and strong coupling limit by employing it for the half-filled 1-D Hubbard model projected onto a single site impurity problem and the half-filled 2-D Hubbard model projected onto a 4-site impurity problem. For the 1-D Hubbard at weak to medium interaction strength, we see an excellent agreement with the full configuration interaction (FCI) results. For the 2-D Hubbard, where an open-shell version of the current implementation was employed, we observed few notable discrepancies from FCI results.
- **Software for excited states and spectroscopy:** We developed a real-time module for the propagation of single-particle states with a general, time-dependent Hamiltonian. The method overcomes limitations of previous approaches and has linear scaling. Additionally, an approach based on the Kadanov-Baym equations for non-linear response in the cumulant expansion for core hole photoemission was developed. Finally, a perturbation theoretical approach to the exact CCGF was developed. We demonstrated that the second-order approximation to the CCGF is nearly equivalent to the Dyson equation with a second order self-energy, and also to the retarded cumulant expansion of Kas and Rehr.
- **Embedding Non-Collinear Two-Component Electronic Structure in a Collinear Quantum Environment:** We have developed a computational framework to embed nonrelativistic, two-

component calculations in a one-component environment. In this framework, both embedding scalar potential and magnetic field can be included to describe the interaction between quantum subsystems. In this current development generalized Kohn-Sham density functional theory electronic structure is embedded in unrestricted Kohn-Sham density functional theory. The formalism developed herein may serve as a useful tool in the modeling of X-ray absorption feature of defects in extended systems.

- **ASCI integration coupled to the MSCF code and parallel scalability:** The implementation is being used to explore Fe-S and FeMoCo complexes. The ASCI code is being restructured into an easily integretable C++ module with call backs for a matrix element builder from an electronic structure code. In addition, we're exploring optimal choices for the ASCI solver, enabling a scalable parallel sparse diagonalization (current implementation is serial) and building an iterative Davidson solver to explore determinant spaces that cannot be tackled with direct diagonalization.
- **Multireference SCGVB(NO)+1+2 Configuration Interaction Method:** We explored the accuracy and limitations of the Spin-Coupled Generalized Valence Bond (SCGVB), recast as a multiconfiguration wavefunction in terms of orthogonal natural orbitals (NOs) and used in multireference (MRCI, MRCC) calculations and compared the results with those of the corresponding CASSCF+1+2 calculations for a broad range of molecular systems. Initial results are quite encouraging.
- **Website: spec.labworks.org:** provides a SPEC project overview, listing of events, presentations, publications, research team members and partners, and the Scientific Advisory Committee.

Future plans:

- Development of time-dependent CC formulation of the GF formalism, derivation and implementation of cumulant Green's function expansion directly from the CC expansion for the time domain.
- Development of self-energy embedding algorithms integrating second-order self-energy with CC self-energy calculated for the valence region.
- Development of parallel implementations of the EOM-CCSD gradients and GF-CCSD formalisms.
- Development of MC-MP4. MP4 has comparable accuracy as "gold-standard" CCSD(T) and its scalable, stochastic implementation marks an important milestone in the development of the MC-MP*n* series. An even more powerful convergence acceleration than the redundant-walker algorithm is required to make MC-MP4 viable. MC-MP2 and MC-GF2 for correlation energy and quasiparticle energy bands of three-dimensional solids will also be developed.
- The grid-based DMC will be upgraded to a more physically motivated real-space grid, such as Becke's radial-spherical grid. We will explore grid-based DMC-like implementations of MP2, CCD, and CCSD, without a fixed-node approximation.
- The derivation of analytical formulas for the second-order perturbation corrections at a finite temperature is underway, with the sum-over-states formulas already derived and numerically verified. We will derive reduced formulas given in terms of molecular integrals, and then seek a linked-diagram theorem in a time-independent, non-Matsubara-Green-function picture.
- Development of scalable implementation of the GW formalism exploring RI approximations as well as virtual space truncation schemes to reduce the computational cost and enable large scale applications. This will form the basis for the Bethe-Salpeter equation (BSE) implementation.
- Utilization of the CCSD and CCSD(T) Green's functions both for embedded and embedding method in SEET and test in molecules displaying strong correlations. Employ SEET with CCSD as a solver for the treatment of molecular crystals.
- Real-time approaches to CCGF methods that are complementary to the frequency space CCGF methods will be jointly developed with PNNL since this approach involves similar Feynman diagrams. We aim to develop a time-dependent approach analogous to the coupled clusters (CC) approximation for the ground state wave-function. This is based on a real time CC-EOM approach and yields a

cumulant representation of the CCGF. Alternative determinantal methods will also be developed to obtain the x-ray absorption spectra using a convolution of a one-body spectrum with the core-hole spectral function.

- Development of relativistic time-dependent equation-of-motion coupled-cluster method (TD-EOM-CC) for valence excitations and extension of relativistic EOM-CC and relativistic embedding methods to studies of X-ray absorption spectroscopy.
- The webpage will provide links to and instructions for the SPEC libraries as soon as they are released. The User Group will be ramping up as the libraries become available. The core group will be expert theorists who can incorporate the SPEC libraries into their code, or code they are already using (e.g. NWChemEx, QCHEM, GAMESS, CFOUR). This group will be invited to attend the annual SPEC User/Development meeting this fall. In addition, we actively maintain contact with the light sources and will organize a symposium in the upcoming SLAC Users annual meeting (Sept. 2019).

Postdocs: Avijit Shee, Jun Zhang, Alexander Kunitsa, Lu T. Xu, David Williams-Young, Chad Hoyer, Bo Peng, Nicholas Bauman, Erdal Mutlu

Students: Alexander E. Doran; Cole M. Johnson; Punit K. Jha, Jasper V. K. Thompson, Lauren Koulias

Selected Publications (since 1 Oct. 2017)

1) J. Warneke, G.-L. Hou, E. Aprà, C. Jenne, Z. Yang, Z. Qin, K. Kowalski, X.-B. Wang and S. S. Xantheas, “Electronic Structure and Stability of $(B_{12}X_{12})^{2-}$ (X = F – At): A Combined Photoelectron Spectroscopic and Theoretical Study”, *Journal of the American Chemical Society* **139** (41), pp. 14749–14756 (2017); https://doi.org/10.1021/jacs.7b08598

2) K. Kowalski, “Properties of coupled-cluster equations originating in excitation sub-algebras”, *The Journal of Chemical Physics* **148** (9), 094104 (2018); https://doi.org/10.1063/1.5010693

3) B. Peng and K. Kowalski, “Green’s Function Coupled-Cluster Approach: Simulating Photoelectron Spectra for Realistic Molecular Systems”, *Journal of Chemical Theory and Computation* **14** (8), pp. 4335–4352 (2018) https://doi.org/10.1021/acs.jctc.8b00313

4) C. M. Johnson, A. E. Doran, S. L. Ten-no, and S. Hirata, “Monte Carlo explicitly correlated many-body Green’s function theory”, *The Journal of Chemical Physics* **149** (17), 174112 (2018) https://aip.scitation.org/doi/10.1063/1.5054610

5) J. Zhang, “Origins of the enantioselectivity of a palladium catalyst with BINOL–phosphoric acid ligands”, *Organic & Biomolecular Chemistry* **16** (43), pp. 8064–8071 (2018) https://doi.org/10.1039/C8OB02271B

6) K. Kowalski, J. Brabec, .B Peng, "Regularized and Renormalized Many-body Techniques for Describing Correlated Molecular Systems: A Coupled-Cluster Perspective", *Annual Reports in Computational Chemistry*, volume 14, 1st Edition, Elsevier, pp. 3–45 (2018) https://www.elsevier.com/books/annual-reports-in-computational-chemistry/dixon/978-0-444-64116-8

7) B. Peng and K. Kowalski, "Green's function coupled cluster formulations utilizing extended inner excitations", *The Journal of Chemical Physics* **149** (21), 214102 (2018) https://doi.org/10.1063/1.5046529

8) M. Mayer, V. van Lessen, M. Rohdenburg, G.-L. Hou, Z. Yang, R. M. Exner, E. Aprà, V. A. Azov, S. Grabowsky, S. S. Xantheas, K. R. Asmis, X.-B. Wang, C. Jenne, J. Warneke, “Rational design of an argon-binding superelectrophilic anion”, *Proceedings of the National Academy (USA)* **116** (17), pp. 8167-8172 (2019) https://doi.org/10.1073/pnas.1820812116

9) L. T. Xu, J. V. K. Thompson, T. H. Dunning Jr., "Spin-Coupled Generalized Valence Bond Description of Group 14 Species: The Carbon, Silicon and Germanium Hydrides, XH_n (n = 1–4)", *Journal of Physical Chemistry A*, **123** (12), pp 2401–2419 (2019) https://doi.org/10.1021/acs.jpca.9b00376

10) B. Peng, R. van Beeumen, D. B. Williams-Young, K. Kowalski, C. Yang, "Approximate Green's Function Coupled Cluster Method Employing Effective Dimension Reduction" *Journal of Chemical Theory and Computation* ASAP article (2019) https://doi.org/10.1021/acs.jctc.9b00172

Arun Yethiraj

Polymers in deep eutectic solvents

Arun Yethiraj

University of Wisconsin-Madison

Abstract

Deep eutectic solvents (mixture of choline chloride and urea) have emerged as an exciting class of green solvents. They are obtained from natural sources, are inexpensive, and their properties are highly tunable. Incorporating these solvents into a polymer matrix via phase separation (followed by crosslinking the polymer) would allow for the creation of materials with the desired solvent properties. The goal of the project is to obtain the phase behavior of polymers in deep eutectic solvents.

We have calculated the phase diagram of PEO in the ionic liquids [BMIM][BF$_4$] and [BMMIM][BF$_4$]. In previous work, we had developed a new method for determining, from computer simulations, the phase behavior of mixtures of complex fluids. The method relied on simulating a large box with the coexisting phases and an interface, and using a concentration correlation function to align the interface from different snapshots, thus obtaining the coexisting concentrations and the phase diagram. The method is successful far from the critical point. We are evaluating machine learning methods to obtain the phase diagram closer to the critical point.

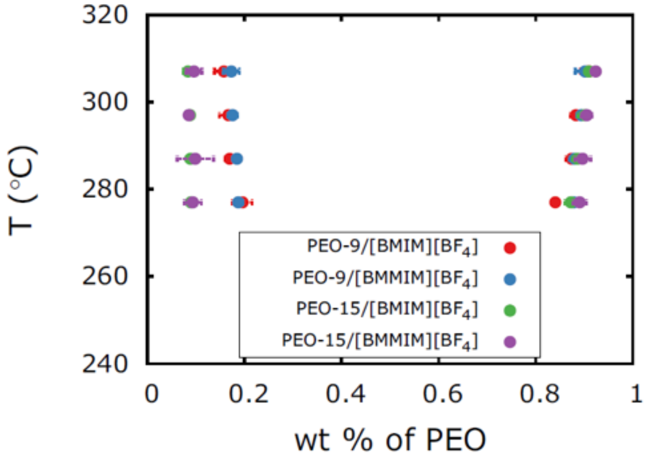


Figure 1: Phase behavior of PEO (9-mer and 15-mer) in the ionic liquids [BMIM][BF$_4$] and [BMMIM][BF$_4$]

We have developed ab initio force fields for choline chloride and urea. The resulting force fields are not accurate, however, for the mixture (when compared to first principles molecular dynamics simulations). We are including additional sites into the molecular model to improve the transferability of the force fields.

The proposed research has three goals. The first goal is to obtain fully atomistic polarizable force fields for choline chloride and urea (from first principles calculations), and coarse-grain these to obtain united atom force fields. The second goal is to obtain a force field for poly (ethylene oxide) (PEO) in this solvent. The third goal is to combine these to obtain the phase behavior of PEO in deep eutectic solvents, for a range of solvent compositions. The fourth goal is to study ion and charge transport in the solutions and thin films.

DE-SC0017877

Polymers in deep-eutectic solvents

Student(s): Hyun-Tae Jung and Kyeong-Jun Jeong

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

1. J. G. McDaniel, C.-Y. Son, and A. Yethiraj, "Ab Initio Force Fields for Organic Anions: Properties of [BMIM][TFSI], [BMIM][FSI], and [BMIM][OTf] Ionic Liquids", *J. Phys. Chem. B* **122**, 4101-4114 (2018).
2. H.-T. Jung and A. Yethiraj, "A simulation method for the phase diagram of complex fluid mixtures", *J. Chem. Phys.* **148**, 244903 (2018).
3. C.-Y. Son, J. G. McDaniel, Q. Cui, and A. Yethiraj, "Conformational and Dynamic Properties of Poly(ethylene oxide) in [BMIM][BF_4] : A Microsecond Computer Simulation Study Using First Principles-Based Force Fields, *Macromolecules* **51**, 5336-5345 (2018).

ECC: Exascale Computational Catalysis

David H. Bross,[1] Eric Bylaska,[2] C. Franklin Goldsmith,[3] Habib N. Najm,[4] Eric T. Phipps,[5]
Branko Ruscic,[1] Cosmin Safta,[4] Khachik Sargsyan,[4] Christian R. Trott,[5] Richard H. West,[6] Judit Zádor[4,*]

[1]*Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL*
[2]*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA*
[3]*School of Engineering, Brown University, Providence, RI*
[4]*Combustion Research Facility, Sandia National Laboratories, Livermore, CA*
[5]*Center for Computing Research, Sandia National Laboratories, Albuquerque, NM*
[6]*Department of Chemical Engineering, Northeastern University, Boston, MA*

Program Scope

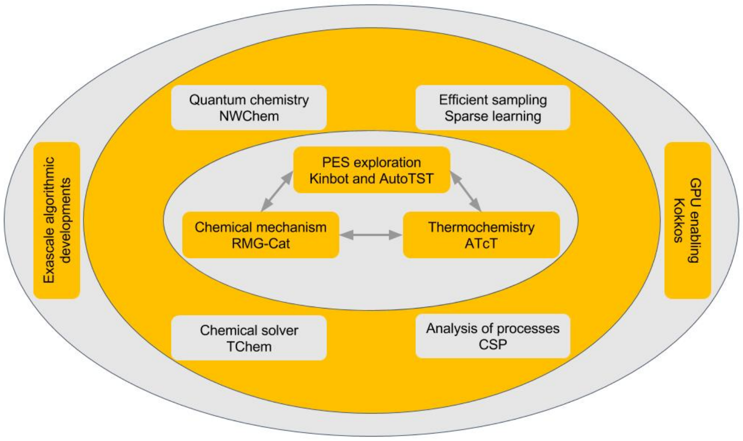
Heterogeneous catalysis is a crucial part of the modern economy, used to upgrade heavy fossil fuels, enable the partial reduction of bio-derived feedstocks, or convert small molecules, such as CO, CO_2 or methane, into larger and more valuable compounds. To achieve these goals most efficiently and selectively it is necessary to design and fine-tune catalysts and operating conditions through a combination of theory and modeling. Our work provides the necessary molecular-level understanding and quantitative description of chemical processes at the catalyst surface and in the gas phase above it to create an exascale enabled toolset for the broad research community to help design catalytic systems that can answer challenges of the 21st century, such as energy security and curbing global warming.

Our goal in this project is to create a computational framework that accelerates discovery and characterization of complex molecular systems. We are targeting coupled heterogeneous/gas-phase reactions and reaction mechanisms with relevance to catalytic conversion of hydrocarbons, oxygenates, and small molecules. We capitalize on recent improvements in theoretical chemistry, combined with improved mathematical software for solving complex problems, and with exascale-size supercomputers to develop a uniquely powerful chemical computational toolset for the research community.

We conduct three major thrusts of research supported by a diverse array of mathematical, software, and algorithmic tools. The hierarchy of the parts of the work is shown on the right. We define the three main areas as follows:

Automated reaction path exploration on multidimensional potential energy surfaces. Using advanced machine learning algorithms coupled to quantum chemistry code suitable for heterogeneous exascale architectures we develop codes that explore reaction pathways for elementary reactions. These algorithms automatically discover previously unknown elementary reaction classes and produce calculations on a large number of homologous systems to build up minable reaction databases.

Automated reaction mechanism generation for heterogeneous catalysis. We develop a complete computational infrastructure that generates reaction mechanisms for heterogeneous catalysis. This stores and recalls reactions and builds



---

[*] Project Director. Address: PO Box 969, Livermore, CA 94551; E-mail: jzador@sandia.gov

them into a mechanism that is able to predict macroscopic observables. Moreover, we solve the underlying kinetic equations efficiently, so that they allow for advanced mechanism analysis, reduction, and uncertainty quantification.

Advanced thermochemistry database. We create a modern, intelligent, user-friendly, and accurate thermodynamic database that is self-consistent and can be grown by us and the broader scientific community. For gas-phase systems we incorporate automatic state-of-the-art energy evaluations and anharmonic corrections and generate thermodynamic properties directly applicable in common kinetics codes, including ours. For heterogeneous systems, we implement methods beyond DFT to calculate energies, and novel approaches for entropy terms.

Recent Progress

The exhaustive exploration and characterization of the relevant elementary chemical pathways on the underlying potential energy surface is an extremely hard problem. Our main goals are to automate the discovery of new reactions pathways for catalytic reactions and generalize them into reaction families, and to rapidly evaluate reaction properties (barrier heights, transition state structures, etc.) for many homologous reactions and cast the resulting information into mineable data.

Our related goals at Sandia for Year 1 are to implement multimodal search algorithms, based on evolutionary or annealing algorithms, for gas-phase reactions, including search acceleration with sparse learning techniques demonstrated on small, gas-phase molecules. We have thus far implemented various established optimization algorithms for low-rank tensor approximations and tested them on simple molecular potential energy surfaces. We are working on extracting analytical Hessians and gradients from these approximations. We also tested several multimodal search algorithms, such as genetic algorithms and simulated annealing for critical point search, as well as implemented targeted saddle point search algorithms (e.g., dimer method), and worked on the parallelization of these codes. We coupled our codes to NWChem for scalability, but via the Atomic Simulation Environment (ASE) we will be able to couple with other electronic structure codes as well. We are also working on coupling these approaches with our heuristic KinBot code in order to further accelerate the search. The related work from Northeastern is described under ‘Future Plans’.

A major goal in catalysis is to predict the performance of novel materials. Accurate prediction of the reactivity and selectivity of catalytic materials requires a detailed list of elementary surface reactions, or a microkinetic mechanism. To this end, we want to enhance and extend RMG-Cat (Reaction Mechanism Generator for Heterogeneous Catalysis), recently developed at Northeastern and Brown, which builds microkinetic models for catalysis in an automated manner and couple RMG-Cat to our other software tools and databases. The immediate goals are outlined under ‘Future Plans.’

Thermochemistry is central to predicting and modeling the properties and behavior of matter. Some current challenges for accurate prediction are creating thermodynamically consistent datasets for a large number of chemical species and incorporating sufficiently rigorous calculations for entropy to allow reliable application of thermodynamic data under a wide temperature range. Over the course of the project we want to develop our Active Thermochemical Tables (ATcT) into a public and interactive database while preserving a strict control over accuracy, and incorporate into automated chemical mechanism calculations, enable the routine inclusion of anharmonic effects for gas-phase species, crucial for accurate entropy and create a suite of methods implemented into ASE to compute the partition function for the coupled, anharmonic motion of adsorbates relative to the catalyst surface.

Our Year 1 goals at Argonne are to create SQL databases for thermochemical networks and design a Non-Rigid Rotor Anharmonic Oscillator (NRRAO) code. Reference data was generated for small, three-atom systems to enable benchmarking of approximate methods of calculating anharmonic partition functions. The reference data for H_2O, HO_2, and $^3CH_2$ was created in collaboration with the Gas Phase Chemical Dynamics group at Argonne (Ruscic, Jasper, Wagner, Harding) from high accuracy potential energy surfaces that were solved using fully variational approaches methods to yield the vibrational energy levels and their computed partition functions. The reference partition functions generated in this work were well converged (~.1%) below 3000 K. The SQL database is being developed. The related planned work on adsorbate thermochemistry is outlined under 'Future Plans.'

NWChem is an open source computational chemistry code developed at PNNL. This is our main electronic structure code in this this project. Over the course of the project we want to create modern interfaces (e.g. web APIs) between NWChem and KinBot and ATcT, fully taking advantage of the GPU and MIC capabilities of NWChem and implement methods beyond DFT to treat heterogeneous catalytic systems.

Our Year 1 goals at PNNL is to add pathways optimization algorithms to NWChem Arrows, implement method of increments and dispersion corrections for surfaces. We created a molecular orbital viewing to EMSL Arrows and other, user-friendly web APIs (https://arrows.emsl.pnnl.gov/api/). Specifically, we added an automatic input generation capability in arrows that demonstrates the use of the bonding penalty function for mapping out reaction pathways or for getting initial pathway structures. We are currently working on implementing BEEF-vdW functional and testing it on molecules and surfaces.

At Sandia we are also developing a GPU-accelerated flexible chemical solver, called TChem++, applicable for catalysis and gas-phase chemistry, including a range of physical embeddings of the solver, e.g., plug flow reactor. Our Year 1 goals are to convert existing C utilities to C++ and add functionality for heterogeneous microkinetic models. Thus far we reviewed the sequence of computations and typical dimensions for various thermodynamic properties and reaction rate computations and added doxygen to the current C++ version. Currently we are working on the implementation of Kokkos structures to C++ class handling thermodynamic properties. In this context, we are exploring the efficiency of several memory layout models for a range of kinetic model sizes, from o(10) to o(10^3) species, and for both OpenMP and GPU-based computations.

Computational predictions from chemical systems computations are difficult to analyze, e.g. to assign cause-and-effect relationships and advance understanding, given the nonlinearity, stiffness, and intricate coupling among reaction processes. This is particularly so in results from large-scale computations with complex chemical systems. Accordingly, there is a strong need for analysis software tools that offer fast and effective capabilities tailored to the analysis of chemical systems. Our goals are to (a) build a GPU-enabled C++ chemical analysis software toolkit tailored for exascale architectures using Computational Singular Perturbation (CSP) and usable for analyzing both gas phase and catalytic chemical models (b) demonstrate effective performance on heterogeneous architectures and large scale chemical data, with both gas phase and catalytic chemical problems.

Our Year 1 goals are to develop the core C++ CSP library classes, providing a basic kernel of CSP operations. We have so far designed the high-level software architecture, defining essential classes and their key functionalities and extended the mathematical formulation of CSP analysis, beyond ODE/PDE systems to include DAE systems of relevance in catalytic systems. We are currently testing the CPU-GPU linear algebra package MAGMA eigensolvers on test matrices. The eigensolution of Jacobian matrices is the most computationally intensive element of the CSP analysis computational budget.

Future Plans

At Northeastern and Brown we had not received funding by the time of this abstract submission. However, we have a detailed plan for contributions as soon as the funds are received.

At Northeastern the goal for Year 1 in the first thrust of research is to improve, accelerate, and generalize the saddle point searches in our AutoTST code. We will create Python classes for molecules and transition states that allow the translation between RMG objects, RDKit objects, and ASE objects, with relative ease (e.g., preserving atom labeling), so that we can use RMG's graph methods and reaction generation, RDKit's distance geometry conformer embedding, and ASE's interface to electronic structure codes. Conformer generation via ASE in AutoTST will be tested, both with a brute force (rotate all the torsions in every combination) and some evolutionary strategies. We will also work on techniques using vibrational mode analysis instead of IRC for saddle point verification. Meanwhile, we will rewrite AutoTST as an independent project (that uses some RMG modules and classes) rather than being part of the core RMG codebase.

Our goals for Year 1 in the second thrust of research at Northeastern and Brown are to implement linear scaling relationships (LSR) and add reaction families, such as Eley-Rideal or bidentate, to RMG-Cat. We will implement LSR in RMG-Cat for binding energy estimation on a range of metals. We will test this on the catalytic combustion of methanol and generate new kinetic models for a range of metal surfaces. This reaction system will eventually be one of our test cases for the other tools; the catalytic partial oxidation of methane and natural gas coupled with gas phase chemistry will be the other one.

At Brown we will work on the theoretical aspects of adsorbate thermochemistry (third research thrust). The traditional approach to estimating the thermochemistry of adsorbates is to use the harmonic oscillator model. For each adsorbate, our new approach will separate the 6 modes of relative motion from the $3N$-6 internal vibrational modes in the partition function. The resulting $3N$-6 new vibrational modes will continue to be calculated using the quantum harmonic oscillator model, while the partition function for the remaining 6 degrees of freedom will be computed directly using classical statistical mechanics. At Brown the dynamics code originating from Argonne, called rotd (Klippenstein, Georgievskii) will be tested and adapted to calculate adsorbate thermochemistry and eventually to predict sticking coefficients. A major challenge is likely the calculation of the accurate energies during the sampling of the PES.

Our goals for the whole team are outlined in our original proposal, and are summarized below in the form of milestones.

	End of Year 1	**End of Year 2**	**End of Year 3**	**End of Year 4**
Automated reaction path exploration	Calculate reaction pathways for highly unsaturated on in other ways challenging gas-phase systems automatically and demonstrate generalization of search	Demonstrate capabilities on known heterogeneous reactions	Generate microkinetic model automatically where all tools demonstrate their individual capabilities as well as their coupling, performance, and scalability on heterogeneous architectures. Mechanism is generated with RMG-Cat, parameters are incorporated from KinBot, AutoTST, and ATcT, which drive NWChem directly or via Arrows. The kinetic ODE is solved with TChem and analyzed by CSP. Target test catalytic systems with coupled gas-phase and heterogeneous chemistry.	Create the ability to generate the building blocks of a kinetic Monte Carlo model of a heterogeneous catalytic system with the synchronized effort of the developed tools. Demonstrate ability on the same systems as listed in Year 3.
RMG-Cat	Generate model with linear scaling and gas-adsorbate reactions	Perform mechanism creation coupled to KinBot and AutoTST		
Thermo-chemistry	Release beta ATcT web version	Release beta version of ATcT on the web with thermo for high temperatures based on NRRAO		
NWChem	Arrows has new functionalities, and method of increments and dispersion corrections are functional	RPA is functional and surface interactions work in Arrows		
TChem	TChem can run RMG-Cat generated mechanisms off-line	Demonstrate direct coupling to RMG-Cat and ATcT and feasability on heterogeneous architectures		
CSP	Develop core CSP code classes	Develop full suite of CSP classes and batched mixed architecture eigensolver		

Grant Numbers and Grant Titles

Exascale-enabled computational tools for complex chemical systems

Postdoc(s): Eric Hermes (Sandia), Fazle Rob (Sandia), Rai Prashant (SNL, partial support)
Student(s): none currently

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

None so far, project started September 2017

ECC: EXASCALE COMPUTATIONAL CATALYSIS

David H. Bross,[1] Eric J Bylaska,[2] C. Franklin Goldsmith,[3] Kyungjoo Kim,[4] Habib N. Najm,[5] Eric T. Phipps,[4] Branko Ruscic,[1] Cosmin Safta,[6] Khachik Sargsyan,[5] Christian R. Trott,[4] Richard H. West,[7] Judit Zádor[5,*]

[1]*Chemical Sciences and Engineering, Argonne National Laboratory, Lemont, IL*
[2]*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA*
[3]*Chemical and Biochemical Engineering Department, Brown University, Providence, RI*
[4]*Center for Computing Research, Sandia National Laboratories, Albuquerque, NM*
[5]*Combustion Research Facility, Sandia National Laboratories, Livermore, CA*
[6]*Computational Science and Analysis, Sandia National Laboratories, Livermore, CA*
[7]*Chemical Engineering Department, Northeastern University, Boston, MA*

PROGRAM SCOPE

Heterogeneous catalysis is a crucial part of the modern economy, used to upgrade heavy fossil fuels, enable the partial reduction of bio-derived feedstocks, or convert small molecules, such as CO, CO_2 or methane, into larger and more valuable compounds. To achieve these goals most efficiently and selectively it is necessary to design and fine-tune catalysts and operating conditions through a combination of theory and modeling.

Our goal in the ECC project (https://ecc-project.sandia.gov/) is to create a computational framework that accelerates discovery and characterization of the complex molecular systems that govern heterogeneous catalysis. We are targeting coupled heterogeneous/gas-phase reactions and reaction mechanisms with relevance to catalytic conversion of hydrocarbons, oxygenates, and small molecules. We have three thrusts (Automated reaction path exploration on multidimensional potential energy surfaces; Automated reaction mechanism generation for heterogeneous catalysis; Advanced thermochemistry database) and an array of mathematical, software, and algorithmic tools that enable them.

RECENT PROGRESS

Development of Sella (https://github.com/zadorlab/sella) began in the summer of 2018 in order to facilitate the large number of saddle point optimizations that will be required by this project. Currently, Sella is capable of rapidly and efficiently optimizing saddle points of molecules, condensed systems, and heterogeneous catalyst systems. In order to avoid costly evaluation of the full Hessian matrix, Sella uses a novel iterative eigensolver that uses finite difference to approximate Hessian-vector products based on Jacobi-Davidson. These Hessian-vector products are also used to update an approximate Hessian matrix using a novel multi-secant TS-BFGS Hessian update method. This approximate Hessian is used both as a preconditioner to subsequent calls to the Jacobi-Davidson eigensolver and in our novel trust radius quasi-Newton geometry optimizer, which is able to converge to saddle points of arbitrary order. We have also systematically implemented constraints in such a way that the dimensionality of the optimization problem is reduced, which in turn improves efficiency and stability.

These developments have been implemented in Sella in an object-oriented way that separates the high-level task of finding a saddle point from the low-level task of finding the lowest curvature direction. New information obtained during optimization steps or iterative diagonalization steps is automatically incorporated into the approximate Hessian matrix. As a result, the code that performs the geometry optimization is extremely simple. We have tested Sella on a benchmark test suite of saddle point optimizations documented on the website optbench.org, and we achieved superior performance. We are also developing a benchmark test suite of molecular saddle point optimization using semi-empirical potential energy surfaces; Sella also performs very well on this benchmark.

---

[*] Project Director. Address: PO Box 969, Livermore, CA 94551; E-mail: jzador@sandia.gov

The combined groups of West and Goldsmith have made two major improvements to RMG-Cat. First, the accuracy of RMG-Cat's thermodynamic predictions is significantly improved. In collaboration with the research group of Prof. Felix Studt at the Karlsruhe Institute of Technology, density functional theory (BEEF-vdW) calculations were performed for 69 adsorbates on the Pt(111) surface. These adsorbates were chosen specifically to include every possible surface species that contains up to two heavy atoms in the HCNO system. This revision marks the first time that RMG-Cat is capable of handling nitrogen-containing adsorbates. Partition functions and subsequent thermodynamic properties were computed from the DFT properties. The new thermodynamic database will improve the accuracy of both small molecules as well as RMG-Cat's ability to estimate the thermochemistry of larger compounds. Second, RMG-Cat can pursue mechanism expansion simultaneously on both the surface and in the gas-phase. RMG-Cat can leverage the extensive library of gas-phase reaction families (currently upwards of 40+ distinct families) for homogeneous/heterogeneously coupled systems.

These two improvements have been demonstrated on the catalytic combustion of methane on platinum. The microkinetic mechanism that RMG-Cat generated was used within plug flow reactor simulations (via the open-source software Cantera). The results successfully confirm that under some operating conditions, the catalyst is capable of inducing light-off in the gas-phase. These results have been submitted for publication in Industrial & Engineering Chemistry Research (currently under review).

AutoTST, our code for automatically predicting transition state geometries and performing fully automated TST calculations of reaction rates, has been re-written as a stand-alone and extensible module, using classes and methods from RMG as needed, rather than being embedded within RMG. It now uses the Atomic Simulation Environment (ASE) interface, so is compatible with many electronic structure codes. Saddle points can now be confirmed to belong to the desired reaction using an analysis of the vibrational modes, rather than a (much more expensive) intrinsic reaction coordinate (IRC) calculation. Fully automated hindered rotor scans for 1D-HR corrections have been implemented for reactants and products, and is close to completion for transition states.

A current challenge for accurate thermodynamic predictions is the creation of a consistent dataset for a large number of chemical species that incorporates sufficiently rigorous estimates for thermophysical properties. We are expanding the Active Thermochemical Tables (ATcT, https://atct.anl.gov/) into a public and interactive database while preserving a strict quality control, and incorporate it into automated chemical mechanism calculations. A preliminary SQL database has been developed with current and prior versions of the thermochemical network being uploaded to it, and we have begun working on a front-end interface to enable external collaborator access. We have also contributed substantial improvements to the existing public ATcT website including a new interactive search functionality for queries of reaction enthalpies.

The motion of an adsorbate relative to the catalyst surface is a large amplitude motion (LAM). Anharmonic corrections to partition functions of non-rigid molecules or assemblies that undergo LAM are a particularly challenging case, as the degrees of freedom undergoing LAM are poorly approximated by a harmonic oscillator, even if NRRAO corrections are included, because the corrections assume that the energy levels can be adequately represented by a low order, $n \leq 3$, polynomial. Moreover, molecules containing two or more coupled LAM modes in most cases require explicit consideration of the PES containing all coupled LAM degrees of freedoms. We have implemented a code using the Colbert-Miller discrete variable representation approach to deal with two coupled LAM modes, and tested this approach on CH_2OH against more rigorous full dimensional (15D) solutions from Lanczos. This work was carried out in collaboration with the Gas Phase Chemical Dynamics groups at Argonne (Ruscic, Harding) and Brookhaven (Yu).

NWChem is an open source computational chemistry code developed at PNNL. This is our main electronic structure code in this this project. Over the course of the project we want to create modern interfaces (e.g. web APIs) between NWChem and KinBot and ATcT, fully taking advantage of the GPU and MIC capabilities of NWChem and implement methods beyond DFT to treat heterogeneous catalytic systems. In this period, we have updated the NWChem's plane-wave code. We implemented vdw-DF and vdw-DF2 dispersion functionals and various GGAs for catalysis, e.g. BEEF. The SCAN functional's implementation is nearing completion as well. We also updated fractional occupation optimizers and fixed various bugs for metallic systems.

Our web API, Arrows (https://arrows.emsl.pnnl.gov/api/) now has a web-based periodic builder written in Javascript (https://arrows.emsl.pnnl.gov/api/periodic). We also developed a web-based queue system that works with DOE HPC computers without the need for using protocols that rely on unsecure passwords storage. We also developed strategies for calculating first and second quantization of periodic 2-electron integrals. A manuscript titled, "Accurate Brillouin Zone Integration for Overlap, One-Electron, Two-Electron Integrals Involving Two Determinants", which describes the first quantization the strategy, is being prepared for publication.

We converted the gas-phase chemistry components of TChem (https://www.sandia.gov/tchem/), our chemical solver, from C to C++ and for performance portability to many-core and GPU-based architectures, we have interfaced TChem with Kokkos. We have completed GPU-enabled workflows for production rates and Jacobian matrix components and we are currently testing the implementation for a set of batch sizes and gas-phase kinetic models to identify performance bottlenecks. We have compared serial, OpenMP, and CUDA implementations and found that the OpenMP version is ~7 times and the CUDA version is ~130 times faster than the serial version of TChem.

We have also developed tools for handling micro-kinetic models necessary for heterogeneous catalysis models. We have developed a parser for Chemkin-format surface kinetic model specifications, and have implemented tools computing surface rate constants.

We have been building an object-oriented C++ library for computational singular perturbation (CSP) analysis of chemical models, including both gas phase and catalytic systems. The library design is flexible, allowing for analysis of general dynamical systems. We have assembled essential elements of the three key classes for the CSP library. The *Model* class provides functionality for defining model structure. The ODE implementation fundamental components are complete and functional. The *Kernel* class provides functionality for eigenanalysis, and the construction of the CSP basis vectors. Its default structure is complete. The *Index* class provides a variety of analysis capabilities for chemical systems, which is essentially complete.

Given that the primary computational cost in this context is the eigendecomposition of Jacobian matrices, we have also built a GPU-enabled batched eigensolver relying on Kokkos for handling data locality and CPU/GPU computational utilization in an exascale setting. Batched algorithms are useful for enhancing the efficiency and scaling of linear algebra implementations on massively parallel architectures.

FUTURE PLANS

Our primary immediate plan is to create a workflow that couples our tools. In the coming year we want achieve the following couplings: RMG-Cat – Sella – NWChem; KinBot – Sella – NWChem; Sella – FitPy; RMG-Cat – TChem – CSP; RMG-Cat – ATcT – NRRAO.

We are currently incorporating Sella into the workflow of KinBot (https://github.com/zadorlab/KinBot). This incorporation will enable direct coupling to NWChem and many other quantum chemistry codes, which will eventually give us access to GPU and exascale capabilities. We are also developing a new workflow using Sella to optimize saddle points for heterogeneous systems predicted by RMG-Cat. Achieving this requires both complex software engineering and the development of new methods.

We have initiated a software product, FitPy, that serves as a wrapper to established uncertainty quantification (UQ) and machine learning libraries, including UQTk, PyTorch, Keras, SciKit-Learn. The main task of FitPy is to perform surrogate approximation of functions (supervised machine learning), in order to approximate PES given an ensemble of configurations. We are exploring the merits of various surrogate forms, such as sparse polynomials or low-rank tensor expansions, as well as neural-networks of varying architectures. Furthermore, we are implementing adaptive workflows for on-the-fly surrogate construction to support Sella for saddle-point search, and to enable computationally intensive tasks that otherwise require infeasibly many PES evaluations, e.g. genetic algorithm search or related optimization tasks. The surrogate construction is augmented by the gradient computation to support requisite optimization or search algorithms.

At Brown we are working on the theoretical aspects of adsorbate themo. Our new approach will separate the 6 modes of relative motion from the $3N$-6 internal vibrational modes and for these degrees of freedom the partition function will be computed directly using classical statistical mechanics. At Argonne we are currently developing and testing a non-rigid-rotor anharmonic oscillator code that implements Wooley's expressions for generating an anharmonic partition function from an input set of constants.

We are merging RMG-Cat with the official master branch of RMG, so that it will be distributed to a much wider user base, will have many more developers maintaining it, and will benefit from many new features being developed in RMG, such as advanced model expansion algorithms and better gas-phase chemistry predictions. We are also adding new reaction families for Eley-Rideal reaction types, and an ability to treat bidentate adsorbates.

AutoTST is currently being debugged and tested on high-throughput calculation of thousands of gas-phase reactions. We anticipate that coupling with Sella will increase the performance and robustness of the saddle point searches. We will then extend it to attempt to predict transition state geometries on a catalyst surface.

We are developing the implementation of RPA in NWChem. Initial implementation of $O(N)$ DFT solver in NWChemEx is also underway.

We will be extending the microkinetic model capability in TChem to handle multiple surface sites. We will augment the range of physical models with a plug-flow reactor model. In the near term the plug-flow model discretization will be implemented and tested in a serial mode. In the longer term, this model will be parallelized and tailored to run on heterogenous computing platforms.

We are in the process of testing the batched eigensolver, in terms of accuracy and performance, relative to other existing libraries, allowing for a range of problem sizes of practical interest. The coupling of this eigensolver to the CSP *Kernel* class is work in progress.

Grant Numbers and Grant Titles: Exascale-enabled computational tools for complex chemical systems
Postdocs: Eric Hermes (SNL), Fazle Rob (SNL), Prashant Rai (SNL, past), Ruben Van de Vijver (SNL, past)
Students: Katrin Blondal (Brown), Emily Mazeau (Northeastern), Nate Harms (Northeastern), David Farina (Northeastern)

UP TO TEN PUBLICATIONS ACKNOWLEDGING THIS GRANTS IN THE LAST 3-4 YEARS

Published or in press

1. D. H. Bross, A. W. Jasper, B. Ruscic, and A. F. Wagner. Toward Accurate High Temperature Anharmonic Partition Functions. *Proc. Combust. Inst.* **37**, 315-322 (2019)
2. T. L. Nguyen, J. Thorpe, D. H. Bross, B. Ruscic, and J. F. Stanton. Unimolecular Reaction of Methyl Isocyanide to Acetonitrile: A High-Level Theoretical Study. *J. Phys. Chem. Lett.* **9**, 2532–2538 (2018)
3. D. H. Bross, H.-G. Yu, L. B. Harding, and B. Ruscic. Active Thermochemical Tables: The Partition Function of Hydroxymethyl (CH_2OH) Revisited, *J. Phys. Chem. A* (in press) (2019)
4. B. Ruscic and D. H. Bross, Thermochemistry. Chapter 1 in: *Mathematical Modeling of Complex Reaction Systems: Pyrolysis and Combustion*, T. Faravelli, F. Manenti, and E. M. Ranzi, Eds. Computer Aided Chemical Engineering Series, Vol. 45, Elsevier: New York (in press) (2019)
5. D. Feller, D. H. Bross, and B. Ruscic. Enthalpy of Formation of $C_2H_2O_4$ (Oxalic Acid) from High-Level Calculations and the Active Thermochemical Tables Approach, *J. Phys. Chem. A* (in press) (2019)

Submitted and currently under review

6. J. Thorpe, C. A. Lopez, T. L. Nguyen, J. H. Baraban, D. H. Bross, B. Ruscic, and J. F. Stanton. High-Accuracy Extrapolated ab initio Thermochemistry. IV. A Modified Recipe for Computational Efficiency, *J. Chem. Phys.* (submitted) (2019)
7. K. Blondal, J. Jelic, E. Mazeau, F. Studt, R. H. West, and C. F. Goldsmith. Computer-generated kinetics for coupled heterogeneous/homogeneous systems: A case study in catalytic combustion of methane on platinum, *Indust. Eng. Chem. Res.* (submitted) (2019)

2019 Computational and Theoretical Chemistry Research PI Meeting (CTC)
May 22 - 24, 2019
Participant List

Christine Aikens
Kansas State University
cmaikens@ksu.edu

Nandini Ananth
Cornell University
ananth@cornell.edu

Edwin Barnes
Virginia Technical Instiute
efbarnes@vt.edu

Tunna Baruah
University of Texas, El Paso
tbaruah@utep.edu

David Bross
Argonne National Laboratory
dbross@anl.gov

Vyacheslav Bryantsev
Oak Ridge National Laboratory
bryantsevv@ornl.gov

Eric Bylaska
Pacific Northwest National Laboratory
eric.bylaska@pnnl.gov

Roberto Car
Princeton University
rcar@princeton.edu

Marco Caricato
University of Kansas
mcaricato@ku.edu

Coray Colina
University of Florida
colina@chem.ufl.edu

Richard Dawes
Missouri University of Science and Technology
dawesr@mst.edu

Barry Dunietz
Kent State University
bdunietz@kent.edu

Francesco Evangelista
Emory University
francesco.evangelista@emory.edu

James Evans
Ames Laboratory/ISU
evans@ameslab.gov

Maria Victoria Fernandez-Serra
Stony Brook University
maria.fernandez-serra@stonybrook.edu

James Freericks
Georgetown University
james.freericks@georgetown.edu

Bruce Garrett
U.S. Department of Energy
bruce.garrett@science.doe.gov

Vikram Gavini
University of Michigan
vikramg@umich.edu

Eitan Geva
University of Michigan
eitan@umich.edu

Evelyn Goldfield
National Science Foundation
egoldfie@nsf.gov

C. Franklin Goldsmith
Brown University
franklin_goldsmith@brown.edu

Mark Gordon
Ames Laboratory/ISU
mgordon@iastate.edu

Niranjan Govind
Pacific Northwest National Laboratory
niri.govind@pnnl.gov

Jeffrey Greeley
Purdue University
jgreeley@purdue.edu

2019 Computational and Theoretical Chemistry Research PI Meeting (CTC)
May 22 - 24, 2019
Participant List

Anastasia Gunina
Ames Laboratory
gunina@ameslab.gov

Hua Guo
University of New Mexico
hguo@unm.edu

Sharon Hammes-Schiffer
Yale University
sharon.hammes-schiffer@yale.edu

Marcus Hanwell
Kitware
marcus.hanwell@kitware.com

John Herbert
Ohio State University
herbert@chemistry.ohio-state.edu

So Hirata
University of Illinois
sohirata@illinois.edu

Edward Hohenstein
SLAC National Accelerator Laboratory
egh4@slac.stanford.edu

Hrant Hratchian
University of California, Merced
hhratchian@ucmerced.edu

Geoffrey Hutchison
University of Pittsburgh
geoffh@pitt.edu

Christine Isborn
University of California, Merced
cisborn@ucmerced.edu

Koblar Jackson
Central Michigan University
jacks1ka@cmich.edu

Seogjoo Jang
CUNY Queens College
sjang@qc.cuny.edu

Lasse Jensen
Pennsylvania State University
jensen@chem.psu.edu

Karl Johnson
University of Pittsburgh
karlj@pitt.edu

Sabre Kais
Purdue University
kais@purdue.edu

Abdelkader Kara
University of Central Florida
abdelkader.kara@ucf.edu

Shiv Khanna
Virginia Commonwealth University
snkhanna@vcu.edu

KAROL KOWALSKI
Pacific Northwest National Laboratory
karol.kowalski@pnnl.gov

Henry Krakauer
College of William & Mary
hxkrak@wm.edu

Jeffrey Krause
U.S. Department of Energy/BES
Jeff.Krause@science.doe.gov

Heather Kulik
Massachusetts Institute of Technology
hjkulik@mit.edu

Jerzy Leszczynski
Jackson State University
Jerzy@icnanotox.org

Benjamin Levine
Michigan State University
levine@chemistry.msu.edu

James Lewis
West Virginia University
james.p.lewis.phd@gmail.com

2019 Computational and Theoretical Chemistry Research PI Meeting (CTC)
May 22 - 24, 2019
Participant List

Xiaosong Li
University of Washington
xsli@uw.edu

Da-Jiang Liu
Ames Laboratory
dajiang@ameslab.gov

Thomas Markland
Stanford University
tmarkland@stanford.edu

Nicholas Mayhall
Virginia Technical Instiute
nmayhall@vt.edu

Alexander Mebel
Florida International University
mebela@fiu.edu

Andrew Medford
Georgia Institute of Technology
ajm@gatech.edu

Thomas F. Miller
California Institute of Technology
tfm@caltech.edu

Raul Miranda
U.S. Department of Energy/BES
raul.miranda@science.doe.gov

Sona Najafi
Virginia Technical Instiute
najafisona@vt.edu

Eric Neuscamman
University of California, Berkeley
eric.neuscamman@gmail.com

Serdar Ogut
University of Illinois, Chicago
ogut@uic.edu

Francesco Paesani
University of California, San Diego
fpaesani@ucsd.edu

Athanassios Panagiotopoulos
Princeton University
azp@princeton.edu

Kyungwha Park
Virginia Technical Instiute
kyungwha@vt.edu

John Pask
Lawrence Livermore National Laboratory
pask1@llnl.gov

Michele Pavanello
Rutgers University, Newark
m.pavanello@rutgers.edu

Mark Pederson
U.S. Department of Energy/BES
mark.pederson@science.doe.gov

Juan Peralta
Central Michigan University
juan.peralta@cmich.edu

John Perdew
Temple University
perdew@temple.edu

Andrew Peterson
Brown University
andrew_peterson@brown.edu

Piotr Piecuch
Michigan State University
piecuch@chemistry.msu.edu

Andrew Rappe
University of Pennsylvania
rappe@sas.upenn.edu

Brenda Rubenstein
Brown University
brenda_rubenstein@brown.edu

Adrienn Ruzsinszky
Temple University
aruzsinszky@temple.edu

2019 Computational and Theoretical Chemistry Research PI Meeting (CTC)
May 22 - 24, 2019
Participant List

Biswajit Santra
Temple University
biswajit.santra@temple.edu

Sapna Sarupria
Clemson University
ssarupr@g.clemson.edu

Henry Schaefer
University of Georgia
ccq@uga.edu

George Schatz
Northwestern University
g-schatz@northwestern.edu

Gregory Schenter
Pacific Northwest National Laboratory
Greg.Schenter@pnnl.gov

Jordan Schmidt
University of Wisconsin, Madison
schmidt@chem.wisc.edu

Gustavo Scuseria
Rice University
guscus@rice.edu

Thomas Settersten
U.S. Department of Energy/BES
thomas.settersten@science.doe.gov

Ron Shepard
Argonne National Laboratory
shepard@tcg.anl.gov

Kevin Shuford
Baylor University
kevin_shuford@baylor.edu

J. Ilja Siepmann
University of Minnesota
siepmann@umn.edu

Wade Sisk
U.S. Department of Energy/BES
Wade.sisk@science.doe.gov

Ryan Steele
University of Utah
ryan.steele@utah.edu

David Strubbe
University of California, Merced
dstrubbe@ucmerced.edu

Joseph Subotnik
University of Pennsylvania
subotnik@sas.upenn.edu

Jianwei Sun
Tulane University
jsun@tulane.edu

Phanish Suryanarayana
Georgia Institute of Technology
phanish.suryanarayana@ce.gatech.edu

Ceren Susut
U.S. Department of Energy/ASCR
Ceren.Susut-Bennett@science.doe.gov

Donald Truhlar
University of Minnesota
truhlar@umn.edu

Zachary Ulissi
Carnegie Mellon University
zulissi@andrew.cmu.edu

Philip Wilk
U.S Department of Energy/BES
philip.wilk@science.doe.gov

Adam Willard
Massachusetts Institute of Technology
awillard@mit.edu

Angela Wilson
Michigan State University
akwilson@msu.edu

Bryan Wong
University of California, Riverside
bryan.wong@ucr.edu

2019 Computational and Theoretical Chemistry Research PI Meeting (CTC)
May 22 - 24, 2019
Participant List

Sotiris Xantheas
Pacific Northwest National Laboratory
sotiris.xantheas@pnnl.gov

David Yarkony
Johns Hopkins Univeristy
yarkony@jhu.edu

Arun Yethiraj
University of Wisconsin
yethiraj@wisc.edu

Judit Zádor
Sandia National Laboratories
jzador@sandia.gov

Dominika Zgid
University of Michigan
zgid@umich.edu

Rajendra Zope
University of Texas, El Paso
rzope@utep.edu