



# Computational and Theoretical Chemistry Virtual Summer Conference Series

Germantown, Maryland  
Summer 2020

## FOREWORD

Plans were already underway for the seventh annual CTC PI meeting scheduled for May 12-14, 2020 when it was canceled due to COVID-19. In response to the cancellation, a few PIs planted the seed of a virtual conference series as a viable alternative. Hence, here we are organizing the 2020 CTC Summer Conference Series. Using repurposed submitted abstracts originally for the PI meeting, we have organized a series of afternoon meetings scheduled to be held monthly over the summer of 2020. Despite the change in style, venue, format, and duration, we sincerely hope this virtual conference series will serve as a platform for collegial discussion and exchange of ideas among the various projects within the CTC program. It is our deep hope that seeds for future collaborations among research groups with mutually complementary expertise will grow from this virtual conference series.

The 2020 CTC virtual summer conference series 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. We thank all of the researchers whose dedication, innovation, and reviewing activities have enhanced the goals of Basic Energy Sciences and made this virtual meeting possible. We look forward to seeing this community build upon its successes and look forward to the next joint meeting.

Special thanks to Sharwyn Fryer and Teresa Crockett from Office of Basic Energy Sciences and Connie Lansdon at 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

Jeff Krause, Aaron Holder, and William Kuo

July 16, 2020

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**2020 Computational and Theoretical Chemistry Virtual Conference Series**  
**July 16, July 30, and August 13**  
**Agenda**

**July 16 (Thursday – all time in EST)**

1:00 PM      *Kick - off*

**Session I: Functional Transition Metal**

1:20 PM      *The FLO-SIC Center: Progress towards efficient density functional theory calculations without self-interaction*  
**Koblar A. Jackson**, Central Michigan University

1:40 PM      *Polarizability and Electron Binding Energies of Water Clusters with FLOSIC and Locally-scaled Self Interaction Correction Methods*  
**Tunna Baruah**, University of Texas at El Paso

2:00 PM      *Break*

2:05 PM      *Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies*  
**Shiv Khanna**, Virginia Commonwealth University

2:25 PM      *CASPT2 Molecular Geometries of Transition Metal Complexes*  
**Bess Vlasisavljević**, University of South Dakota

2:45 PM      *Data-Directed Synthesis of Multicomponent Materials for Light-Driven Hydrogen Production from Oxygenates*  
**John R. Kitchin**, Carnegie Mellon University

3:05 PM      *Break*

**Session II: Generalized Solvents**

3:10 PM      *Computational Chemical Science Center: Chemistry in Solution and at Interfaces (CSI)*  
**Roberto Car**, Princeton University

3:30 PM      *Next generation quantum-based molecular dynamics: simulations of reactive chemical systems*  
**Anders M. N. Niklasson**, Los Alamos National Laboratory

3:50 PM      *Probing the partial activation of water by ions and radicals*  
**Ryan P. Steele**, University of Utah

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**July 30 (Thursday – all time in EST)**

**Session III: Complex Chemical Transformation**

- 1:00 PM *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**, University of Minnesota, Minneapolis
- 1:20 PM *Theoretical and Experimental Studies of Elementary Hydrocarbon Species and their Reactions*  
**Henry F. Schaefer**, University of Georgia
- 1:40 PM *ECC: EXASCALE COMPUTATIONAL CATALYSIS*  
**Judit Zádor**, Sandia National Laboratories, Livermore
- 2:00 PM *Break*
- 2:05 PM *Electrocatalysis at Liquid-Solid Interfaces: Principles and Reactivity-Stability Trends*  
**Jeff Greeley**, Purdue University
- 2:25 PM *Theory and Code Developments and Applications to Surface Science, Heterogeneous Catalysis, and Intermolecular Interactions*  
**Mark S. Gordon**, Iowa State University and Ames Laboratory
- 2:45 PM *Non-equilibrium statistical mechanical and coarse-grained modeling of catalytic systems*  
**Jim W. Evans**, Ames Laboratory
- 3:05 PM *Break*
- 3:10 PM *Accurate wave functions expressed as polynomial product states*  
**Gustavo E. Scuseria**, Rice University
- 3:30 PM *Novel Relativistic Electronic Structure Theories for Actinide-Containing Compounds*  
**Lan Cheng**, Johns Hopkins University
- 3:50 PM *Quantum Chemical Treatment of Strongly Correlated Magnetic Systems Based on Heavy Elements*  
**Laura Gagliardi**, University of Minnesota, Minneapolis

**2020 Computational and Theoretical Chemistry Virtual Conference Series**  
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**Agenda**

**August 13 (Thursday – all time in EST)**

**Session IV: Photodriven Processes**

- 1:00 PM      *Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC)*  
**Sotiris S Xantheas**, Pacific Northwest National Laboratory
- 1:20 PM      *New Single- and Multi-Reference Coupled-Cluster Methods for High Accuracy Calculations of Ground and Excited States*  
**Piotr Piecuch**, Michigan State University
- 1:40 PM      *Ab initio geochemistry of hydrous phases*  
**Renata M. Wentzcovitch**, Columbia University
- 2:00 PM      *Break*
- 2:05 PM      *Electron and Electron-Nuclear Dynamics of Open Quantum Subsystems*  
**Michele Pavanello**, Rutgers University
- 2:25 PM      *Surface Plasmon Enhanced Chemistry*  
**George C. Schatz**, Northwestern University
- 2:45 PM      *Designing and Screening of Organic Sensitizers for Highly Efficient Dye-Sensitized Solar Cells: In Silico Approaches*  
**Jerzy Leszczynski**, Jackson State University
- 3:05 PM      *Break*

**Session V: Quantum Information System**

- 3:10 PM      *Towards Improved Simulation on Quantum Computers*  
**Bryan K. Clark**, University of Illinois at Urbana Champaign
- 3:30 PM      *Space-Time Quantum Information from the Entangled States of Magnetic Molecules*  
**Wilson Ho**, University of California, Irvine
- 3:50 PM      *Wrap - up*

**Driven similarity renormalization group approaches for near-degenerate states:**

Chenyang Li, Nan He, Shuhe Wang, Nicholas Stair, Renke Huang, Francesco A. Evangelista

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

**Abstract**

**Program Scope.** Project **DE-SC0016004** aims to study and develop new multireference many-body theories based on the driven similarity renormalization group (DSRG), a new many-body formalism introduced by our group [*J. Chem. Phys.* **141**, 054109 (2014)]. In the past four years, we have developed multireference DSRG (MR-DSRG) methods to treat dynamical electron correlation effects in molecular systems. The DSRG is a convenient framework to derive numerically-robust multireference theories with electron correlation treated perturbatively (second- and third-order) or at a level comparable to that of coupled-cluster methods [*Annu. Rev. Phys. Chem.* **70**, 052416 (2019)]. The goal of the multi-PI project **DE-SC0019374** is to develop algorithms, benchmark sets, and software to solve quantum chemistry problems with quantum computers.

**DE-SC0016004 — Recent progress**

In the past year, we have attempted to reduce the cost of MR-DSRG computations and developed the main formalism in two new directions. First, we have developed an efficient version of the MR-DSRG(2), a nonperturbative approximation scheme with one- and two-body substitutions (a method comparable in accuracy to CCSD). Our new code uses factorized two-electron integrals obtained either via Cholesky decomposition or density fitting, and in this way it avoids storage of large integral files. We have also investigated ways to reduce the cost to perform the unitary transformation of the Hamiltonian and found that a simple, non-interacting virtual orbital (NIVO) approximation, is crucial to reducing both the CPU and memory costs of the MR-DSRG [*J. Chem. Theory Comput.*, **15**, 4399 (2019)]. Using this new code, we can now perform routine MR-DSRG(2) applications with up to 500 basis functions. This point was demonstrated in our computation of the automerization barrier of cyclobutadiene using a large  $5\zeta$  basis set.

As part of our longer-term plan to implement linear response properties of the MR-DSRG methods, we have also published a paper on analytic energy gradients. This work treated the specific case of second-order DSRG perturbation theory in the limit of a Slater determinant reference [*J. Chem. Phys.* **151**, 044118 (2019)]. The main finding of this paper was that efficient and stable response equations could be formulated for the DSRG despite the

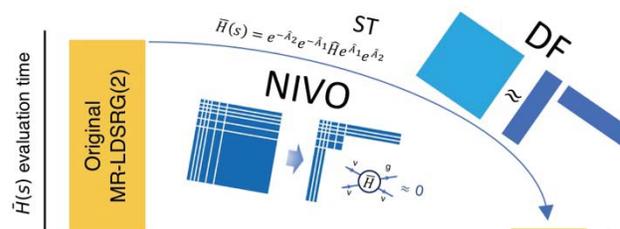


Figure 1. Efficient implementation of the MR-DSRG(2) method. Cost reduction achieved by combining a density fitting approximation of the two-electron integrals with the noninteracting virtual orbital (NIVO) approximation.

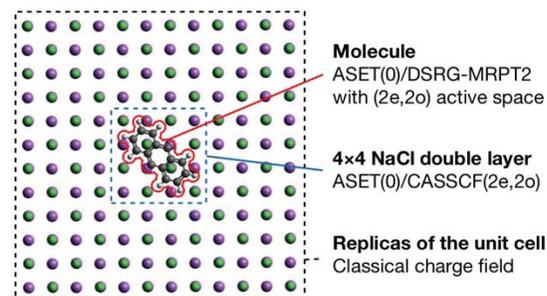


Figure 2. Example of a system studied with our active-space embedding theory (ASET). A 9,10-anthracene diradical physically adsorbed on a NaCl double layer.

presence of a regularizer in the energy expression and the requirement that the orbitals must diagonalize the Fock matrix. This result suggested that analytic energy gradients for the multireference DSRG are viable, and we are now working on the extension of the gradient formalism to this significantly more complex case. Another problem we have started to solve is how to apply the DSRG methods to large-scale problems that can naturally be partitioned into a *system* composed of few atoms (a reaction center, a chromophore) plus an *environment* (solvent molecules, surface). To enable such kind of computations, we have implemented a simple, yet effective, active-space embedding theory (ASET) for multireference methods. This technique has allowed us to extend the application of the MR-DSRG to model the interaction of open-shell species with surfaces. For example, we were able to compute the singlet-triplet gap of the 9,10-anthracyne diradical on a NaCl bilayer (see Fig. 2), simulating a recent experiment that observed this intermediate via atomic force microscopy.

Lastly, we have collaborated with the Lian group at Emory and published a paper on the direct triplet sensitization of oligothiophene by quantum dots [*Chem. Sci.* **10**, 6120 (2019)]. This paper observed Dexter-type triple energy transfer from a quantum dot to an acceptor oligothiophene molecule, demonstrating photon upconversion systems for systems that are more stable and tunable than the more extensively studied polyacenes.

### DE-SC0019374 — Recent progress (work by this PI)

Our work on quantum computing has led to two publications from this PI. Our first paper is a collaboration with the Chan and Scuseria groups [*J. Chem. Phys.* **151**, 244112 (2019)]. In this work, we proved that certain types of trial wave functions based on unitary coupled-cluster theory can exactly represent any quantum state. This work also showed how to construct exact representations of many-body states using only one- and two-body operators, providing a theoretical foundation for building exact trial states for variational quantum eigensolver algorithms.

Taking inspiration from recently introduced quantum imaginary-time evolution algorithms, our second paper [*J. Chem. Theory Comput.* **16**, 2236–2245 (2020)] studied a new class of quantum Krylov algorithms in which a correlated many-body basis is generated via real-time quantum dynamics (see Fig. 3). This basis is then used to represent a solution of the Schrödinger equation, leading to a generalized eigenvalue problem that is solved by a classical computer. This work showed how to construct efficient quantum circuits to evaluate the matrix elements that arise in quantum Krylov methods and benchmarked the accuracy of this new approach using a series of small molecules.

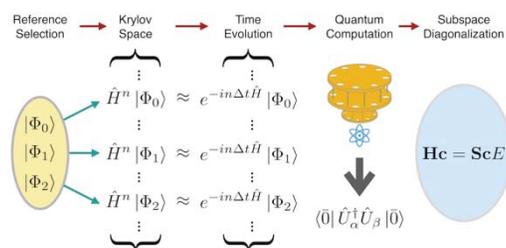


Figure 3. Outline of the quantum Krylov algorithm.

### Future plans

- Formulations of multireference analytic energy gradients of DSRG methods.
- Extend the ASET to include system-environment interactions and apply this approach to other molecule surface problems.
- Extension of quantum Krylov algorithms to excited states.
- Development of benchmark sets for quantum computing algorithms.
- Hybrid quantum-classical algorithms for quantum computers based on the DSRG.

## Grant Numbers and Grant Titles

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

**Student(s):** Shuhe Wang, Nan He

### DE-SC0019374 —Quantum Chemistry for Quantum Computers

**Postdoc(s):** Chenyang Li

**Student(s):** Nicholas Stair, Renke Huang

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

#### DE-SC0016004

1. Evangelista, F. A., Perspective: Multireference coupled cluster theories of dynamical electron correlation. *J. Chem. Phys.* **149**, 030901 (2018).
2. 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).
3. Li, C.; Evangelista, F. A., Multireference Theories of Electron Correlation Based on the Driven Similarity Renormalization Group. *Annu. Rev. Phys. Chem.* **70**, 052416 (2019).
4. 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).
5. Wang, S.; Li, C.; Evangelista, F. A., Analytic gradients for the single-reference driven similarity renormalization group second-order perturbation theory, *J. Chem. Phys.* **151**, 044118 (2019).
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7. Xu, Z.; Jin, T.; Huang, Y.; Mulla, K.; Evangelista, F. A.; Egap, E.; Lian, T., Direct triplet sensitization of oligothiophene by quantum dots, *Chem. Sci.* **10**, 6120 (2019).
8. He, N.; Evangelista, F. A., A zeroth-order active-space frozen-orbital embedding scheme for multireference calculations, *J. Chem. Phys.* **152**, 094107 (2020).

#### DE-SC0019374

9. Evangelista, F. A.; Chan, G. K.-L.; Scuseria, G. E., Exact parameterization of fermionic wave functions via unitary coupled cluster theory. *J. Chem. Phys.* **151**, 244112 (2019).
10. Stair, N. H.; Huang, R.; Evangelista, F. A., A Multireference Quantum Krylov Algorithm for Strongly Correlated Electrons. *J. Chem. Theory Comput.* **16**, 2236 (2020).

## Understanding Plasmon Decay and Plasmon-Enhanced Photocatalysis using Electron and Electron-Nuclear Dynamics

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### 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. Upon excitation of the system at the longitudinal plasmon resonance of the nanowire, the  $N_2$  bond length elongates; for strong incident electric fields, the molecule dissociates (Figure 1a). The presence of the silver nanoparticle enhances excitation into antibonding orbitals of  $N_2$  (Figure 1b). We are currently examining how increasing the length of the nanowire (which increases the strength of the near-field present after plasmonic excitation, but also decreases the plasmon resonance energy) affects the minimum electric field strength required for dissociation. Moreover, we are considering how arrays of silver nanowires can be utilized to increase the efficiency of the plasmon-enhanced photocatalysis process. Recently, we have also 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.

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 within several 10s of fs. These interband transitions occur at twice the incident frequency, and are greatly affected by the intensity of the incident radiation. The

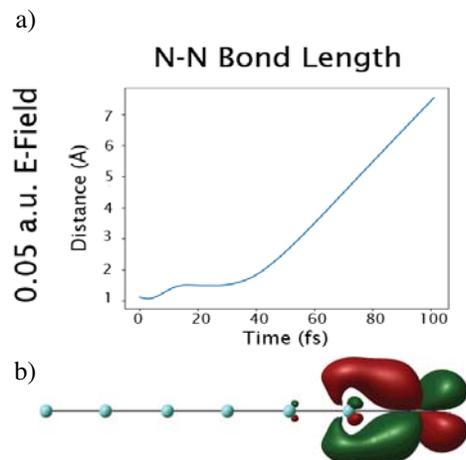


Figure 1. a) Dissociation of  $N_2$  after excitation of the longitudinal plasmon resonance of the silver wire. b) An antibonding  $N_2$  orbital (LUMO+3). The  $N_2$  molecule is arranged in an end-on fashion along the long axis of the silver wire.

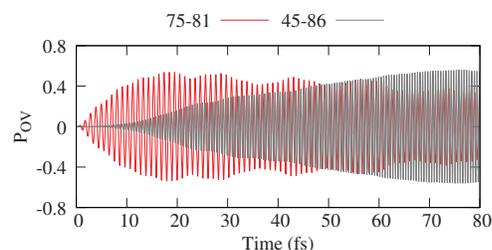


Figure 2. Decay of dipole-allowed  $1P \rightarrow 1D$  transition (75-81) into two-photon-allowed  $1S \rightarrow 1F$  transition (45-86).

time variations of density matrix elements corresponding to occupied and virtual orbital pairs show that the one-photon allowed transitions, which have been excited due to the incident electric field, experience ultrafast decay into high energy transitions, specifically to two-photon allowed transitions (Figure 2). 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.

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 3). This occurs due to coupling with a “dark” electronic state. 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.

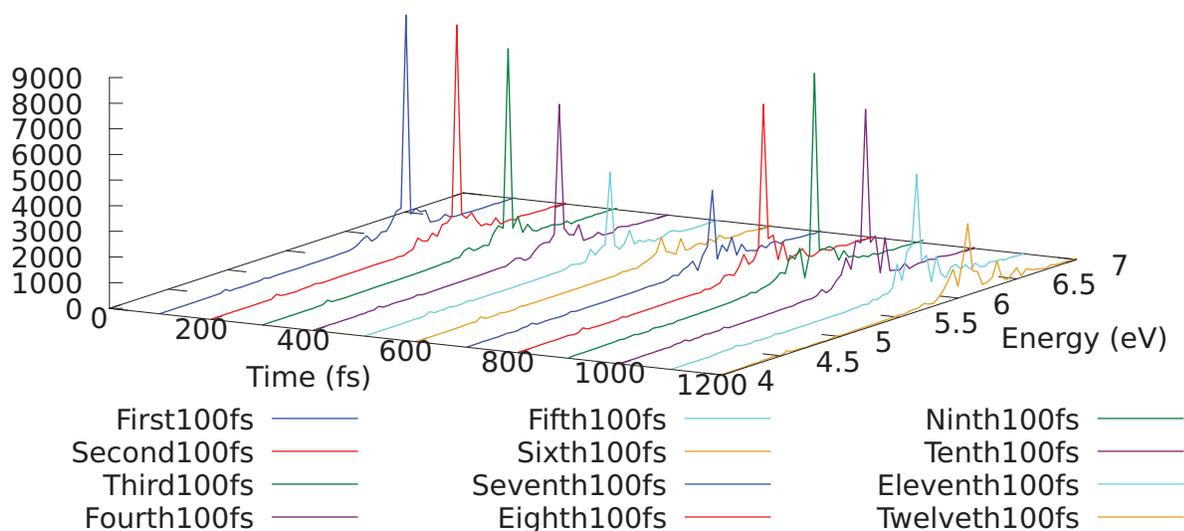


Figure 3. Short-time Fourier transforms of the  $z$  dipole moment after electronic excitation of naphthalene in the  $z$  direction and vibrational excitation of mode 32 ( $B_{1u}$  symmetry), showing the decay and revival of the collective excitation.

## 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 U. Kuda-Singappulige, Olivia Hull, Pratima Pandeya, Yuchen Wang

## Publications

- Ultrafast Nonlinear Plasmon Decay Processes in Silver Nanoclusters. G. U. Kuda-Singappulige, D. B. Lingerfelt, X. Li, C. M. Aikens, submitted to *J. Phys. Chem. C*.
- Electronic Structure and Nonadiabatic Dynamics of Atomic Silver Nanowire-N<sub>2</sub> Systems. O. Hull, D. B. Lingerfelt, X. Li, C. M. Aikens, under revision in *J. Phys. Chem. C*.
- Electron Relaxation Dynamics in [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>-1</sup> (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, MPA, PET) Thiolate-Protected Nanoclusters. R. D. Senanayake, C. M. Aikens, *Phys. Chem. Chem. Phys.*, **2020**, 22, 5272-5285.
- Understanding Plasmon Coupling in Nanoparticle Dimers using Molecular Orbitals and Configuration Interaction. F. Alkan and C. M. Aikens, *Phys. Chem. Chem. Phys.*, **2019**, 21, 23065-23075.
- Theoretical Investigation of Relaxation Dynamics in the Au<sub>18</sub>(SH)<sub>14</sub> Thiolate-Protected Gold Nanocluster. R. D. Senanayake, C. M. Aikens, *J. Chem. Phys.* **2019**, 151, 094702/1-10.
- 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, *J. Phys. Chem. C*, **2019**, 123, 14734-14745.
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- Theoretical Investigation of Relaxation Dynamics in Au<sub>38</sub>(SH)<sub>24</sub> 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.
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- Photoluminescence Origin of Au<sub>38</sub>(SR)<sub>24</sub> and Au<sub>22</sub>(SR)<sub>18</sub> 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<sub>25</sub>(SH)<sub>18</sub>]<sup>-1</sup> 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).
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# Electron attachment to solvated nucleobases

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Electron transfer processes in solution phase are ubiquitous in nature, and as such, gaining understanding of these intrinsic dynamics is of fundamental importance across a range of interdisciplinary fields. The study of damage to DNA arising from low energy electrons produced by radiation represents one such important field. Studies modelling the electronic structure of nucleobases and reactions, such as dissociative electron attachment, have been carried out previously using high-level *ab initio* methods, predominantly in the gas phase. While gas phase *ab initio* studies provide insight into the intrinsic electronic structure and dynamics of nucleobases, they often neglect the effect of both micro- and bulk solvation, therefore offering limited insight into the reaction dynamics of DNA in biological environments. Conversely, many of the studies that focus on the bulk solution phase properties neglect the intrinsic dynamics of individual chemical species, failing to capture the intricacies of chemical reactivity. In order to gain a true insight into the electronic structure and dynamics of nucleobases in the solution phase a bridge between the two modelling approaches is required.

To gain understanding and accurately model electron damage in large biomolecules such as DNA, the Matsika group employs a bottom-up approach, using uracil in the gas and solvated phases as a model system. When low energy electrons attach to nucleobases they create metastable states (resonances), and a proper description requires obtaining both the energy and the lifetime (width) of the states. As the gas phase is tractable by high-level electronic structure calculations, we have benchmarked the ability of different levels of theory to reproduce the position and width of resonances of bare uracil. The stabilization approach and complex absorption potential method were used with EOM-EA-CCSD and a specialised basis set, able to mimic the continuum, to produce these results.

Moving towards the solution phase, we have investigated the influence of micro-solvation on the resonances of the uracil anion, starting with complexes with a single water molecule. The uracil anion with a single water molecule is still tractable with the high-level calculations used for the bare uracil anion, however adding further water molecules quickly becomes unfeasible. Additional calculations were run, in which the water molecule is instead treated with an effective fragment potential (EFP) and was shown to give good agreement with the full *ab initio* calculations, providing a method to move closer to modelling electron attachment to fully solvated uracil. Four stable isomers of the uracil water cluster were investigated, giving additional insights into stabilization effects as related to solvation site around the uracil core.

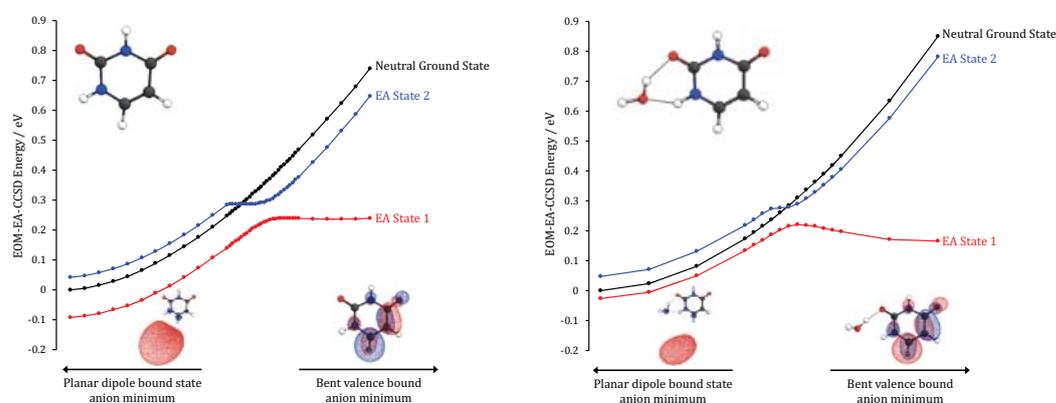


Figure 1. Potential energy surfaces showing the interconversion of the ground state of the bare uracil anion, left, and the microsolvated uracil anion, right, using EOM-EA-CCSD and a specialised basis set able to represent both the continuum, the valence bound anion and the non-valence dipole bound state. Both the dipole bound state and the valence bound anion geometries were optimised using MP2 and a pathway between the two minimum energy geometries were obtained using linear interpolation of internal coordinates to find the avoided between the two anion ground states. The ground state of the uracil anion is shown in red, with orbitals representative of the character of the ground state inset. The neutral reference state is shown in black.

Non-valence states of anions are widely accepted to be important as ‘gateway states’ to the formation of anions in the gas phase. The ground state of the bare uracil anion in the gas phase is a non-valence dipole bound state, where the excess electron is bound by the sufficiently large dipole moment of the neutral core rather than conventional electrostatic forces of a valence state. Anion photoelectron spectroscopy experiments have determined that the dipole bound state of uracil is the ground anionic state in the gas phase. We are investigating the interconversion of the non-valence state to the valence bound anion along specific reaction coordinates, using EOM-EA-CCSD with a specialised basis set able to describe both valence and non-valence states accurately (Figure 1). Through the incremental addition of water molecules around the neutral uracil core, we will investigate how the coupling of the anion dipole bound state and valence state changes, and the fate of the dipole bound state following hydration. This will offer insight into experimental observations of the formation of valence bound state of uracil following micro-solvation with a single water molecule in the gas phase. Extrapolating to more water molecules will give insight in how solvated electrons interact with the bases. The dipole bound state should play a key role in this interaction.

We are working with Prof. **Klein**’s group to model the solvated uracil anion. We are using snapshots obtained using DFT-based molecular dynamics as starting points to investigate the non-adiabatic photodynamics of uracil, from a microsolvated to fully solvated environment (Figure 2). Specifically, we have been investigating how the position of water molecules around the uracil core stabilizes resonances. Additionally, we are untangling the solvation stabilization energy from geometric distortions, allowing us to partition the stabilization energy into vibrational and solvation effects.

Through thorough exploration of the potential energy surfaces of bare uracil, through microsolvation, to fully solvated uracil, we will produce a comprehensive foundation for the exploration of ground and excited state non-adiabatic dynamics. The **Maitra** group at Rutgers is developing an exact factorization surface hopping model to be used in non-adiabatic dynamics of the solvated electron in bulk. The **Maitra** and **Matsika** groups will collaborate to apply that method to model the dynamics of the solvated electron transfer to the uracil nucleobase, once we have a more accurate description of their potential energy surfaces.

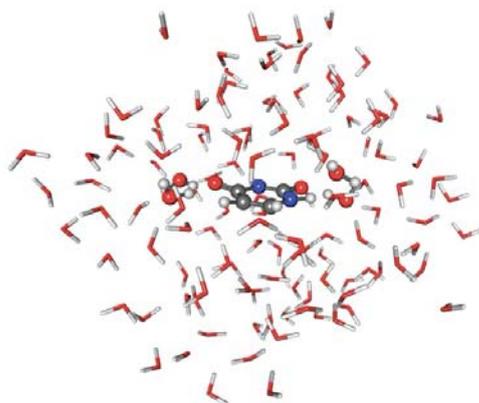


Figure 2. A snapshot of the solvated uracil nucleobase calculated using DFT-MD simulations of 128 water molecules. The water molecules directly interacting with the nucleobase and the nucleobase itself are depicted using the ball and stick scheme, while the water molecules that form the bulk solution are depicted with the wire scheme.

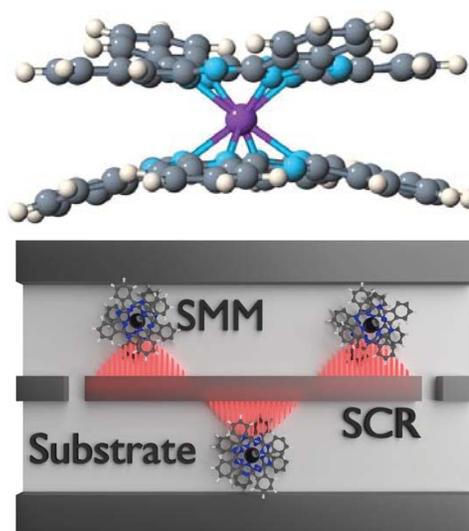
## Grant DE-SC001934: Chemistry in Solution and at Interfaces

**Postdocs:** Cate Anstöter, Mark Dello-Stritto

## Ab initio design of quantum molecular magnets for information applications

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**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  $\text{TbPc}_2$  (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  $\text{TbPc}_2$ -based SMMs for QIP functionality. The  $\text{TbPc}_2$  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<sub>2</sub>-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 ISF-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<sub>2</sub> due to its extremely attractive features, but the techniques we are developing will be general and transferable to other molecules and other qubits. The 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 have investigated how different chemical environments influence magnetic properties of terbium-based SMMs using first-principles relativistic multireference methods.<sup>1</sup> We performed complete active space self-consistent field calculations including relativistic spin-orbit interactions for representative Tb-based SMMs such as TbPc<sub>2</sub> and TbPcNc in three charge states. Our calculations show that the ligand type and other details of the molecular geometry do not affect the gap between the ground-state and first-excited doublets. On the other hand, higher-energy levels have a strong dependence on these details. Our results provide insights into the mechanisms of magnetization relaxation in Tb-based SMMs. It is known that lanthanide-based single-ion magnetic molecules can also have large magnetic hyperfine interactions. These interactions play a central role in the electrical control and inter-qubit coupling of SMM qubits. Therefore, we have also investigated the magnetic hyperfine and nuclear quadrupole interactions for a <sup>159</sup>Tb nucleus in TbPc<sub>2</sub> using multiconfigurational ab initio methods including spin-orbit interaction.<sup>2,3</sup> We found that the magnetic hyperfine coupling is dominated by the interaction of the Tb nuclear spin with electronic orbital angular momentum. The asymmetric 4f-like electronic charge distribution leads to a strong nuclear quadrupole interaction with significant transverse terms for the molecule with low symmetry. The ab initio calculated electronic-nuclear spectrum, including the magnetic hyperfine and quadrupole interactions, is in excellent agreement with experiment findings. We further found that the transverse quadrupole interactions significantly influence the avoided level crossings in magnetization dynamics and that the molecular distortions affect mostly the Fermi contact terms as well as the transverse quadrupole interactions. Going forward, we will use these results to further improve the model Hamiltonians we use in our gate designs and to determine what adjustments should be made to the experimental device setup to achieve stronger qubit-resonator interactions and the best quantum logic gate performance.

*Quantum Embedding:* Although we observed excellent performance from the embedding model we developed last year,<sup>4</sup> very large systems can still be computationally expensive due to the large number of atomic orbitals which need to be transformed in a calculation. In order to improve the efficiency, it becomes necessary to remove the unimportant virtual orbitals from the embedded high-level calculation. While this has been attempted before, it was not done in a rigorous or robust

manner. Over the past year, we developed a solution to this problem using a concept we introduced called “concentric localization”.<sup>5</sup> The idea here is to project the virtual space onto a local subspace of the embedded region, and then SVD the Fock matrix coupling between the active virtual and the remaining virtuals. This numerically robust procedure is repeated recursively to generate a sequence of virtual orbital “shells” which have rapidly diminishing importance to the physics of the embedded system. This method<sup>5</sup> removes the bottleneck from the embedded calculations and opens up applications to much larger systems. This software can be accessed from the Mayhall Group website, and github account (<https://github.com/mayhallgroup/PsiEmbed>). Our next steps will be to finish the implementations and benchmark the methods and then start applying these methods to TbPc<sub>2</sub>-based compounds.

*ISF-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<sub>2</sub> 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. Building on the work in our first publication,<sup>6</sup> (the software of which can be accessed at <https://github.com/mayhallgroup/psi4fockci>) we have recently completed two implementations of this methodology: an open-source python module which can be used with PSI4 (to be released after documentation is completed), and a more optimized C++ version implemented in the widely distributed Qchem software, (code should be part of the next official release). We are currently working on applying these methods to chemical systems to better understand the nature of spin-couplings in mixed metal systems. In order to apply the RAS(h,p)-nSF-EA methods to the target TbPc<sub>2</sub> systems, inclusion of spin-orbit coupling effects is necessary. This year, we have completed the first implementation of SOC interactions for the RAS(h,p)-nSF-EA methods. The implementation and numerical benchmarking is reported in Ref. 7, and the software will be released soon.

*Model Hamiltonians and quantum gate simulations:* We made further improvements to a model Hamiltonian that describes two SMM qubits coupled to a superconducting microwave cavity resonator. Using realistic experimental parameters in the model, we estimated the achievable qubit-resonator interaction strength. We found that while this electrical coupling mechanism is much stronger than the magnetic interactions proposed in earlier works, the system does not yet lie comfortably in the strong-coupling regime where the interaction strength substantially exceeds the spin dephasing time and cavity loss rate.<sup>8</sup> We showed that with further improvements in the device geometry and substrate, it should be possible to achieve fast, high-fidelity entangling gates between two cavity-coupled SMM qubits. We have also developed new control schemes for improved initialization and readout in SMM qubits. We did this by building a geometric framework that assists with the design of control pulses that implement Landau-Zener sweeps through an avoided crossing while dynamically suppressing charge noise effects. This method is useful not only for reducing a main source of errors in the initialization and readout of SMM qubits,

but is also generally applicable to other types of qubits that utilize avoided crossings for these purposes or for implementing entangling gate operations. In the next phase of the project, our focus will be on incorporating the results from our ab initio calculations into our model Hamiltonians to identify optimal parameter regimes and device components for cavity-coupled SMM qubits. We will also continue to improve our techniques for designing gates in these systems and to explore possible quantum algorithmic advantages that come from utilizing the higher energy levels of the SMM qubit.

**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. Pederson, R., Wysocki, A. L., Mayhall, N. J., Park, K. (2019). Multireference Ab Initio Studies of Magnetic Properties of Terbium-Based Single-Molecule Magnets, *Journal of Physical Chemistry A*, 123, 6996-7006. <https://doi.org/10.1021/acs.jpca.9b03708>
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## Polarizability and Electron Binding Energies of Water Clusters with FLOSIC and Locally-scaled Self Interaction Correction Methods

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### Abstract

The Fermi-Lowdin orbital based self-interaction correction (FLOSIC) scheme has so far been applied to test several molecular properties by our group and others over the last few years. One common trend that was seen that the FLOSIC corrections often tend to be excessive for a number of properties. Perdew and Santra have earlier shown that self-interaction correction degrades the behavior of functionals at the uniform gas limit. The Perdew-Zunger orbital by orbital self-interaction correction reduces the error in stretched bond situation but the errors in equilibrium properties on the other hand are overcorrected. A new scheme was proposed to scale the SIC energy density by introducing a scaling factor  $z_\sigma(\vec{r}) = \frac{\tau_\sigma^W(\vec{r})}{\tau_\sigma(\vec{r})}$ , where  $\tau_\sigma^W = \frac{|\nabla\rho_\sigma|^2}{8\rho_\sigma}$  is the von Weiszacker kinetic energy density and  $\tau_\sigma$  is the kinetic energy density of spin  $\sigma$ . This factor is an iso-orbital indicator that has the value 1 in one-electron region and equals zero in the uniform gas region. The local scaling is done as a post self-consistent correction to the total energy. The local self-interaction correction (LSIC) with LDA shows very promising behavior in that it maintains the PZSIC behavior in the stretched bond cases but scales down corrections of the equilibrium properties.

We have applied the FLOSIC to examine the electron delocalization by calculating the static dipole polarizabilities of small water clusters. The effect of self-interaction error (SIE) on the static dipole polarizabilities of water clusters is modelled with three increasingly sophisticated, non-empirical density functional approximations (DFAs), the local spin density approximation (LSDA), the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA), and the Strongly Constrained and Appropriately Normed (SCAN) meta-GGA using the Perdew-Zunger self-interaction-correction (PZ-SIC) energy functional in the FLOSIC framework. Our results show that while all three DFAs overestimate the cluster polarizabilities, the description systematically improves from LSDA to PBE to SCAN. The self-correlation free SCAN predicts polarizabilities quite accurately with a mean absolute error (MAE) of 0.58 Bohr<sup>3</sup> with respect to coupled cluster singles and doubles (CCSD) values. Removing SIE using PZ-SIC correctly reduces the DFA polarizabilities, but over-corrects, resulting in underestimated polarizabilities in SIC-LSDA, SIC-PBE, and SIC-SCAN. To reduce the overcorrection, we applied the local SIC with LDA in a quasi self-consistent formulation. In this formulation the scaling factor is calculated using the density at each iteration but the variation of the factor is ignored. Our calculated water cluster polarizabilities shows that LSIC-LDA mean average error is only 0.30 Bohr<sup>3</sup> compared to the CCSD(T) values. This calculation shows the possibilities of improving the SIC-DFA methodology.

The description of excess charge in atoms and molecules is challenging for semilocal and global (hybrid) DFAs. We have tested the FLOSIC methodology on singly charged water cluster anions to

assess the self-interaction errors. Accurate description of excess electron is challenging for standard semi-local and (global) hybrid density functional approximations. The self-interaction error on the vertical detachment energies of water clusters anions was assessed with the local spin density approximation (LSDA), Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation, and the strongly constrained and appropriately normed (SCAN) meta-GGA functionals. Our results show that for the relative energies of isomers with respect to reference CCSD(T) values, the uncorrected SCAN functional has the smallest deviation of 21 meV, better than that for the MP2 method. The performance of SIC-SCAN is comparable to that of MP2 and is better than SIC-LSDA and SIC-PBE, but it reverses the ordering of the two lowest isomers for water hexamer anions. Removing self interaction error (SIE) corrects the tendency of LSDA, PBE, and SCAN to over-bind the extra electron. The vertical detachment energies (VDEs) of water cluster anions, obtained from the total energy differences of corresponding anion and neutral clusters, are significantly improved by removing self-interaction and are better than the hybrid B3LYP functional, but fall short of MP2 accuracy. Removing SIE results in substantial improvement in the position of the eigenvalue of the extra electron. The negative of the highest occupied eigenvalue after SIC provides an excellent approximation to the VDE, especially for SIC-PBE where the mean absolute error with respect to CCSD(T) is only 17 meV, the best among all approximations compared in this work.

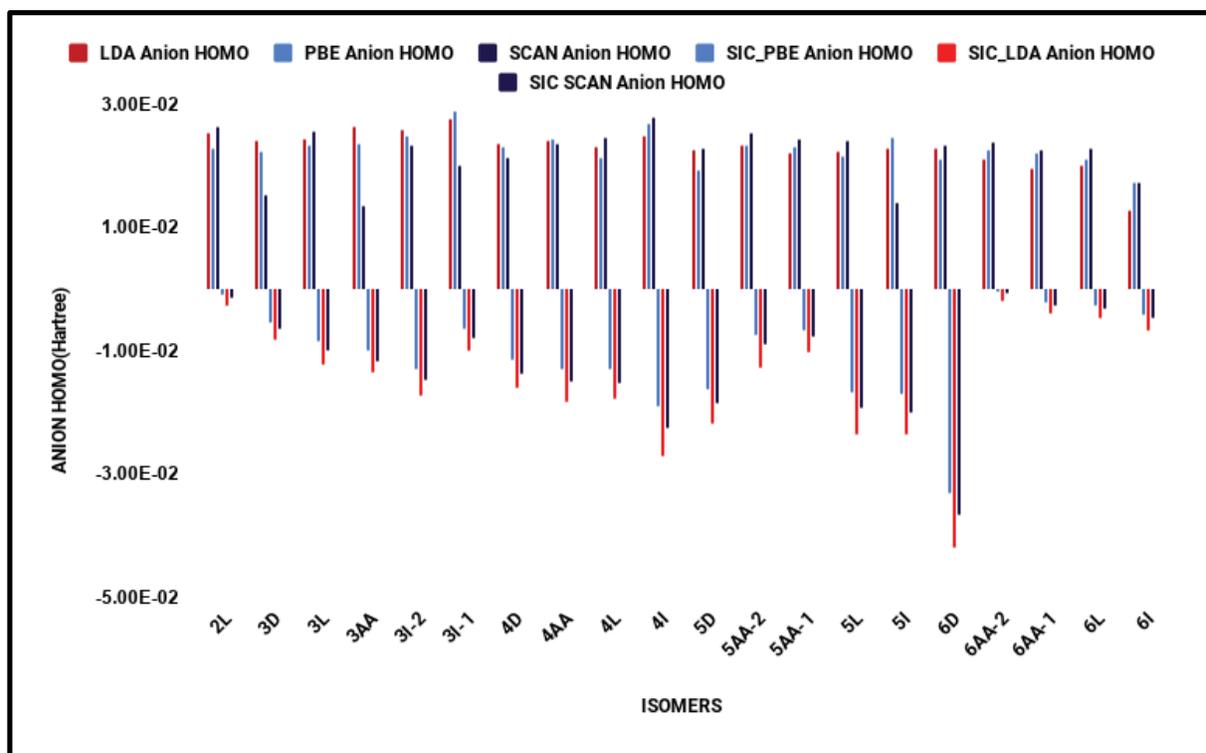


Fig. 1: Eigenvalues of the highest occupied molecular orbital of the water cluster anions.

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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, Po-Hao Chang.**

**Student(s): Carlos Diaz, Prakash Mishra.**

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1. Improvements in the orbitalwise scaling down of Perdew-Zunger self-interaction correction in many-electron regions, Yoh Yamamoto, Selim Romero, Tunna Baruah, and Rajendra Zope, *J. Chem. Phys.* **152**, 174112 (2020).
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## Hydration Mechanisms in Nanoparticle Interaction and Surface Energetics

Award DE-SC-0004406

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### Program scope

The project aims to advance molecular-level understanding, prediction and control of nanoscale hydration in salt solutions under the effects of confinement and external fields. It relies on the development of state-of-the-art simulation algorithms in statistical mechanics to study complex processes in open systems, and equilibrium and nonequilibrium molecular dynamics to address dynamic responses and dissipative processes. Studies of wetting and dispersibility of ionizing nanoparticles aim to uncover predictive relations between electrowetting, functionalization, and morphology of the particles. Permeation of nanoporous electrodes at preset voltage underlies the function of ultracapacitors. Transitory regulation of wetting in nanoporous media by applied voltage spans an array of applications in materials, energy storage, and separation sciences. The physically related modulation of nanoparticle solubility by ionization can extend the range of the nanomaterial applications, improve processing techniques, and potentially alleviate environmental concerns.

### Recent progress

**Dielectric behavior of confined solution and implications for field-enhanced imbibition<sup>9</sup>.** Building on the previous developments in Grand Canonical simulations of polarizable water and salts, we analyze dielectric and absorption responses of model water and solutions in a porous medium subject to strong electric fields. Comparisons between nonpolarizable and polarizable (gaussian-charge on spring BK<sub>3</sub>-AH) force fields involves nontrivial adaptations of expanded ensemble Monte Carlo methodologies, including biased multi-particle moves, and considerable increases of computational load. Fig. 1 shows the mean dielectric constant  $\epsilon_f = \langle \frac{1}{\epsilon_{\perp}(z)} \rangle_{d_f}^{-1}$  in a

planar nanopore, measured across the confined aqueous film of thickness  $d_f$ . In contrast to comparisons between the two force fields in the bulk phase, the polarizable model of *confined* solution predicts a *lower* mean dielectric constant than the nonpolarizable one. The difference is explained by the reduction of the molecular dipole in the interfacial layer (inset in Fig. 1) when using the polarizable force field, a result consistent with quantum mechanical simulations at aqueous interfaces. Although the reduced dipole moment of the interfacial BK<sub>3</sub> water still exceeds the constant value of the nonpolarizable model, its reduction relative to the bulk phase value affects pore-bulk partitioning and *weakens* the influence of applied electric field on the absorption

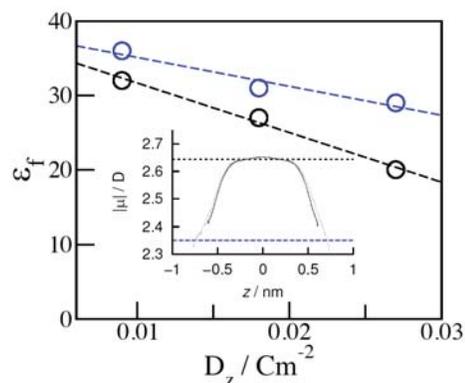


Fig.1 Mean dielectric constant inside a confined aqueous film (black: BK<sub>3</sub>, blue: SPC/E) as a function of applied electric displacement  $D_z$ . Inset: Average dipole moment of a polarizable (BK<sub>3</sub>) water molecule as a function of position inside the 1.64 nm wide apolar confinement. Blue dashed line corresponds to the fixed dipole of the nonpolarizable (SPC/E) model<sup>9</sup>.

propensity. These differences affect *in silico* predictions for the function of supercapacitors and batteries relying on electrolyte permeation of porous electrode materials. Efficiency improvements necessary for systematic open ensemble modeling of salt effects with polarizable force fields are planned in future work.

**Solution Dynamics in Spherical Nanocages**<sup>7</sup>. Local diffusion represents an important determinant of reaction kinetics in spherically confined systems, a geometry that is common to many chemical nanoreactors. Applying a newly developed method to study position-dependent, anisotropic diffusion tensors in the confinement, we unveil and characterize a surprisingly rich diffusion dynamics of confined water. The pronounced anisotropy of diffusion components predicted by the model agree with explicit molecular dynamics simulations. The approach is applicable to transport of solutes to and from reaction sites at nanoreactor interfaces. A detailed analysis of hydrogen bond kinetics, intimately coupled with local diffusion, shows a single set of elementary rate constants is sufficient to accurately describe the kinetics of hydrogen bond breaking and formation in nonuniform water. Residence times of hydrogen bonding partners are well correlated to averaged diffusion constants obtained by the new procedure.

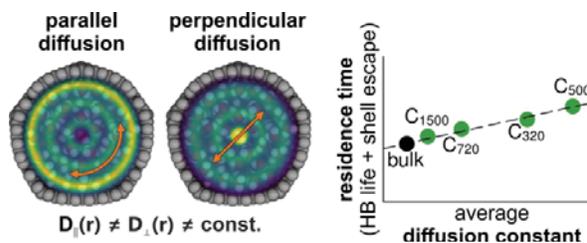


Fig.1 L: anticorrelated components of spatially varying solvent diffusivities along and normal to confining wall; (R) size dependence of mean coordination shell residence times in spherical nanoconfinements<sup>7</sup>.

**Electric field effect on ion mobilities in room temperature ionic liquids**<sup>8</sup>. Remarkable electrochemical stability, excellent conducting properties, and extremely low volatility invite the use of ionic liquids in a range of energy applications. Our research addresses the variation of conductance and ion diffusivities under strong electric fields potentially achievable in nanoscale EDL supercapacitors. Using atomistic molecular dynamics of model ionic liquids, we consider the behavior of highly flexible ionic liquid 1-butyl-3-methylimidazolium bis (trifluoromethyl-sulfonyl imide with significant electronic polarizability captured by the drude-particle force field. Electric and diffusive mobilities under a strong external field showed considerable anisotropy and a remarkably nonlinear response to the field. While electric mobilities along the direction of the field increase through the alignment and conformational changes, an even bigger enhancement results from the disruption of local cage structure of coordinating counterions. In very strong fields, this disruption leads to up to two orders of magnitude increase of conductance as well as ion diffusivities in *both* the direction along and perpendicular to the field. Fig. 2 illustrates the change in parallel diffusivities (computed after the drift correction) and very similar changes are observed in migration mobilities of the ions and in their diffusivities normal to the field. The strong deviations from ohmic resistance revealed in the present study have considerable implications for the estimated dissipation losses in ionic-liquid supercapacitors.

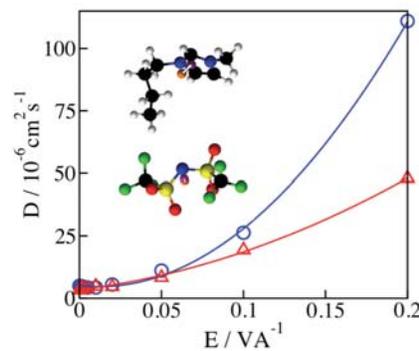


Fig. 2 Enhanced mobilities of 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide cation and anion under static electric field  $E$ <sup>8</sup>.

### Future plans

Predictive modeling of superficial-energy storage during forced electrolyte-pore absorption motivates ongoing methodology developments for computations of chemical potentials and open ensemble

simulations of pore/bulk partitioning at extreme pressures and applied fields. Extensions to polarizable force fields require algorithmic advances for efficient sampling in fractional-exchange open ensemble simulations. A dynamic variation of the controlled electric potential molecular dynamics is being developed to address temporal responses to pressure and electric stimuli in energy-storage contexts.

#### **Ten publications acknowledging the award DE-SC-0004406 in 2018 and 2019**

- (1) B. S. Jabes, D. Bratko, A. Luzar, Extent of surface force additivity on chemically heterogeneous substrates at varied orientation, *J. Phys. Chem. B* **122**, 3596 (2018).
- (2) S. Gehrke, M. von Domaros, R. Clark, O. Holloczki, M. Brehm, T. Welton, A. Luzar and B. Kirchner, Structure and lifetimes in ionic liquids and their mixtures, *Faraday Discuss.* **206**, 219 (2018).
- (3) B. S. Jabes, D. Bratko, A. Luzar, Curvature dependence of the effect of ionic functionalization on the attraction among nanoparticles in dispersion, *J. Chem. Phys.* **148**, 222815 (2018), ), Special issue on Ions in Water.
- (4) N. Ojaghlo, H. V. Tafreshi, D. Bratko, A. Luzar, Dynamical Insights into the Mechanism of a Droplet Detachment from a Fiber, *Soft Matter* **14**, 8924 (2018), featured on issue cover.
- (5) C. D. Daub, N. M. Cann, D. Bratko and A. Luzar, Electrokinetic flow of aqueous electrolyte in amorphous silica nanotubes, *Phys. Chem. Chem. Phys.* **20**, 27838 (2018). Among the *PCCP* 'Hot articles' for the year.
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- (8) R. Clark, M. von Domaros, A. J. S. A. A. Luzar, B. Kirchner, T. Welton, Effect of an external electric field on the dynamics and intramolecular structures of ions in an ionic liquid, *J. Chem. Phys.* **151**, 164503 (2019).
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# Aqueous Interfaces with Metals and Metal Oxides

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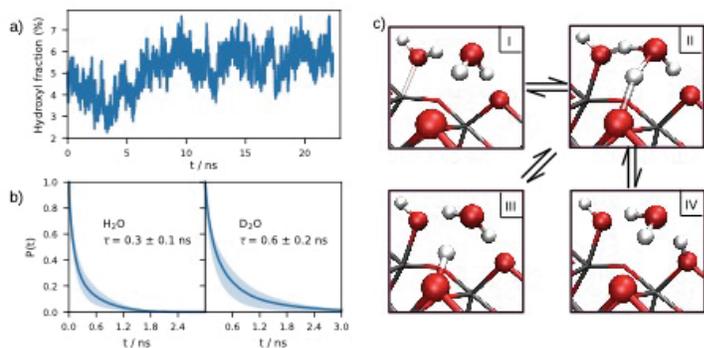
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## Abstract

Interfaces play a central role in transport and reactive processes associated to energy-water issues of interest to DOE, from photocatalytic applications for fuel production and environmental recovery, to water treatment membranes and electrode materials for electrochemical desalination, to effects of the acidity/basicity at hydrophobic interfaces, to electron transfer processes in biochemistry.

In **Project 1**, our long-term goal is to characterize the structure and reactivity of prototypical water-metal oxide interfaces, particularly the aqueous interfaces with titania ( $\text{TiO}_2$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). These interfaces are important in many fields of science and technology, from geochemistry and photo-electrochemistry to biomedical devices.

We have initially focused on the acid-basic properties of the water interface with anatase, the  $\text{TiO}_2$  polymorph more relevant for photocatalysis and energy applications. Although the  $\text{TiO}_2$  photocatalytic efficiency depends significantly on the medium acidity, the mechanism of proton transfer on  $\text{TiO}_2$  surfaces is still unclear even for the case of well-defined crystalline surfaces. To address this issue, we have investigated the anatase-water interface using molecular dynamics with an *ab initio*-based deep neural network potential. The ability of neural networks to reproduce the *ab initio* potential energy surface of the anatase–water interface together with their scalability has allowed us to substantially extend the size and time scales of our *ab initio* simulations for this system. By combining the computationally efficient neural network potential with enhanced sampling techniques, we have also been able to reconstruct the free energy surface of water dissociation and proton transport at the interface.



**Figure 1** a) Time evolution of the surface hydroxyl coverage at the anatase (101)–water interface, as obtained from deep neural network molecular dynamics simulations. b) Survival probability of surface hydroxyl groups at the aqueous ( $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ) interface as a function of time. In both plots  $\tau$  denotes the average lifetime of terminal hydroxyl groups. c) Mechanisms of proton transfer reactions at the anatase (101)–water interface.

Our simulations of the interface structure show a dynamical equilibrium of molecular and dissociative adsorption of water on TiO<sub>2</sub>. Water dissociation occurs via solvent-assisted concerted proton transfer to form a pair of short-lived hydroxyl groups on the TiO<sub>2</sub> surface (**Figure 1**). Molecular adsorption of water is 8.0±0.9 kJ/mol lower in free energy than the dissociative adsorption, giving rise to a 5.6±0.5% equilibrium water dissociation fraction at room temperature.

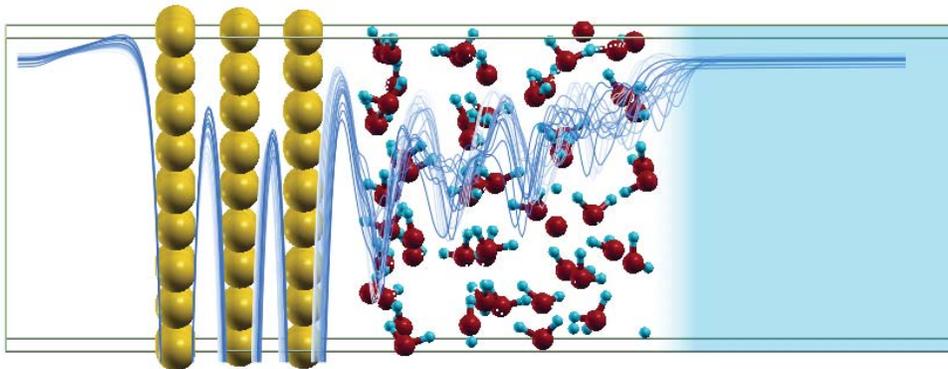
We plan to extend this work to investigate proton transfer reactions between bulk water and the TiO<sub>2</sub> surface. The chemical equilibrium of these reactions governs the experimentally accessible acid-base constants of the TiO<sub>2</sub> surface in water, thus providing a more direct contact of our simulations with experiment. Due to the relevance of acid-basic equilibria to the surface chemistry of TiO<sub>2</sub>, our model might be key to understanding phenomena ranging from surface functionalization to photocatalytic mechanisms.

In future work we will also tackle the water oxidation reaction on hematite. Fe<sub>2</sub>O<sub>3</sub> is a well-studied inexpensive photoanode for water splitting, with a high predicted intrinsic water-splitting activity, but suffers from low carrier lifetimes. *Ab initio* molecular dynamics trajectories will be carried out to characterize the aqueous interfaces of pure and hole-doped hematite at the level of hybrid DFT. These trajectories will elucidate the electronic and structural effects localized excitons may have on catalytic surface chemistries that follow photoexcitation. From representative trajectories, and the associated structures, we will perform the more accurate multiconfigurational correlated wavefunction (CW) calculations to more robustly account for the influence of an electron hole and excited electronic states in the reaction energetics of the water oxidation reaction. This will be achieved using the newly developed capped density functional embedding theory (capped-DFET). Capped-DFET allows for the partitioning of large covalent and ionic systems into fragments, and the evaluation of the fragments' interaction from DFT. Smaller fragments containing the active site therefore may be described using CW, while also incorporating environmental effects through a quantum-mechanically-derived effective potential.

In **Project 2** our main goal is to understand the properties of the electrical double layer (EDL) at aqueous metal electrode interfaces under voltage bias. Electrode-liquid interfaces under voltage bias demonstrate anomalous electrostatic and structural properties that are influential in their catalytic and technological applications. While mean-field and empirical models of the EDL that forms in response to the applied bias do not capture the instantaneous inhomogeneities that polarizable electrolyte and solvent molecules engender, emerging methods for determining the electrode potential in density functional theory (DFT) calculations<sup>2-4</sup> have made controlled-potential simulations of the EDL accessible.

As a first representative example, we have started studying relatively inert Au electrodes in contact with pure water. We perform Born-Oppenheimer *ab initio* molecular dynamics (AIMD) calculations of electrified Au(111) slabs interfaced with liquid water using a combined explicit-implicit solvent approach (**Figure 2**). The excess charges localized on the model electrode are held constant and the electrode potentials are computed dynamically, elucidating the equilibrium fluctuations of interfacial electric fields and the system's capacitive properties. The effects of applied voltages, positive and negative, on the interfacial structure, dynamics, and vibrational spectroscopic properties of water in the EDL are quantified and compared to experiment.

In future work, these controlled-potential simulations will provide a framework for further investigation of more complex or reactive species in the EDL and broadly for understanding crucial electrochemical interfaces *in situ*.



**Figure 2** - Representative illustration of the model electrochemical half-cell (Au atoms are gold in color, O atoms are red, H atoms are cyan) with its periodic boundaries. At left of the Au slab is vacuum, at its immediate right is a region of explicit water molecules, then a region of continuum water solvent, designated by the light blue color. Superimposed in blue are the electrostatic potentials, plane-averaged parallel to the surface, of the system at different simulation times as a function of the surface-normal coordinate. The opaquer curves correspond to later simulation times.

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**Postdocs:** Zachary K. Goldsmith

**Students:** Marcos Calegari Andrade, Linfeng Zhang

## **Computational Chemical Science Center: Chemistry in Solution and at Interfaces (CSI)**

Director: Roberto Car<sup>1,2</sup>; Deputy Directors: Athanassios Z. Panagiotopoulos,<sup>1,3</sup> and Annabella Selloni<sup>1,2</sup>

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### **Abstract**

CSI is a collaborative project uniting PIs at Princeton University, at Temple University, at Stony Brook University (SUNY) and at Rutgers University-Newark. A complete list of the senior investigators, postdoctoral associates and graduate students can be found on the center website (<http://chemlabs.princeton.edu/ccsc/>). The center was created with a DOE award having September 15<sup>th</sup> 2018 as the starting date. CSI is fully operational since the fall of 2019 as most of the newly recruited postdoctoral associates started their activity then. While the main scientific activity in 2020 has proceeded as planned, the COVID-19 outbreak has forced us to modify our regular schedule. In particular, postdocs/students visits/exchanges among sites have been canceled, our bi-weekly seminar series has been interrupted, in person PI meetings, the SAB review meeting originally scheduled for June, and the 2 days hands-on workshop on the software tools developed at CSI originally scheduled for July have all been cancelled. Some of these activities have been replaced by virtual zoom meetings (e.g. the PI meeting and the seminar series with a reduced pace). Zoom meetings between subgroups working at different projects are made regularly, and we will convert the July hands-on workshop to an open virtual workshop via zoom. The SAB review meeting will also be done remotely. The impossibility of traveling and having in person meetings is also slowing down on-going collaborations with other centers and academic institutions in the US and abroad.

While a detailed overview of the ongoing scientific progress can be found in the abstracts submitted by the various teams associated to the center, a few highlights that mark important milestones achieved so far are listed below.

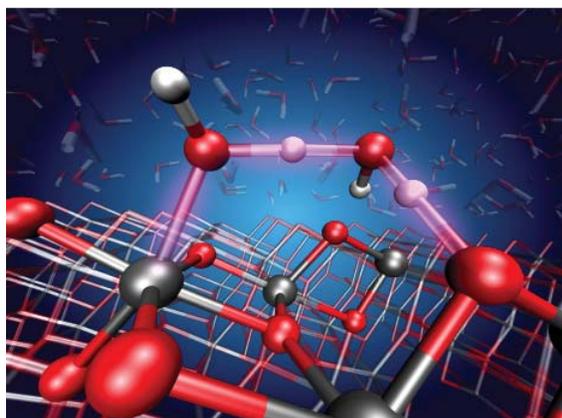
1. The deep potential (DP) methodology has been made accessible to the molecular simulation community via two open-software tools: DeePMD-kit for driving DPMD simulations, and DP-GEN for generating DPs by training with DFT data. The DPs are reactive potentials that reproduce accurately DFT at a small fraction of the computational cost. A recent study made at CSI with the DP methodology found that hydroxylation processes occur at the interface between titania (anatase) and liquid water<sup>1</sup> (Fig. 1). These processes occur on the ns timescale and cannot be observed in the short trajectories accessible with direct AIMD simulations. In addition to facilitating studies of interfacial water, the DP methodology is currently used at CSI in investigations of phase equilibria and liquid crystallization, of deeply undercooled water, and of electrolyte solutions. In some of these studies the DP methodology has been combined successfully with modern enhanced sampling techniques, such as enhanced variational sampling and the corresponding multi-thermal, multi-baric simulations.

2. The DP methodology has been extended to model the polarization and polarizability surfaces<sup>2,3</sup> allowing the calculation of infrared, Raman, and SFG spectra. The approach is based on deep neural networks (DNN) that reproduce accurately the environmental dependence of the electronic Wannier centers and can describe the change of dielectric properties upon molecular dissociation (Fig. 2). Open software tools extending the DP methodology to model dielectric properties will soon be made available to the molecular simulation community.

3. DPMD has been optimized on hybrid CPU/GPU computer architectures, achieving excellent scaling on the Summit supercomputer at ORNL, where DPMD simulations can harness about 40 percent of peak performance, i.e. ~80 PFLOPS out of 200 PFLOPS peak performance. With the computational power of Summit it is possible to perform 12 DPMD steps per second for a system with more than 100 million atoms, opening the way to molecular dynamics simulations with DFT accuracy for systems of unprecedented size (Fig. 3).

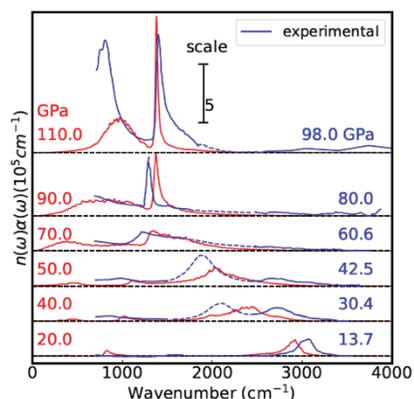
4. Progress has been made to improve DFT functional energies and forces with ML techniques<sup>4</sup>.

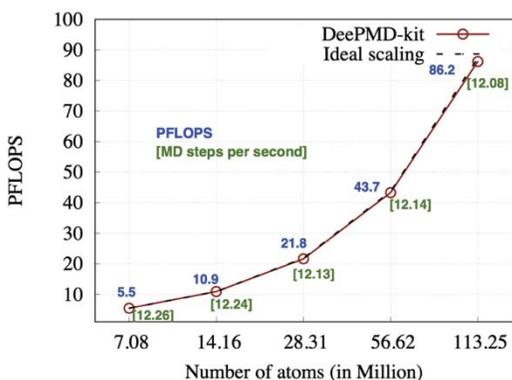
5. Various functional approximations of DFT have been used to model the Al<sub>2</sub>O<sub>3</sub>(001)-H<sub>2</sub>O interface, finding that an accurate interfacial structure could be achieved only when modeling electron exchange-correlation with the SCAN meta-GGA functional<sup>5</sup>. The role of nuclear quantum fluctuations on the solvation structures of simple ions in water has been elucidated with PI-AIMD simulations based on the SCAN functional<sup>6</sup>.



**Fig. 1** The transition state for proton transfer leading to hydroxylation of the TiO<sub>2</sub> interface with liquid water. This figure was displayed in the internal cover of the issue of *Chemical Science* that reported the work<sup>1</sup>. Hydroxylation and de-hydroxylation processes occur continuously on the ns time scale.

**Fig. 2** The change in infrared absorption in the transition from ice VII to ice X under pressure at 300 K. The calculated spectra using the DP methodology for the polarization are reported in red. Experimental diamond anvil cell data are in blue (dashed lines correspond to frequency ranges in which the experimental signal is not available and are obtained with oscillator fits). Ice VII is a molecular crystal with a disordered proton distribution satisfying the ice rules. Ice X is an ionic crystal with a BCC oxygen sublattice in which the protons occupy sites in the middle of the O-O bonds. The DP polarization methodology does not rely on identification of molecular dipoles and can describe seamlessly the change of dielectric properties during the pressure induced transition<sup>2</sup>.





**Figure 3** Weak scaling of DPMD for copper systems on Summit. Each GPU holds 4,139 atoms, and the corresponding number of nodes scales from 285 to 4,560 throughout the tests. Notice that the number of MD steps per second is held approximately constant. The simulation with  $\sim 113$  million atoms achieves a performance of  $\sim 86$  PFLOPS on Summit, which is about 40 percent of the peak performance of the machine.

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**Students:** Princeton: M. Calegari Andrade, Y. Chen, Z. Ding, M. N. Barbosa Muniz, B. Yang, S. Yue, L. Zhang; Stony Brook: S. Dick, A. Wills

# Building Reliable Models of Functionalized Amorphous Silicate Surfaces

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## 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.<sup>1</sup> 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.

Active sites of catalysts on amorphous oxide supports have a distribution of local environments due to the structural and topological disorder of the support.<sup>2</sup> Contributions to the overall disorder includes both *quenched* and dynamically disordered degrees of freedom. Quenched disorder, *e.g.*, in the connectivity of the SiO<sub>2</sub> network, requires energy changes on the order of 100 kJ/mol to rearrange. In contrast, surface hydroxyls form a *dynamically disordered* H-bond network because smaller thermal fluctuations are sufficient to rearrange them. A key milestone for the success of this project is the construction of reliable models of such functionalized amorphous silicate surfaces. These surfaces will serve as the basis to build models of the stationary points along the reaction coordinate for the catalytic cycle. In turn, these models of the reactants, transition states, and products will be used to train the machine learning algorithm for the extrapolation of the activation energy. Therefore, we have dedicated the past year to creating a robust computational protocol for the construction of the functionalized surfaces. This is not an easy task, because of the glassy nature of these materials. In fact, for a given average density of functional groups per unit area, there are multiple metastable minima that can be populated. The distribution of this population depends on the experimental technique employed for the synthesis of the material. A large number of synthetic approaches for amorphous and mesoporous silica have been reported in the literature, all of which take place on timescales beyond the capabilities of direct computer simulations. Thus, we have invested a lot of effort to determine what computational strategy is the most reliable in reproducing key experimental features.

The Laird group has been working to generate realistic amorphous silica surfaces with varying silanol density using reactive potentials – specifically the ReaxFF, which has been shown to work well for the amorphous silica-water interface.<sup>3</sup> A reactive potential has an advantage in that one does not need to rely on *ad-hoc* protocols for the addition of silanol groups to the surface – in this work we expose the bare silica surface to water and let the silanization of the surface occur naturally. We produce our initial silica slabs starting with bulk simulations from the Thompson group using the BKS potential. These bulk

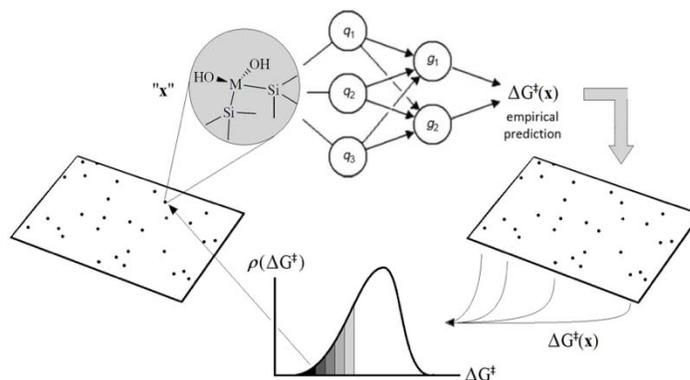


Figure 1 Scheme of the importance learning algorithm for the sampling of the active sites with low activation energy on an amorphous silica surface.

silica samples are then heated to 4000K to melt the structure and then cooled back to 298K using varying cooling rates, which we then examine to optimize and characterize the procedure. The periodic boundary conditions in the  $z$  direction are removed to form amorphous silicate slab. Water is introduced afterwards to form a silica-water interface, which is then heated to 800K to increase the rate of silanol formation. We are currently examining how the concentration and relative location of surface silanol groups at the surface varies with the parameters of the formation protocol (*e.g.*, annealing rates and temperatures). Thus, we will be able to provide the Baron and Caricato groups with a large data set of amorphous silicate surfaces to use in the catalytic rate calculations.

Complementary to and in concert with these efforts, the Thompson group is using classical force fields to develop silica slab and mesopore models. The general approach is that described above with ReaxFF (melt, expand in  $z$  to make a slab, cool at varying rates). The classical force fields require a different technique for functionalizing the resulting surface with surface  $-OH$  groups. This is done by selecting Si-O bonds (by length or randomly) and adding an H to the O atom and an  $-OH$  to the Si; this procedure preserves charge neutrality and permits variations in both the density and distribution of silanols on the surface. Our results indicate that defects within the silica structure (*e.g.*, over- and under-coordination) increase with faster cooling rate. Some defects appear preferentially at the surface, such as ring structures with only two or three Si atoms. The control of these various properties of the silica surface models will enable exploration of their influence on the catalytic properties of grafted and embedded metal active sites.

Once functionalized surfaces are obtained from the classical MD simulations, they need to be doped with the metal center and refined with quantum mechanical (QM) simulations. Given the size of the models, the best compromise between cost and accuracy is obtained with density functional theory (DFT), using modern hybrid functionals. However, even at this level of theory, performing geometry optimizations using periodic boundary conditions is too demanding. Therefore, we resort to cluster models containing a large portion of amorphous silica surrounding the metal center (about 200 atoms) to preserve the metastable amorphous character of the surface. Considering that hundreds or thousands of such model clusters will be necessary for the training of the machine learning model, it is necessary to determine the best computational procedure to find the DFT energy minima of the doped surface starting from the MD undoped model. Specifically, we ask how large the DFT-optimized cluster should be, and whether the geometry relaxation should be performed in sequential steps for larger and larger portions of the cluster or all at once.

The Peters and Caricato groups are working to understand how the quenched and dynamically disordered degrees of freedom can be accurately preserved when small cluster models are made from larger silica support models. The Peters group has created a lattice model with quenched structural disorder and a dynamically disordered H-bond network to study how both types of disorder influence the grafting energy of a Cr metal complex, shown in Figure 3. Monte Carlo procedures are being used to sample different H-bond configurations

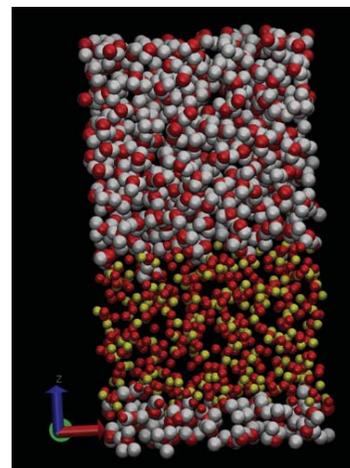


Figure 2 Snapshot of ReaxFF simulation of silica-water interface after annealing to 298K.

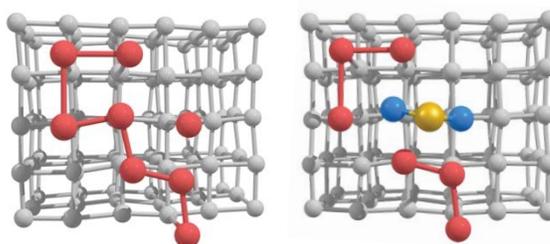


Figure 3 Disordered lattice model of the hydrogen bond network between silanols (red) before (left) and after (right) grafting of a metal center (yellow) to create an  $M(OSi\equiv)_2$  site.

across an ensemble of non-uniform sites. These simplified models allow the treatment of very large samples, so that near-convergence with bulk behaviour can be reached. Simultaneously, the Caricato group is testing the trends for the Cr grafting energy on production-level clusters with full DFT simulations. Initial results on both the lattice model and the full clusters show that the preoptimization of the slab, before grafting of the metal, may be necessary to obtain smooth optimizations of the metal doped cluster. This is an indication that the MD structures are rather far away from the DFT minimum structure. Thus, directly grafting the surface would create particularly strained initial geometries that would make the subsequent geometry optimization difficult and unstable. An example of this behavior is reported in Figure 4, which reports the grafting energy using relaxed regions of the cluster surrounding the metal center of different sizes (the Relaxed Radius indicates the size of the relaxed region), starting from either a pre-optimized or an MD initial structure. In this case, a region of 8 Å radius is necessary to obtain convergence in the grafting energy, and using a pre-optimized structure allows a smooth convergence of the grafting energy towards the right value.

The main goals for the near future are: 1) To produce functionalized amorphous silicate surfaces from classical MD simulations, either by direct insertion of OH groups or via a water reaction using reactive force fields; 2) To dope the surfaces with metal centers and determine initial minima and transition state structures; 3) To optimize a protocol for the automatic generation of these energy stationary points along the reaction coordinate. 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).

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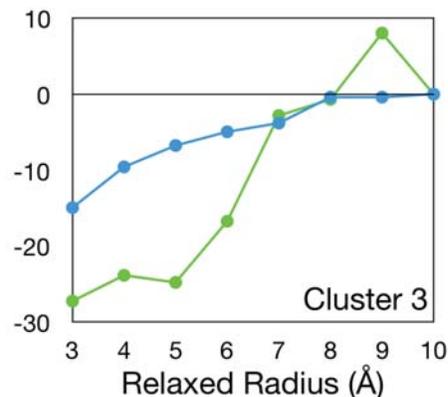


Figure 4 Geometry optimization of a Cr-grafted cluster using a pre-optimized structure (blue) or directly from the MD structure (green). The y axis reports the relative energy in kcal/mol.

## Quantum Mechanical Evaluation of Alternative Photovoltaic Materials

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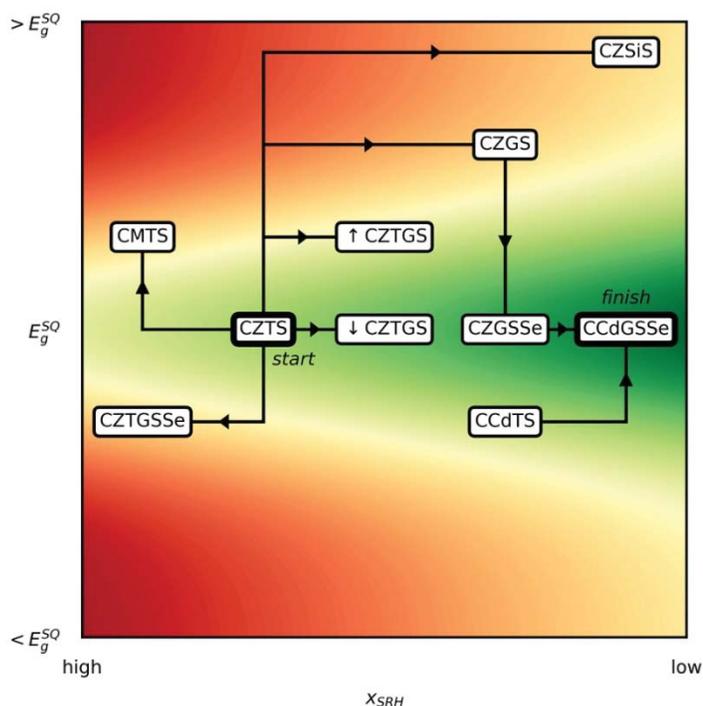
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### Abstract

This abstract reports our continued exploration of how to suppress the formation of Shockley-Read-Hall (SRH) recombination centers in  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS), an inexpensive solar cell material, via first principles thermodynamics calculations. We also report on quantum-dynamics simulations of another promising optoelectronic material,  $\text{WSe}_2$ . We begin with the former and end with the latter.

Defect thermodynamics play a significant role in the efficiency of solar cells, especially those based on CZTS and  $\text{Cu}_2\text{ZnGeS}_4$  (CZGS). For example, the  $\text{Cu}_{\text{Zn}}+\text{Zn}_{\text{Cu}}$  antisite cluster causes electrostatic potential fluctuations in CZTS that reduce its open-circuit voltage ( $V_{\text{oc}}$ ) (*Chem. Mater.* **2016**, *28*, 864–869). Previous publications reported that defect clusters involving the  $\text{Sn}_{\text{Zn}}$  antisite, such as  $2\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}$ , create localized electronic states within the band gap that trap charge carriers (*Appl. Phys. Lett.* **2013**, *101*, 223901), thus promoting their nonradiative recombination via the SRH mechanism (*Phys. Rev.* **1952**, *87*, 835–842; *Phys. Rev.* **1952**, *87*, 387). To determine the extent to which defects affect solar cell performance, quantitative predictions of defect formation energies are necessary. Density functional theory (DFT) is the primary tool used for such calculations; however, no studies as yet have compared predictions across semilocal and hybrid exchange-correlation (XC) functionals. Therefore, how quantitative DFT is for modeling defects in CZTS and CZGS remains unclear.

To address this, we performed DFT calculations using semilocal and hybrid XC functionals as well as Hubbard  $U$  corrections. We assessed XC influence on predictions of bulk stability and defect energetics in CZTS and CZGS. We find that the strongly constrained and appropriately normed (SCAN) meta-generalized-gradient-approximation (meta-GGA) XC functional systematically underbinds compounds



containing Ge, thus requiring adjustment of their formation energies to obtain Ge chemical potentials and Cu-Zn-Ge-S quaternary phase diagrams consistent with experiments. We also quantify the variability in DFT defect formation energies associated with different XC treatments. We connect this variability to defect-induced charge delocalization (Wexler et al., manuscript under review).

Cd doping can significantly improve performance of CZTS solar cells by suppressing disorder-inducing  $\text{Cu}_{\text{Zn}}+\text{Zn}_{\text{Cu}}$  and  $2\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}$  antisite defects under certain synthesis and doping conditions (*Chem. Mater.* **2018**, *30*, 4543). We recently collaborated with experimentalists who fabricated and characterized  $\text{Cu}_2\text{CdSnS}_4$  (CCdTS) solar cells (*Adv. Energy Mater.* **2019**, *9*, 1902509), while we used DFT to calculate the bulk and defect energetics of CCdTS under various synthesis conditions. To evaluate bulk and defect energies, we used SCAN XC because unlike GGA XC, SCAN's errors are systematic and it has the firmest theoretical underpinning (satisfying all 17 known constraints for XC functionals; *Phys. Rev. Lett.* **2015**, *115*, 36402). As in our previous work on Cd- and Ag-doped CZTS (*Chem. Mater.* **2018**, *30*, 4543), we considered three chemical scenarios relevant during synthesis or operation to evaluate defect formation energies, namely, Cu-rich, constrained Cu-poor, and Cu-poor. Importantly, CCdTS suppresses formation of  $2\text{Cu}_{\text{Cd}}+\text{Sn}_{\text{Cd}}$  SRH recombination centers across Cu chemical potentials, as indicated by higher formation energies and time-resolved photoluminescence (PL) decay times ( $>0.72$  eV under Cd-rich conditions and  $\tau_1-\tau_2=6.8-44.7$  ns, respectively) than in pure CZTS (0.67 eV under Zn-rich conditions and  $\tau_1-\tau_2=0.5-2.4$  ns). Complete Cd-substitution, however, does not alter formation of the  $V_{\text{oc}}$ -reducing  $\text{Cu}_{\text{Zn}}+\text{Zn}_{\text{Cu}}$ . However, complete Cd-substitution decreases the formation energy of Cu-vacancies, which increases the band gap of CCdTS into the ideal photovoltaic range, as indicated by the increase in the room-temperature steady-state PL intensities of CCdTS vs. pure CZTS (published in *Adv. Energy Mater.* **2019**, *9*, 1902509).

We recently devised an ion substitution strategy involving complete Cd- and Ge-substitution and partial selenization to suppress the low-formation-energy  $2\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}$  antisite clusters, ultimately arriving at an optimal composition of CCdGSSe. Full Cd- and Ge-substitution roughly doubles the formation energy of the deep-trap-inducing  $2\text{Cu}_{\text{Cd}}+\text{Ge}_{\text{Cd}}$ . We predict that partial selenization optimizes the band gap with respect to the Shockley-Queisser limit. In addition to providing a new, practical ion-substitution strategy, we elucidated the origin of defect suppression and promotion by Ge and Se, highlighting the key role of the inert pair effect and metal-chalcogen bond covalency, respectively. The ideal thermodynamic and electronic characteristics possessed by CCdGSSe should invigorate research on kesterite-based solar cells, specifically those that explore the rich materials optimization space afforded by ion substitution and post-quinary compounds (Wexler et al., manuscript in preparation).

In addition to CZTS, we also collaborated with experimentalists seeking to understand the synthesis of nanocrystalline  $\text{Fe}_2\text{GeS}_4$  (FGS), a potential low-cost PV absorber (manuscript under review). Our collaborators identified a modified FGS synthesis that utilizes a less expensive, air-stable Ge precursor (Ge-gly instead of  $\text{GeI}_4$ ), greener S precursor (S powder instead of TMS-S), and decreased reaction time. To verify that FGS was synthesized using the new procedure, the experimentalists measured the Raman spectrum of the as-synthesized sample. Because no experimental standards are available for the Raman spectrum of FGS, we used the GGA+ $U$  ( $U=3.7$  eV on Fe atoms) XC framework to compute the spectrum for FGS. Briefly, the Raman activity of a given vibrational mode can be obtained by calculating the derivative of the macroscopic dielectric tensor with respect to the corresponding normal mode coordinate. GGA+ $U$  calculations enable estimation of Raman activities, which in convolution with the wavelength and intensity of irradiation used in experiments, yields the Raman intensities. The orthorhombic space

group  $Pnma$  describes FGS, with the point group symmetry of  $D_{2h}^{16}$ . In turn, the 28 atoms present within the unit cell of  $\text{Fe}_2\text{GeS}_4$ , leads to 84 possible normal vibrational modes. The  $D_{2h}$  character table indicates that there should be four fundamentally active Raman modes:  $A_g$ ,  $B_{1g}$ ,  $B_{2g}$ ,  $B_{3g}$ . Importantly, the observed spectrum features an intense peak at  $\sim 350 \text{ cm}^{-1}$  with a few weak peaks on either side, in close agreement with the GGA+ $U$ -predicted intense peak at  $\sim 345 \text{ cm}^{-1}$  (and a minor peak at  $\sim 400 \text{ cm}^{-1}$ ). Thus, the robust agreement between theoretical predictions and experimental synthesis indicates successful synthesis of FGS with the new precursors. We now turn to our work on  $\text{WSe}_2$  (*J. Am. Chem. Soc.*, **2019**, *141*, 10451).

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 and strategies for performance improvement. We conducted a first-principles quantum dynamics investigation of charge-carrier dynamics in pristine and defective  $\text{WSe}_2$  monolayers with three of the most probable defects, Se vacancies, W vacancies, and  $\text{Se}_\text{W}$  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  $\text{Se}_\text{W}$  antisites also slightly accelerate recombination, the predicted mechanism differs 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  $\text{Se}_\text{W}$  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  $\text{WSe}_2$  monolayers.

Recent theoretical work (*Nano Lett.* **2017**, *17*, 7962) predicted that sulfur vacancies in a  $\text{MoS}_2$  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 also the mechanisms behind these dynamical processes differ. The most common intrinsic point defects frequently are chalcogen vacancies in TMDs. Normally, the mechanisms found in one material transfer 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  $\text{WSe}_2$  monolayers among the three most probable point defects. Although the  $\text{Se}_\text{W}$  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 reported for  $\text{MoS}_2$ . 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  $\text{WSe}_2$  monolayers.

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### **Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications**

**Postdocs:** Robert B. Wexler, Lesheng Li, Gopalakrishnan Sai Gautam, Xing Zhang, Kuang Yu, Thomas P. Senftle

**Graduate student:** Nima Alidoust

**Undergraduate student:** Sam Berman

### **10 Publications Acknowledging These Grants in the Last Three Years**

S. Hadke, S. Levchenko, G. S. Gautam, C. J. Hages, J. A. Márquez, F. Oliva, V. Izquierdo-Roca, E. A. Carter, T. Unold, and L. H. Wong, “Suppressing deep traps and band-gap fluctuations in  $\text{Cu}_2\text{ZnSnS}_4$  using Cd cation substitution,” *Adv. Energy Mater.* 1902509 (2019). [doi: 10.1002/aenm.201902509](https://doi.org/10.1002/aenm.201902509)

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## Novel Relativistic Electronic Structure Theories for Actinide-Containing Compounds

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### Abstract

#### Program Scope:

The present project deals with development of new quantum-chemical methods, algorithms, and computer programs for treating relativistic effects and application to heavy-element spectroscopy and chemistry (see Figure 1). The method-development work is focused on relativistic exact two-component (X2C) theory and X2C-based coupled-cluster methods, aiming to provide enhanced capabilities for accurately treating scalar-relativistic, spin-orbit, and electron-correlation effects in heavy-element containing systems. The application work is focused on understanding electronic and vibrational structures of heavy-element containing (especially actinide-containing) molecules in collaboration with experimental groups.

#### Recent Progress in theory work:

An atomic mean-field (AMF) version of the mean-field spin-orbit approach within the exact two-component (X2C) framework has recently been formulated and implemented [1, 2]. The X2CAMF approach provides accurate spin-orbit integrals with coupling

between scalar-relativistic and spin-orbit effects. The computational cost of constructing these integrals is negligible with exploitation of the local nature of spin-orbit coupling to enhance computational efficiency without significant loss of accuracy. The perturbative treatment of spin-orbit coupling at the coupled-cluster levels of theory with the use of the X2CAMF spin-orbit integrals has been shown to provide accurate treatment of spin-orbit coupling for heavy-element containing molecules, e.g., the prototypical  $\text{ThO}^+$  molecule, for which the computed vibronic levels for low-lying electronically excited states are in excellent agreement with experimental measurement.

Recent work on non-perturbative treatment of spin-orbit coupling within X2C has been focused on the formulation and implementation of analytic gradients for relativistic coupled-cluster methods. The implementation for the evaluation of one- and two-particle density matrices for the spin-orbit coupled-cluster singles and doubles (SO-CCSD) method has been completed. With ongoing implementation for the orbital-relaxation contributions, we are working toward a first implementation of analytic gradients for CC methods with spin-orbit coupling included at the orbital level.

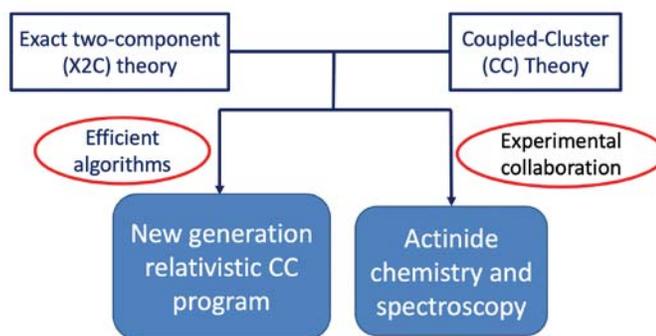
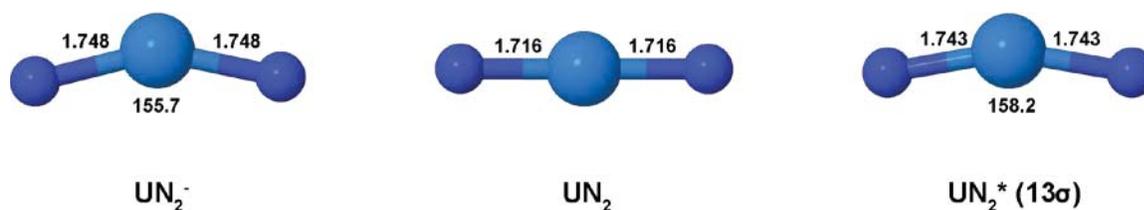


Figure 1. A schematic summary of the present project.

### Collaboration with experimental groups:

Computational studies of electronically excited states of the UN<sub>2</sub> molecule using relativistic coupled-cluster techniques have been performed to interpret the photoelectron spectrum of UN<sub>2</sub><sup>-</sup>, in collaboration with the group of Kit Bowen supported by the DOE Heavy Element Chemistry Program [3]. The vibrational structures in the photoelectron spectrum simulated using the discrete variable representation (DVR) method and relativistic coupled-cluster potential energy surfaces are in good agreement with the experimental spectrum. Relativistic equation-of-motion coupled-cluster calculations with spin-orbit coupling included at the orbital level have also provided accurate excitation energies and have helped assign the excited state features in the photoelectron spectrum. Beside simulation of the spectrum, the computations have found that both electron attachment and electronic excitation significantly bend the UN<sub>2</sub> molecule and elongate its U≡N bond (see Figure 2), which has interesting implications to the activation of UN<sub>2</sub>. The DVR technique implemented here has also been used to solve the sophisticated vibronic structures of the YbOH molecule [4].



**Figure 2.** Computationally optimized structures of the ground states of UN<sub>2</sub><sup>-</sup> and UN<sub>2</sub> as well as of the 13σ<sub>g</sub> electronically excited state of UN<sub>2</sub>, labeled here as UN<sub>2</sub><sup>\*</sup>(13σ).

### Future Plans:

The immediate next step in method-development work is to complete the implementation for the orbital-relaxation contributions to analytic gradients of the spin-orbit coupled-cluster singles and doubles with a noniterative triples [SO-CCSD(T)] method. This will be a first implementation of analytic gradients for coupled-cluster methods with spin-orbit coupling included at the orbital level. This implementation will enable efficient and accurate calculations of geometry and frequencies for actinide-containing molecules at SO-CC level of theory.

Collaborative work with the group of Kit Bowen is being focused on the photoelectron spectrum of ThOH<sup>-</sup>, in which computations are playing an important role in determining the geometries and excitation energies of ThOH. Calculations of absorption spectrum for the UN<sub>2</sub> molecule will also be performed to obtain useful information to facilitate experimental search for the spectrum, which is being carried out in the groups of Michael Heaven and Tim Steimle supported by DOE Heavy Element Chemistry Program.

### Grant Number and Grant Title:

The work described above was supported by Department of Energy, Office of Science, Office of Basic Energy Sciences under contract number DE-SC0020317: *Development of Novel Relativistic Electronic Structure Methods for Actinide-Containing Compounds*.

**List of students/postdocs supported (months):**

1. Postdocs: Junzi Liu (6)
2. Graduate student: Ayush Asthana (12)

**List of Publications Acknowledging the Grant:**

- [1] C. Zhang and L. Cheng “Performance of an atomic mean-field spin-orbit approach within exact two-component theory for perturbative treatment of spin-orbit coupling” *Mol. Phys.* accepted (2020).
- [2] D. A. Matthews, L. Cheng, M. E. Harding, F. Lipparini, S. Stopkowicz, T.-D. Jaga, P. G. Szalay, J. Gauss, and J. F. Stanton “Coupled cluster techniques for computational chemistry: the CFOUR program package.” *J. Chem. Phys.* accepted (2020).
- [3] G. Liu, C. Zhang, S. Ciborowski, A. Asthana, L. Cheng, and K. Bowen “Mapping the Electronic Structure of Uranium (VI) Dinitride (UN<sub>2</sub>) Molecule.” *J. Phys. Chem. A submitted* (2020).
- [4] E. T. Mengesha, A. T. Le, T. C. Steimle, C. Zhang, L. Cheng, B. L. Augenbraum, Z. Lansner, and J. Doyle “Branching ratios, radiative lifetimes and transition dipole moments for YbOH.” *J. Phys. Chem. A* accepted (2020).

## Towards Improved Simulation on Quantum Computers

Bryan K. Clark<sup>1</sup>

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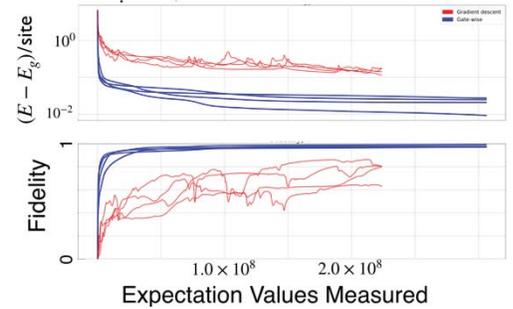
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### Abstract

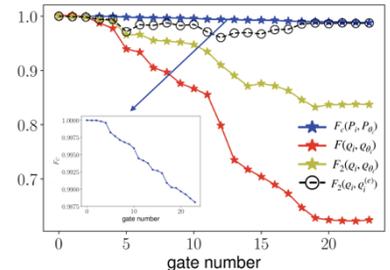
Quantum simulation is one of the most promising problems in which we might anticipate speed-ups using near term quantum computers (most commonly known as NISQ processors). For example, variational quantum eigensolvers (VQE) use quantum circuits as the variational ansatz for performing variational Monte Carlo.

This work is focused on developing the algorithmic tools and approaches necessary for improving such simulations. In one recent ongoing effort, we have been improving the optimization in variational quantum eigensolvers. While theoretically simple, the process of actually finding the optimal quantum circuit is highly non-trivial. While various techniques have been used, the current standard is to approach this problem using stochastic gradient descent (SGD). SGD can be effective but can converge slowly and get stuck in local minima. We are developing a new optimization technique for VQE, gate-wise optimization. This new technique is inspired by classical DMRG approaches which are among the most efficacious approaches to finding ground states. Gate-wise optimization has a number of advantages over standard techniques. We have seen, on empirical studies of condensed systems, convergence that is significantly faster in terms of total quantum resources used. Also, while gate-wise optimization is not guaranteed to find a global minima, it is able to tunnel through local minima in which SGD would be stuck. It additionally has the feature that it puts the “classical computation” back in quantum-classical hybrids returning a significant amount of computational effort to classical machines. The future effort on this work is focused on determining the generalizability of this new approach and benchmarking the tradeoff in different optimization schemes.

Another recently completed project has focused on improving the classical emulation of quantum circuits. Many aspects of quantum computing algorithms for simulations must be tested empirically. While eventually this can be done on actual quantum machines, classical testing is an important first step. Toward that end, it is key to having efficient emulation techniques. We have recently developed a new approach for quantum circuit emulation based on the POVM



*Preliminary data showing Energy-difference from the ground state and fidelity for gate-wise approach and a variant of gradient descent for an XXZ Hamiltonian.*



*Various fidelities of a VQE circuit to prepare the ground state of a transverse field Ising model.*

formalism. In this formalism, quantum states (generically with positive and negative amplitudes) gets mapped onto positive probability distributions; quantum gates get mapped onto semi-stochastic matrices. While these probability distributions require an exponential amount of memory to represent, we can store approximate compact representations of these states in various machine learning architectures – in our case we use a transformer. We then develop a novel algorithm to update the parameters of the transformer after the application of a quantum gate. At polynomial cost, this gives us an approximate evolution of the quantum circuit. We test our algorithm on (among other things) a VQE circuit. We find that the algorithm is particularly efficacious at producing the correct probability distribution for the POVM measurements corresponding to the POVM basis we were using. This suggests that one may be able to target our emulation methods to the measurements and observables we wish to extract from our quantum circuits. Our next step in this work is to determine whether one can go beyond being locked to a variational manifold.

We have also developed a new approach to generate unitary circuits (equivalently matrix-product operators) for diagonalizing many-body Hamiltonians. (This is particularly effective in the context of many-body localized systems which are common in disordered interacting Hamiltonians). This new approach is based on using a new efficient tensor-network version of the Wegner-Wilson flow we have developed. While currently not especially practical, the next phase of this work will be to determine how to optimally represent the MPO as a quantum circuit, how to perform the tensor operations directly on a quantum computer, and better categorize the class of Hamiltonians on which this procedure is effective (if only to partially diagonalize the system).

Finally, we have developed a new classical algorithm to back out parent Hamiltonians from symmetries. This has led to the development of a new class of spin liquids that may be useful for topological quantum computing and quantum error correction as well as a general approach to find parent Hamiltonians for Majoranas. We are now working on using this technique to develop validation and benchmarking of VQE algorithms.

DE-SC0020165: Porting classical approaches for quantum simulations to quantum computers.

**Student(s):** Lucas Slatery, Di Luo, Benjamin Villalonga, Eli Chertkov

### **Publications Acknowledging this Grant**

1. Carrasquilla, Juan, Di Luo, Felipe Pérez, Ashley Milsted, Bryan K. Clark, Maksims Volkovs, and Leandro Aolita. "Probabilistic Simulation of Quantum Circuits with the Transformer." *arXiv preprint arXiv:1912.11052* (2019).
2. Chertkov, Eli, Benjamin Villalonga, and Bryan K. Clark. "Engineering Topological Models with a General-Purpose Symmetry-to-Hamiltonian Approach." *arXiv preprint arXiv:1910.10165* (2019).
3. Yu, Xiongjie, David Pekker, and Bryan K. Clark. "Bulk Geometry of the Many Body Localized Phase from Wilson-Wegner Flow." *arXiv preprint arXiv:1909.11097* (2019).

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

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**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<sub>2</sub>, ROO·, ·QOOH, HCO, NO<sub>2</sub>, 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.

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).

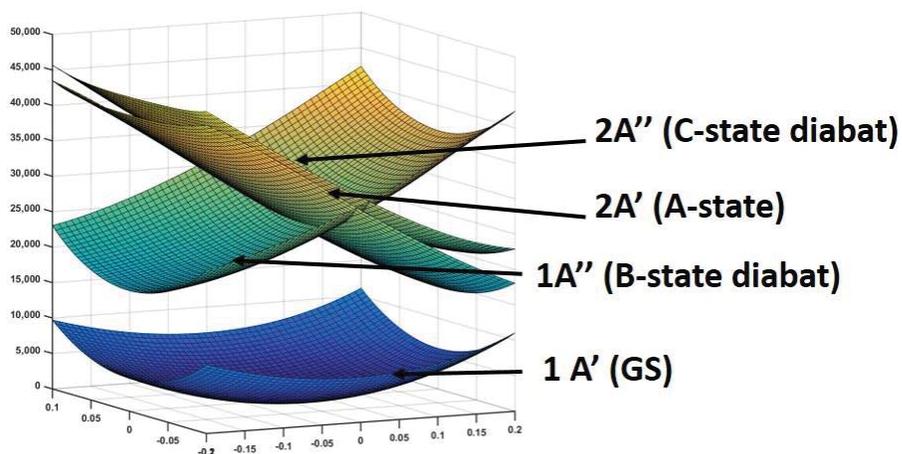
**Recent Progress:** This section describes recent progress achieved along various directions of the project occurring over the past 13 months since the project began in March 2019 (start date of this project was 03-01-2019).

Seven new articles citing DOE support have been published (or are under review) since early 2019.<sup>1-7</sup> A book chapter came out at the end of 2018,<sup>8</sup> citing prior DOE support since the start of this project was slightly delayed. Some critical mass seems to have been reached as two invited articles are now pending. A *JPCA* feature article and a review for *Ann. Rev. of Phys. Chem.* are both due in June 2020.

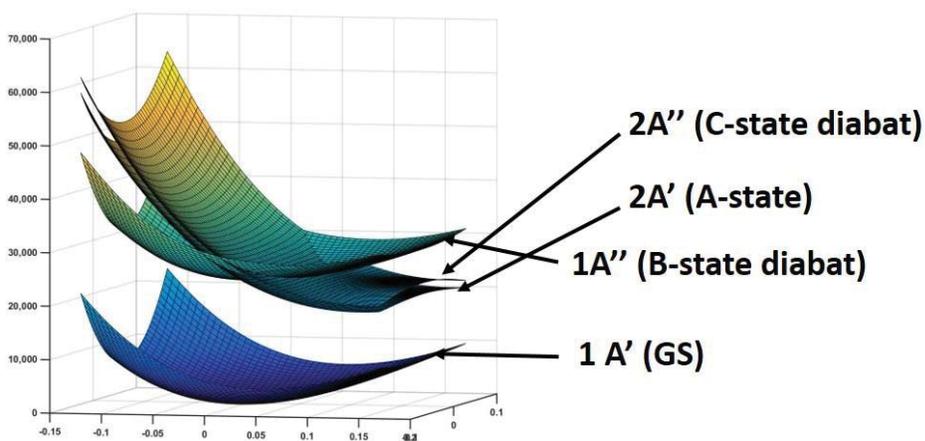
The thermochemistry project spearheaded by graduate student Bradley Welch and in collaboration with Branko Ruscic and David Bross (both from ANL) has resulted in a family of user-friendly scripts implementing the thermochemistry protocol on parallel HPC clusters. This was initially reported in a publication focused on a family of methylperoxy species,<sup>6</sup> and has since been extended to general benchmarks on over 200 small molecules.<sup>9</sup> These scripts have already been extended to other projects by myself and by undergraduate students. Graduate student Bradley Welch defended his thesis and graduated with his PhD. He has recently moved to pursue a postdoc position under the guidance of Angela Wilson at Michigan State University.

A main thrust mentioned above has been on robust calculation and fitting of energy and property surfaces for strongly coupled and intersecting excited electronic states. We have made some excellent progress in this area and recently completed fitting 20 different states and property surfaces in the notoriously tricky NO<sub>2</sub> system. Rovibrational calculations solving an exact Hamiltonian were used to compare the bound states on the ground electronic state with experiment. The RMSE for the 76 levels up to 7000 cm<sup>-1</sup> above ZPE are 14.1 and 82.2 cm<sup>-1</sup> for MRCI(Q) and MRCI based PESs respectively. This confirmed the anticipated necessity of using the Davidson correction, which can introduce some technical issues when applied to high-lying intersecting states. The Davidson corrected ground state PES is the most accurate produced to date and the accuracy does not degrade for the higher energy levels. This will enable predictive quality calculations to be performed for a number of states and processes.

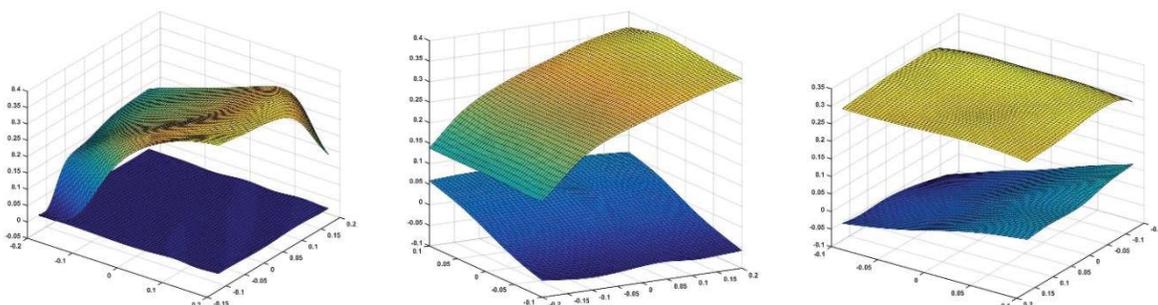
Success was achieved with a much greater challenge in NO<sub>2</sub>, that of diabaticization and fitting of a number of strongly coupled and intersecting excited state energy and property surfaces. Some examples are shown in Figures 1-3 and use of these to study the complex photophysics of this system are underway.



**Figure 1:** The two  $A''$  states ( $B + C$ ) are plotted in the diabatic representation for modes  $(v_1, v_3)$ , and the  $A'$  symmetry is added to the plot. The  $A'$  state is seen to closely shadow the dark  $C$ -state.



**Figure 2:** Same as Figure 1, but as a function of coordinates  $(v_2, v_3)$



**Figure 3:** (left)  $\langle 1.1 | \mu_x | 1.2 \rangle$  and  $\langle 1.1 | \mu_x | 2.2 \rangle$  are plotted in atomic units for modes  $(v_1, v_2)$ .  $\langle 1.1 | \mu_x | 2.2 \rangle$  is zero for  $C_{2v}$  geometries (when mode 3 is not displaced). (middle)  $\langle 1.1 | \mu_x | 1.2 \rangle$  and  $\langle 1.1 | \mu_x | 2.2 \rangle$  are plotted in atomic units for modes  $(v_1, v_3)$ . (right)  $\langle 1.1 | \mu_x | 1.2 \rangle$  and  $\langle 1.1 | \mu_x | 2.2 \rangle$  are plotted in atomic units for modes  $(v_2, v_3)$ .

Further progress was also made with time dependent quantum scattering with two papers by postdoc Ndengue being published.<sup>4,5</sup> Ndengue continues to collaborate with our group, but has accepted a permanent position at the newly established ICTP-East African Institute for Fundamental Research, University of Rwanda. Ndengue (originally from Cameroon) is very pleased with this successful outcome.

#### **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 18 months**

<sup>1</sup> Yang, Dongzheng, Junxiang Zuo, Jing Huang, Xixi Hu, Richard Dawes, Daiqian Xie, and Hua Guo. "A Global Full-Dimensional Potential Energy Surface for the K<sub>2</sub>Rb<sub>2</sub> Complex and Its Lifetime." *The Journal of Physical Chemistry Letters* 11, no. 7 (2020): 2605-2610.

<sup>2</sup> Shanyu Han, Carolyn E. Gunthardt, Richard Dawes, Daiqian Xie, Simon W. North, and Hua Guo, "Origin of the 'Odd' Behavior in the Ultraviolet Photochemistry of Ozone: Solving a 30 Year Old Mystery" PNAS MS# 2020-06070

<sup>3</sup> E. Q. Sanchez, R. Dawes. K. Lee, M.C. McCarthy, "Automated construction of potential energy surfaces suitable to describe vdW complexes with highly-excited nascent molecules: the rotational spectra of Ar--CS(v) and Ar--SiS(v)" JPC A (jp-2020-02685g).

<sup>4</sup> Ndengué, Steve A., Yohann Scribano, David M. Benoit, Fabien Gatti, and Richard Dawes. "Intermolecular rovibrational bound states of H<sub>2</sub>OH<sub>2</sub> dimer from a MultiConfiguration Time Dependent Hartree approach." *Chemical Physics Letters* 715 (2019): 347-353.

<sup>5</sup> Han, Shanyu, 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.

<sup>6</sup> Welch, Bradley K., Richard Dawes, David H. Bross, and Branko Ruscic. "An Automated Thermochemistry Protocol Based on Explicitly-Correlated Coupled-Cluster Theory: The Methyl-and Ethylperoxy Families." *The Journal of Physical Chemistry A* 123, 5673 (2019).

<sup>8</sup> Dawes, Richard, and Ernesto Quintas-Sanchez. "The Construction of ab initio-based potential energy surfaces." *Rev. Comput. Chem* 31 (2018): 199-264.

<sup>9</sup> Welch, Bradley K., Richard Dawes, David H. Bross, and Branko Ruscic. (in prep).

**Presenter: Barry D. Dunietz**

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

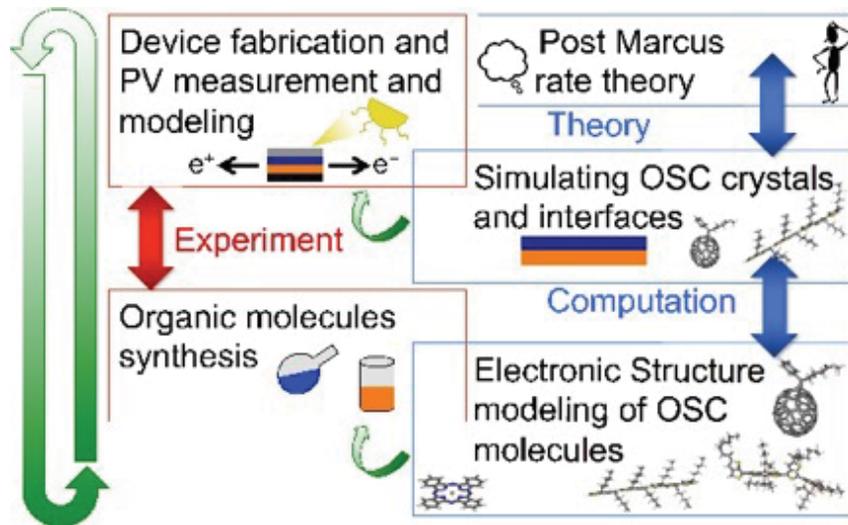
Margaret S. Cheung<sup>1</sup>, Barry D. Dunietz<sup>2</sup>, Eitan Geva<sup>3</sup>

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, that go beyond widely used simplifications, to achieve realistic descriptions of CT processes. This approach properly addresses the contribution of molecular environment at ambient conditions to the CT processes. Our approach achieves unique insight on CT processes that is most relevant to relevant experimental efforts.

The investigated processes span multiple scales in space and time, a challenge that we have overcome by developing an integrative approach that combines analytical rate theories, quantum mechanical calculations, and computer simulations. Our closely collaborative team that is 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).

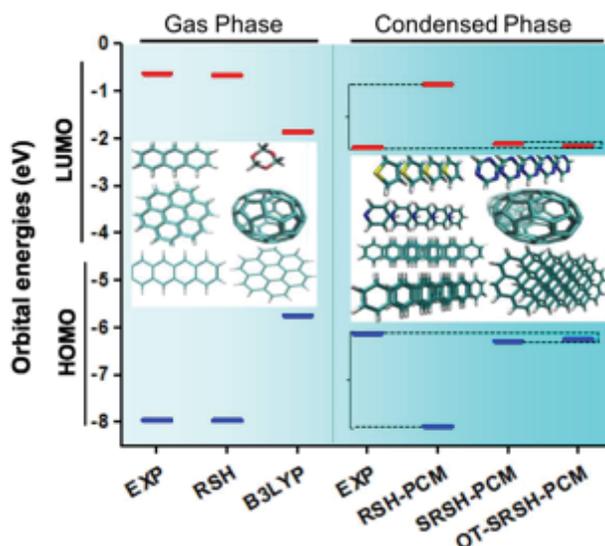


**Figure 1:** A multiscale and multi PI computational program to investigate charge transfer and transport in experimentally relevant molecular interfaces. Our program combines state-of-the-art electronic structure calculations, molecular dynamics simulations in the framework of quantum dynamical hierarchy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

achieves physically relevant frontier orbitals with electron removal and addition energies that reproduce well measured energies in the condensed phase. 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 of benchmark set of molecular crystal, where our screened RSH-PCM (SRSH-PCM) values are in excellent agreement with the measured ionization potentials and electron affinities.

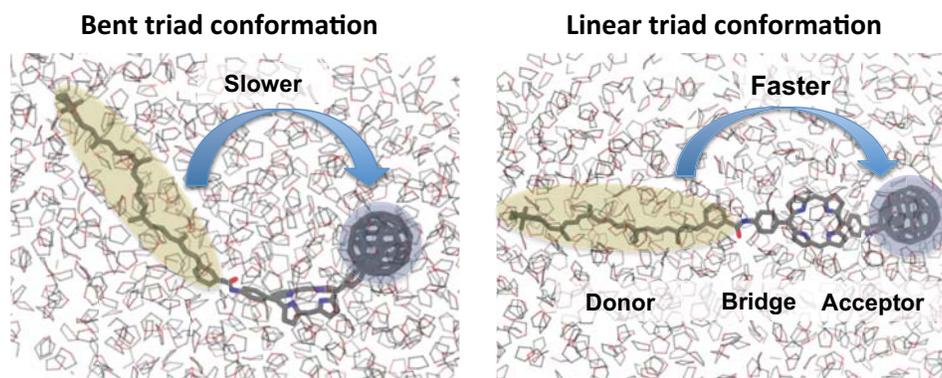


**Figure 2:** Average frontier orbital (HOMO and LUMO) energies, in eV, calculated in the gas phase and in various combinations with a PCM compared to the averaged benchmark IP and EA energies in gas and thin-film forms (Exp.). The SRSH-PCM and OT-SRSH-PCM present excellent agreement with the measured value in the crystal phase. (*J. Chem. Theory Comput.* **14** (2018) 6287) More recent benchmarking show the success of the SRSH-PCM framework in calculating excited charge transfer states (*J. Chem. Theory Comput.* **15** (2019) 4305), and triplet excitations (*J. Chem. Theory Comput.* **xx** (2020)).

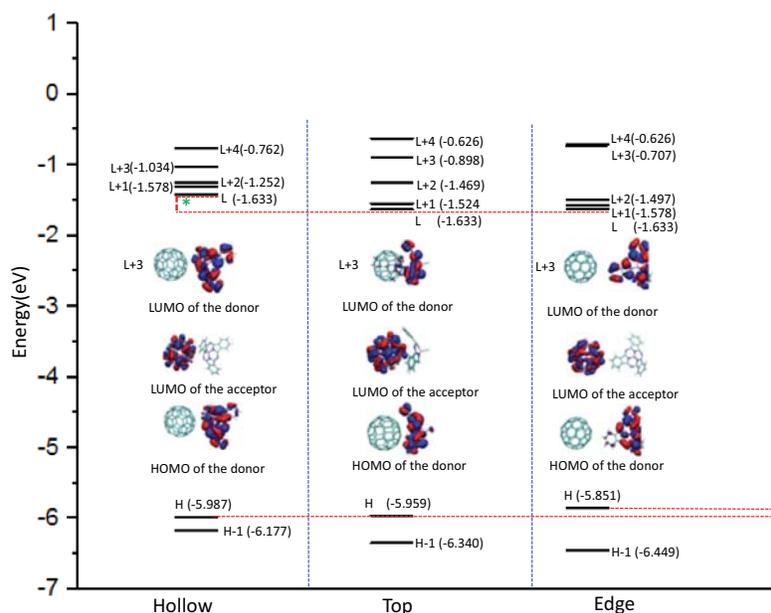
*In the second part,* we study photo induced CT in a complex molecular system of a solvated triad to understand the relationship of the CT to conformational flexibility. See illustrated in Figure 3. In this study we report for the first time the application of the hierarchy of approximations based on 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 the 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 study CT processes through an interface of SubPC and C<sub>60</sub>, 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. (*Phys. Rev. App.* **xx** (2020)) 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 developed 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 (*J. Chem. Phys.*, **160** (2019) 034101). 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. (*J. Chem. Phys.*, **151** (2019) 074103.)



**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<sub>60</sub> 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

- Discovery and characterization of an acridine radical photoreductant  
Buddhadev Maiti, Kunlun Wang, Scott D. Bunge, Robert J. Twieg and Barry D. Dunietz, *Nature*, **580** (2020) 76-80.
- Molecular-Level Exploration of the Structure-Function Relations Underlying Interfacial Charge Transfer in the Subphthalocyanine C<sub>60</sub> Organic Photovoltaic System  
Tinnin, S. Bhandari, P. Zhang, H. Aksu, B. Maiti, E. Geva, B. D. Dunietz, X. Sun, M. S. Cheung *Phys. Rev. App.* **XX** (2020) XXX.
- Efficient Charge Generation via Hole Transfer in Dilute Organic Donor–Fullerene Blends  
Y. Song, A. Schubert, X. Liu, S. Bhandari, S. R. Forrest, B. D. Dunietz, E. Geva, J. P. Ogilvie *J. Phys. Chem. Lett.*, **11** (2020) 2203-2210
- Screened Range-Separated Hybrid Functional with Polarizable Continuum Model Overcomes Challenges in Describing Triplet Excitations in the Condensed Phase Using 'TDDFT'  
K. Begam, S. Bhandari, B. Maiti, B. D. Dunietz *J. Chem. Theory Comput.* **XX** (2020) XXX.
- Combining the Mapping Hamiltonian Linearized Semiclassical Approach with the Generalized Quantum Master Equation to Simulate Electronically Nonadiabatic Molecular Dynamics  
E. Mulvihill, X. Gao, Y. Liu, A. Schubert, B. D. Dunietz, and E. Geva *J. Chem. Phys.*, **151** (2019) 074103.
- Quantitative accuracy in calculating charge transfer state energies in solvated molecular dimers using screened range separated hybrid functional within a polarized continuum model  
S. Bhandari, B. D. Dunietz *J. Chem. Theory Comput.*, **15** (2019) 4305.
- A modified generalized quantum master equation for simulating electronically nonadiabatic 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<sub>60</sub> 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  
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## Non-equilibrium statistical mechanical and coarse-grained modeling of catalytic systems

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### Abstract

Analysis of either the kinetics of catalytic reaction-diffusion processes, or the in-operando dynamics of catalyst surfaces or nanoclusters, constitute non-equilibrium phenomena where precise molecular-level modeling is desired (but where coarse-grained modeling may also be required to access experimental time and length scales). Recent activities have explored different aspects of these challenges: (i) In contrast to a traditional picture where catalyst metal surfaces are static, exposure to chemisorbed species can dramatically enhance fluxional dynamics. Exposure of coinage metal surfaces to even trace amounts of S can accelerate the decay of metal nanostructures by 1-2 orders of magnitude. From DFT analysis of energetics and kinetic modeling (integrated with low-T STM experiment), we show that this acceleration results from the formation of metal-S complexes which facilitate mass transport. A goal is to incorporate this surface dynamics into modeling of catalytic reaction processes. (ii) For catalytic conversion reactions in nanoporous materials, the interplay between inhibited transport within the pores and catalytic reaction produces anomalous kinetics. Molecular-level modeling is required to quantify the propensity for passing of reactant and produce species, and this propensity provides input to coarse-grained modeling of reaction yield. Applying this approach elucidates the strong dependence of yield for PNB conversion to aldol on pore diameter in mesoporous silica. (iii) A new effort explores the post-synthesis dynamics of metallic nanocrystals or nanoclusters (NCs). Shape-controlled synthesis on NCs can optimize catalytic properties, but these non-equilibrium shapes evolve back to equilibrium Wulff shapes. Supported metal NC catalysts can degrade due to NC diffusion and coalescence (or sintering). Evolution is controlled by diffusion of metal atoms across the NC surface in numerous local environments. We develop a stochastic model incorporating a realistic description of such surface diffusion and apply it to characterize such NC evolution.



### DOE Grant DE-AC02-07CH11358: Tools for Modeling of Catalysis on Multiple Scales

Personnel associated with the above projects: PIs: Jim Evans; Mark Gordon; Theresa Windus. Staff Scientists: Da-Jiang Liu; F. Zahariev. Students: King C. Lai; Jiyoung Lee; Yulim Kim.

### PROGRAM SCOPE

This theoretical Chemical Physics project 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 explores molecular-

level descriptions and analysis of: (i) the interplay between anomalous transport and catalytic reaction in functionalized mesoporous materials; (ii) chemisorption and heterogeneous catalysis on metal surfaces and nanoclusters; (iii) assembly and stability of catalytic nanomaterials.

## RECENT PROGRESS

### *Complex formation and enhanced mass transfer on coinage metal surfaces with trace additives*

Detailed characterization of chemisorption is key to describe reactant ordering in catalysis, but also possible chemisorption-induced restructuring and dynamics of metal surfaces by reactants or impurities (promoters or poisons). We focused on the effect of sulfur (S) which can produce ordered adlayers, reconstruction, and metal-S complex formation on coinage metals. Extensive DFT analysis, sometimes combined with statistical mechanical analysis, is integrated with low-T STM studies from collaborators for a comprehensive exploration of low-energy structures. Recent analysis explored the stability of  $MS$ ,  $MS_2$ ,  $M_2S_3$ ,  $M_3S_3$ ... complexes for  $M = Ag, Cu, Au$  systematically comparing adsorbed and gas-phase behavior within a Hess' law framework.<sup>7,8</sup> Also, M-S complexes (which can facilitate M transport) are generally more stable on (111) than (100) surfaces, consistent with observed greater enhancement of surface dynamics on the former.

### *Catalytic Reactions in Functionalized Nanoporous Materials*

Recent efforts have considered catalytic conversion reactions occurring inside linear nanopores of zeolites, functionalized mesoporous silica (by the Ames Lab catalysis group), etc.. Previous analyses had produced limited characterization of low reactivity due to inhibited transport into pores. We showed that mean-field reaction-diffusion equation (RDE) treatments fail to describe such behavior, instead developing a successful "generalized hydrodynamic" treatment.<sup>1</sup> A key parameter is the propensity for reactants and products to pass each other in the pore, a quantity which can be assessed by suitable Langevin simulations.<sup>1</sup> System specific multi-scale modeling was employed to elucidate an observed strong dependence of yield on pore diameter for PNB conversion to an aldol product in amine-functionalized mesoporous silica. Langevin simulation incorporating hydrodynamic diffusion tensors for PNB and aldol was first performed to determine passing propensity as a function of pore diameter. This parameter was input to coarse-grained stochastic modeling to describe reaction-diffusion kinetics, and revealed the desired strong pore diameter dependence in a specific regime of reaction relative to diffusion rate.<sup>10</sup>

### *Assembly and stability of catalytic metal nanomaterials.*

Solution-phase synthesis of metallic nanoclusters (NCs) has recently achieved remarkable control over shape and structure enabling optimization of properties, e.g., for catalysis. For example, if (100) facets are preferred for selectivity or reactivity, then fcc nanocubes can be synthesized. But such metastable nanocubes can reshape. Similarly, supported metal NC catalysts can degrade through coarsening, either via Ostwald Ripening (OR) or Smoluchowski Ripening (SR). The latter involves cluster diffusion and coalescence. On the nanoscale, reshaping diffusion and coalescence are typically mediated by diffusion of metal atoms across the NC surface. Evolution can occur on the time scale of seconds to tens of minutes, so stochastic modeling (rather than MD) is required. We develop such model with a realistic description of surface diffusion for diverse local environments (across and between facets, along step edges and around kinks) in contrast to previous efforts using a generic prescription of activation barriers (which fails dramatically for metal surfaces).<sup>2,5</sup> The model is applied to analyze nanocube reshaping, NC coalescence (capturing the experimental time scale for sintering of a pair of 4 nm Au NCs), pinch-off of elongated NCs, and diffusion of epitaxially supported NCs (revealing a complex oscillatory decrease of diffusivity with size, explained through analytic theory identifying the diffusion path and energetics).<sup>2,3,5</sup>

Other work on NC synthesis has explored the formation kinetics of intermetallic NCs,<sup>4</sup> and the potential to protect NCs from oxidation and coarsening via intercalation in layered materials.<sup>6</sup>

#### *Other projects.*

Reactions sometimes occur under “extreme” conditions such as high-pressure heterogeneous catalysis, where high pressures mean high coverages of reactant species on the “crowded” surface, and thus limited mobility or mixing of reactants. In this regime, text book chemical kinetics fails, and behavior can be dominated by fluctuations. We analyze discontinuous catalytic poisoning transitions for a benchmark Schloegl model for autocatalysis obtaining fundamental insights into differences between such non-equilibrium and classic equilibrium phase transitions.<sup>9</sup>

### **FUTURE PLANS**

Future research efforts will include the following: **(i)** Development of molecular-level system-specific analysis for catalysis in nano- and meso-porous materials in collaboration with Ames Lab Catalysis scientists. With the *Windus* and *Gordon groups*, we aim to apply FF-MD and EFP-MD analysis to assess: ordering of confined solvents; solvent-mediated diffusivity and interactions of reactant and product species; etc. This key information will provide input to our coarse-grained modeling. **(ii)** Energy- and environment-relevant catalysis on surfaces of metals, pnictides, and oxides with experimental collaborators, including DFT analysis of energetics and kinetic modeling **(iii)** Development of reliable theoretical frameworks to reliably catalytic reaction-diffusion kinetics including catalytic poisoning and spatiotemporal behavior in regimes where mean-field kinetics fails. **(iv)** Modeling of catalytic nanomaterials will continue exploration of the synthesis and stability of metallic nanoclusters (NCs), including intermetallics. New studies of single-atom-alloy (SAA) catalysis synthesis, and single-atom-catalysts (SAC) are also planned.

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# Machine learning accurate exchange and correlation functionals of the electronic density

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## Abstract

In the Stony Brook node we (student Sebastian Dick and PI Fernandez-Serra) have been working continuously on applying machine learning methods to develop new accurate exchange and correlation functionals in the framework of density functional theory (DFT). Our work started as a proof of concept. We showed in our first publication [1] that it is possible to learn from the density to improve the exchange and correlation energy. We coined these new DFT functionals **Machine Learned Correcting Functionals (MLCFs)**. Our goal was, rather than replacing DFT, to complement it. The principal concept of our original approach could be termed "Informed Machine Learning". In contrast to many deep learning based methods, we argue that all the available physical insight into a problem should be used to 'help' the ML-model make its predictions and minimize its generalization error. In MLCFs, this translates to DFT assuming the role of a data-preprocessor that maps the atomic coordinates to a self-consistent electron density which is inputted into an artificial neural network (ANN). The ANN then computes corrections to the energy and force calculations originally made with DFT. Thus MLCFs draw upon and optimize the strengths of DFT, which is effective in calculating electrostatic forces, but fails to accurately describe interactions rooted in quantum mechanics. At the same time, DFT provides a solid foundation which the ML-model can fall back on when faced with unseen scenarios in which it will likely fail to make accurate predictions.

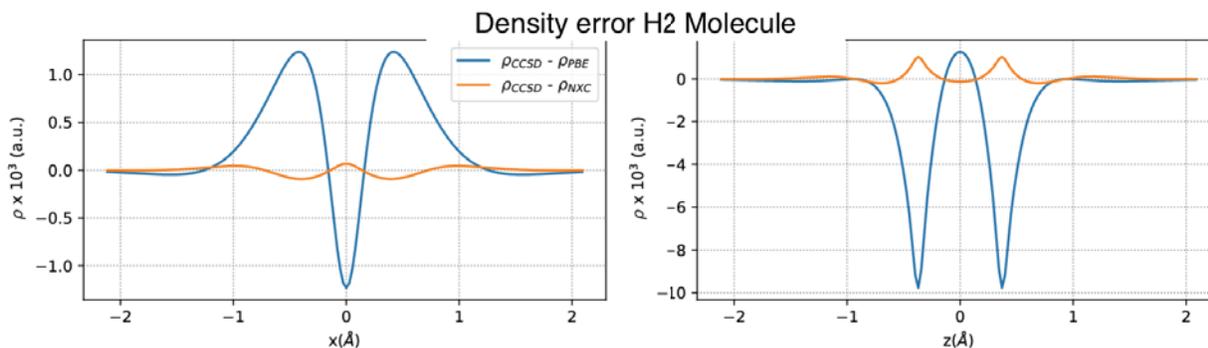
While MLCF were shown to work efficiently in publication [1], the question remained about it being possible to really obtain a real density functional, and its corresponding functional derivatives. The last 6 months we have been working on this the work is almost (pending small revisions) accepted for publication in Nature Communications [2]. In this last work we propose a pathway to construct fully machine-learned functionals that depend explicitly on the electronic density and implicitly on the atomic positions and are built on top of physically motivated functionals. These functionals are created for a specific data-set and hence are not universal. They follow the philosophy of other optimized density functionals which opt to prioritize the system-dependent accuracy over their transferability. However, transferability is still attained, even if not explicitly imposed. We show that it is possible to take the functional derivative of MLCFs thus creating semilocal ML density functionals that can be used in self-consistent calculations. We call this overall method NeuralXC.

Currently our group is working on two fronts, which aim to link with the machine learning efforts developed by Car's group in Princeton. (i) On one side our student Alec Wils is working on understanding the role of quantum mechanical and polarization effects on ion-ion interactions in liquid water. His study aims to decouple the differences observed between classical force field results and ab initio results in the potential of

mean force between equal and opposite charged ions in liquid water. He already has a very large amount of data that can be used to optimize a DEEP-MD force field for Na and Cl ions in water. Before the COVID19 crisis, we had already planned a week long visit by Alec to Princeton to work with the group of professor Car on learning how to use DEEP-MD. This visit has been cancelled, but we plan to re-organize this trained to happen virtually.

(ii) On the other side, with student Sebastian Dick we are continuing our path to search for fully machine learned functionals. In the next level of development, we are now working on developing a ML method where, instead of fitting to the exact total energy of the system we fit to the exact exchange and correlation potential. While our published results indicate that fitting a model to the total energy certainly improves the prediction of energies and forces it does little to improve electron densities.

Hence, we have designed a path to solve this problem by fitting to the exact potential instead. Our preliminary results are very encouraging. Assuming the exact potential for a given system is known, we can use it to define an extended loss function. We use the term "exact" in the sense that it reproduces the reference ground state density associated with the reference energy. The figure below shows how a functional trained in this fashion is able to reproduce the exact density for the H<sub>2</sub> molecule.



One dimensional cuts of the electron density. (left) Electron density on an axis orthogonal to the bonding axis, with the Hydrogen atom positioned at  $x = 0$ . (right) Electron density along the bonding axis. Both plots were computed for an H<sub>2</sub> molecule at experimental equilibrium geometry ( $d = 0.74 \text{ \AA}$ ), a configuration that was not contained in the training set.

Our work is complementary to the work going on at the Princeton main node. We expect that our interactions will be stronger as soon as my student Alec Wils starts using DEEP-MD.

**DE-SC0019394, Chemistry at Solutions and Interfaces, CCS Center Grant**

**Student(s):** Sebastian Dick, Alec Wils.

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

1. Learning from the density to correct total energy and forces in first principle simulations, Sebastian Dick and Marivi Fernandez-Serra, J. Chem. Phys. 151, 144102 (2019).
2. Machine Learning a Highly Accurate Exchange and Correlation Functional of the Electronic Density, Sebastian Dick and Marivi Fernandez-Serra, <https://doi.org/10.26434/chemrxiv.9947312.v1>

# Excited-State and Nonadiabatic Molecular Dynamics Methods with Broad Applicability

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## Abstract

Electronically excited states play a pivotal role in the capture, transformation, storage, and emission of radiative energy. Despite much recent progress for small model systems, excited state properties and dynamics in many larger molecular devices and materials have remained elusive for experiment and theory. Nonadiabatic transitions between electronic states turn radiative energy into heat and are particularly difficult to control. This project aims to develop new electronic structure and nonadiabatic molecular dynamics (NAMD) methods to simulate, predict, and ultimately control the flow and transformation of excitation energy in a wide-range of light-driven molecular devices such as dyes, photocatalysts, and fluorescence emitters.

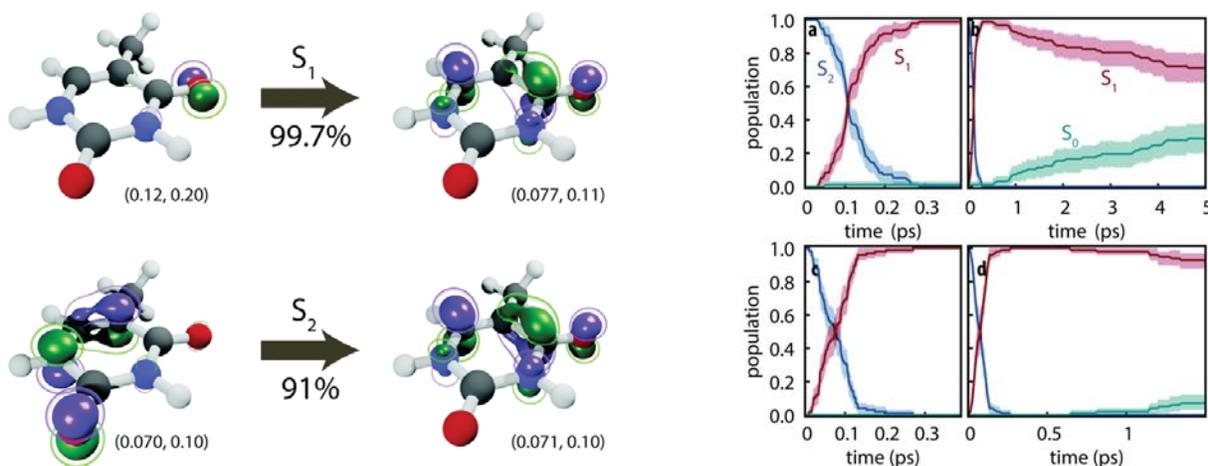


Figure 1: Left panel: Dominant natural transition orbitals (NTOs) for the  $S_1$  ( $n \rightarrow \pi^*$ ) and  $S_2$  ( $\pi \rightarrow \pi^*$ ) electronic states of thymine. The corresponding singular value is shown under the arrow. For each NTO, isovalues are shown below the corresponding orbital and chosen to contain approximately 25% (inner) and 50% (outer) of the total orbital density. All excitations at the Franck-Condon geometry. Right panel: Excited-state populations measured over trajectory swarms using (a and b) def2-SVP and (c and d) def2-SVPD basis sets. Shaded regions show the 95% bootstrap confidence interval. Panels (a) and (c) show the short time behavior while panels (b) and (d) show the picosecond behavior. Note the different time scales in (b) and (d) [1].

A highlight of the present reporting period was the development of a fully analytical NAMD implementation using time-dependent hybrid density functional theory (TDDFT) that includes couplings between arbitrary

states [1], thus enabling first-principles simulations of nonadiabatic radiationless decay processes beyond the first excited state. This work extends the first general-purpose hybrid TDDFT-based NAMD approach for molecular systems we have built with continued support from DOE-BES during the past seven years, and completes an important part of the current project. Our scheme is based on quadratic response theory [2, 3] and includes orbital relaxation terms [4] neglected in previous approaches; simultaneous computation of multiple derivative couplings and energy gradients enables resource-efficient multistate nonadiabatic molecular dynamics simulations in conjunction with Tully's fewest switches surface hopping (SH) method.

We assessed the thus obtained multistate TDDFT-SH scheme by simulating ultrafast decay of UV-photoexcited thymine, for which accurate gas-phase data from ultrafast spectroscopy experiments are available, see Fig. 1. The results agree well with the experimentally observed time constant, unlike previous multiconfigurational self-consistent field and second-order algebraic diagrammatic construction calculations. For thymine, the computational cost of a single TDDFT-SH time-step including the lowest 3 states, all couplings and gradients, is  $\sim 5$  times larger than the cost of a single Born-Oppenheimer dynamics time step for the ground state in our implementation. Thus, ps nonadiabatic dynamics simulations using multistate hybrid TDDFT-SH for systems with up to  $\sim 100$  atoms are possible without drastic approximations on single workstation nodes.

Another important example show-casing the impact of our methodology period was the experimental validation of a mechanism for 5-methoxyquinoline (5-MeOQ) photobasicity predicted by TDDFT-SH simulations [5]. The latter had suggested that the rate-determining step for photoinduced protonation of 5-MeOQ is hole transfer from photoexcited 5-MeOQ to adjacent water molecules within  $\sim 5$  ps followed by rapid electron-coupled proton transfer and deactivation to the ground state. However, this result is at variance with the traditional "Förster" picture of an excited acid-base equilibrium, and we hesitated to publish it until further experimental evidence in the form of kinetic isotope effect measurements became finally available last year. In conjunction with simple thermodynamic arguments and correlated wavefunction calculations, the absence of a significant kinetic isotope effect provided strong evidence for the proposed ultrafast redox-catalyzed proton transfer mechanism.

### **Grant Numbers and Grant Titles**

DE-SC0018352 Excited-State and Nonadiabatic Molecular Dynamics Methods with Broad Applicability

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

**Postdocs:** Shane M. Parker, Eva von Domaros

**Graduate Students:** Luke Nambi Mohanam, Gabriel Phun, Saswata Roy

**Undergraduate Students:** Alan Robledo, Tianyin Qiu

## Select Publications Acknowledging the Above Grants

- [1] S. M. Parker, S. Roy, and F. Furche: Multistate hybrid time-dependent density functional theory with surface hopping accurately captures ultrafast thymine photodeactivation, *Phys. Chem. Chem. Phys.* **21**, 18999–19010, 2019.
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# Quantum Chemical Treatment of Strongly Correlated Magnetic Systems Based on Heavy Elements

Award Number: DE-SC0002183

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## Program Scope

The objective of this project is to develop and employ novel quantum chemical methods in order to study the chemistry of systems containing actinides, and transactinides, with special focus on actinide-based single molecule magnets.

We model inherently multireference magnetic systems containing heavy elements with powerful embedding methods that will enable the calculation of electron correlation energy for extended systems. Commonly used magnetic materials that have potential applications in information storage, quantum information processing and spin electronics work thanks to the spin interactions between neighboring units in the bulk. Single molecule magnets (SMMs) can reduce the length scale of magnetic materials because they exhibit slow relaxation of the magnetization of purely molecular origin, and are thus able to retain their magnetization for a long time. The actinide and trans-actinide elements, because of their large spin-orbit coupling and the radial extension of the 5f orbitals, are promising for the design of both mononuclear and exchange-coupled molecules. Indeed, new actinide SMMs have emerged, and are already demonstrating encouraging properties.

Actinide based SMMs have near-degeneracy electron correlation effects and are thus inherently multiconfigurational systems. Their electronic structure cannot thus be accurately represented by a single Slater determinant approach, such as density functional theory (DFT). To overcome this limitation, we develop and exploit new methodologies for extended systems that go beyond current Kohn-Sham DFT. A balanced quantum mechanical treatment of their electronic structure requires a multiconfiguration (MC) wave function as a starting point for adding dynamic electron correlation. So far we have mainly explored mono-actinide SMMs, while the long term goal is to explore multi-actinide SMMs and their interaction with the environment vibrations, an effect that is crucial in quantum information processing where spin-phonon relaxation is the ultimate origin of decoherence of solid-state electron spin qubits at room temperature.

## Recent Progress

1) We computationally investigated some actinide metallabiphenylene complexes, namely  $(C_5Me_5)_2An(2,5-Ph_2\text{cyclopentadienyl}[3,4]\text{cyclobuta}[1,2]\text{benzene})$ , synthesized in the group of Dr. Kiplinger (Fig. 1). DFT and multireference calculations were performed to investigate the electronic structure of these species, the antiaromatic character of the cyclobutadiene ring and the aromatic character of the benzene ring. Spectroscopic evidence, molecular orbital compositions, and natural bond orbital calculations suggest significant covalency of the uranium  $f^2$  electrons with the carbon-containing fragment.

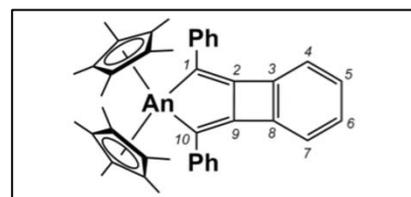
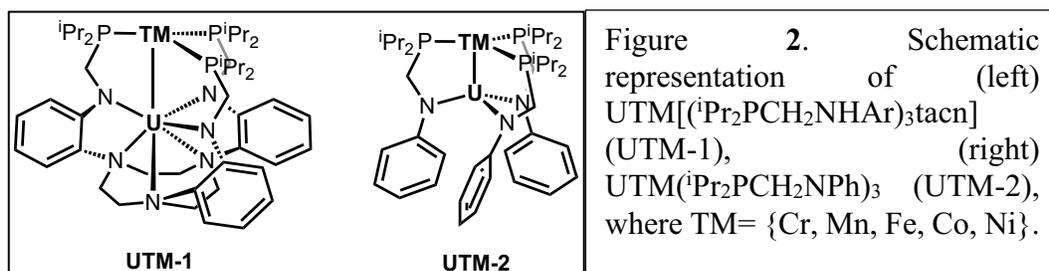


Figure 1. Structure of the actinide metallabiphenylene complexes. An=Th, U.

2) In collaboration with several PIs in the HEC program, including Eric J. Schelter, Thomas E. Albrecht-Schmitt, and Suzanne C. Bart, we investigated an isostructural family of *f*-element compounds (Ce, Nd, Sm, Gd; Am, Bk, Cf) of the redox-active dioxophenoxazine ligand (DOPO<sup>q</sup>; DOPO = 2,4,6,8-tetra-*tert*-butyl-1-oxo-1*H*-phenoxazin-9-olate). We explored the electronic structure of this new family, by performing complete active space self-consistent field (CASSCF) calculations, which revealed these systems to be largely ionic in contrast to previous studies, where berkelium and californium typically have a small degree of covalent character. As part of this collaboration we have also explored Cf(DOPO<sup>q</sup>)<sub>2</sub>(py)(NO<sub>3</sub>) (py = pyridine) where the nitrate anion is hypothesized to form via the alpha-radiolysis-induced reaction of pyridine with water. Computational analysis of the electronic structure of the complex reveals that the Cf<sup>III</sup>-ligand interactions are largely ionic.

3) We computationally explored novel heterobimetallic complexes featuring an uranium atom paired with a first-row transition metal using density functional theory and multireference wave function based methods. The synthetically inspired metalloligands U{(iPr<sub>2</sub>PCH<sub>2</sub>NAr)<sub>3</sub>tacn} and U(iPr<sub>2</sub>PCH<sub>2</sub>NPh)<sub>3</sub> (Fig. 2) were investigated. We reported the presence of multiple bonds between uranium and chromium, uranium and manganese, and uranium and iron. The calculations predicted a 5-fold bonding between uranium and manganese in the UMn(iPr<sub>2</sub>PCH<sub>2</sub>NPh)<sub>3</sub> complex, which is unprecedented in the literature.



4) The electronic structures and magnetic anisotropies for compounds [An(COT)<sub>2</sub>] (An = U<sup>III</sup>/U<sup>IV</sup>, Np<sup>III</sup>/Np<sup>IV</sup> and Pu<sup>III</sup>/Pu<sup>IV</sup>, COT = cyclooctatetraene) were characterized using scalar relativistic density functional theory calculations and second-order perturbation theory based on a complete active space self-consistent field reference, including also spin-orbit coupling. The degree of participation of 5*f* orbitals in actinide-ligand bonding and the associated metal-ligand covalency is found to trend as U > Np ≥ Pu for both the tetra-positive and tri-positive An complexes. A spin-Hamiltonian analysis indicates only weak single-molecule magnet (SMM) characteristics for [U(COT)<sub>2</sub>]<sup>-</sup> and [Np(COT)<sub>2</sub>] complexes and no significant SMM behavior for the other complexes. (Fig. 3) The weak SMM behavior in [U(COT)<sub>2</sub>]<sup>-</sup> and [Np(COT)<sub>2</sub>] is attributed to a subtle interplay between local symmetry and ligand-field splitting. Such a result suggests that magnetic anisotropy in 5*f*<sup>8</sup> ions can be modulated in general by electrostatic ligand field design. In particular, σ-donor ligands oriented 180 degrees relative to one another will have a maximal influence on the 5*f*-orbital ligand field splitting, while pi-donors like cyclopentadiene and COT generate ligand field influences that have more acute angles associated with corresponding atoms on the individual ligands. These observations rationalize the differences in SMM characteristics for [U(Bc<sup>Me</sup>)<sub>3</sub>] (Bc<sup>Me</sup> = dihydrobis(methylimidazolyl)borate) and [U(Bp<sup>Me</sup>)<sub>3</sub>] (Bp<sup>Me</sup> = dihydrobis(methylpyrazolyl)borate) and indicate strategies to design new actinide-based SMMs with high magnetic relaxation barriers.

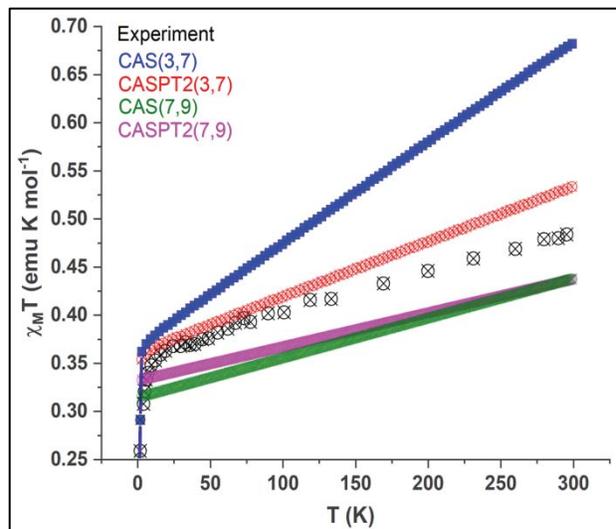


Figure 3. Experimental and *ab initio* computed magnetic susceptibilities for  $[\text{Np}^{\text{IV}}(\text{COT})_2]$ . The black crossed circles are experimental data. The blue, red, pink, and green circles are *ab initio* computed magnetic susceptibilities with CAS(3,7), CASPT2(3,7), CAS(7,9), and CASPT2(7,9) active spaces.

## Future Plans

Actinide-ligand complexes frequently contain a large number of strongly-correlated electronic degrees of freedom in their wave functions, which renders traditional multiconfiguration self-consistent field (MCSCF) approaches like the CASSCF method problematic due to the factorial explosion of the computational cost of the latter with respect to the size of the active space. However, in many of these systems, the strongly correlated electronic degrees of freedom are centered around separable units, for example distant actinide nuclei or weakly-entangled monomers, and a low-scaling local correlation or fragmentation approach to the MCSCF framework may generate realistic chemical models.

Along these lines, we recently introduced the localized active space self-consistent field (LASSCF) method for strongly-correlated systems characterized by weakly-entangled subunits. LASSCF was originally conceived as a generalization of density matrix embedding theory (DMET), but unlike the latter, LASSCF generates a true wave function for the whole molecule and provides an upper bound to CASSCF and full configuration interaction (FCI) energies. LASSCF produces a localized active space (LAS) wave function, which is an approximation to a CASSCF wave function in which the active space is split into one or more non-overlapping, unentangled subspaces. This approximation to CASSCF eliminates the inherent factorial operation and storage cost explosion with increasing system size that is associated with handling a single configuration interaction (CI) vector spanning a direct-product basis of orbitals. Initial tests of LASSCF showed that it reproduces the results of comparable CASSCF calculations, as long as the strong electron correlation of the test system was localized and short-range.

In the next grant period we will extend the LASSCF method to fully minimize the energy with respect to all orbital rotations, rendering it truly variational. This will hopefully improve the robustness and guess dependence of the LAS wave function. We are currently investigating some di-uranium species and exploring different ways of partitioning such systems in terms of active spaces. Magnetic susceptibilities and J coupling constants will be computed for these species.

**Postdoc(s):** Jing Xie, Carlo Alberto Gaggioli

**Student(s):** Prachi Sharma

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## Computational studies of metastable and non-equilibrium phase behavior in supercooled and glassy water

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### Abstract

Water is a ubiquitous substance in the chemical, biological, and energy sciences. Due to its importance in numerous natural and industrial processes, there is a long history of research characterizing water's physical properties. These efforts have revealed strikingly anomalous behavior relative to other fluids, including liquid water's observed maximum in density, and sharp increases in compressibility, heat capacity, and the magnitude of the thermal expansion coefficient upon cooling. Despite water's well-studied nature, finding a definitive explanation for the source of such anomalies is an area of vigorous research activity and debate. One theory is that under strongly supercooled conditions and high pressures, water undergoes a liquid-liquid phase separation into metastable high-density and low-density liquid states (HDL and LDL, respectively). In the pressure-temperature plane, this line of liquid-liquid coexistence terminates in a liquid-liquid critical point (LLCP), and the thermodynamic implications of the liquid-liquid transition can be traced to explain many of water's anomalies. Computer simulation techniques have led the charge in studying this phenomenon, as they are not in general affected by rapid crystallization, the occurrence of which in experiments places the temperatures and pressures where the liquid-liquid transition is theorized to occur outside the range accessible by current experimental techniques.

Further richness in the phase behavior of water is revealed when liquid water is rapidly quenched into the glassy state (producing the so-called amorphous ices). Experimentally, at least two types of amorphous ice have been discovered, which exist in low-density and high-density forms (LDA and HDA, respectively) separated by a first order-like transition. Despite the natural analogies between the non-equilibrium LDA-HDA transition in glassy water and the metastable LDL-HDL transition in simulations of supercooled liquid water, it is unclear whether the experimentally observed polyamorphism in glassy water necessarily constitutes proof of the existence of LDL, HDL, or an LLCP in real water.

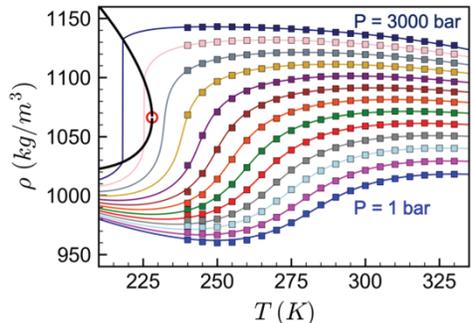
Given the robust debate around these issues, and the advantages of computer simulations in studying these phenomena, there is a need for ever more advanced computational approaches to further illuminate water's liquid-liquid transition and clarify its relationship to polyamorphism in glassy water. In this work, we combine state-of-the-art techniques in computational quantum chemistry, classical statistical mechanics, molecular simulation, and machine learning to shed light on these topics. In the first part, we use the Deep Potential Molecular Dynamics (DPMD) method to generate a neural network-based model of water obtained from high-accuracy density functional

theory calculations. We then use advanced molecular simulation techniques to obtain the thermophysical properties of this model and examine these results for behavior consistent with a liquid-liquid transition. In the second part, we perform non-equilibrium molecular dynamics (MD) simulations of popular classical atomistic and coarse-grained models of water undergoing rapid isobaric cooling. Starting from the liquid state, we track the long-range structure of water as a function of temperature and pressure, as the system is quenched out of equilibrium to form LDA and HDA ice.

In Project 1, we first use an active learning procedure to generate a deep-potential (DP) neural network model for water. In this approach, we train a deep neural network to represent the potential energy surface (PES) of water obtained from *ab-initio* calculations. The trained DP translates the local environment of an atom to *ab-initio*-level atomic energies and forces at a fraction of the computational cost, which can then be used to drive an MD simulation. We prepare the training data with density functional theory (DFT) calculations using the SCAN functional, which has recently shown promise in accurately predicting the thermophysical properties of water. We train the DP on more than 32,000 configurations that cover a range of conditions from  $0 \text{ K} < T < 2500 \text{ K}$  and  $0 < P < 300 \text{ GPa}$ . This general-purpose DP model allows us to explore water’s properties as predicted by the underlying SCAN PES, but at simulation speeds commensurate with the system sizes and time scales necessary for studies of supercooled water phase behavior, which was previously impossible with standard *ab-initio* simulation methods due to their large computational expense.

Via isothermal-isobaric MD simulations, we confirm that the DP model qualitatively reproduces key trends in the thermophysical properties of supercooled liquid water (not shown here for brevity), including the density maximum upon cooling, the increase in isothermal compressibility upon cooling, and the increase in diffusivity at increased pressure. After establishing that this DP model qualitatively reproduces the key features of experimental supercooled water, we use DPMD simulations in the multithermal-multibaric (MTMB) ensemble to efficiently obtain the thermophysical properties of this model over a wide range of temperatures and pressures. Figure 1 shows the density of water obtained from these MTMB simulations at  $240 \text{ K} < T < 330 \text{ K}$  and  $1 \text{ bar} < P < 3000 \text{ bar}$ . The shapes of the isobars are strongly suggestive of the existence of a liquid-liquid critical point; in order to estimate its location we fit these MTMB simulation results to a phenomenological two-state equation of state (TSEOS) model, which represents water as a mixture of high-entropy (high-density) and low-entropy (low-density) structures. The equation of state well-represents the trend in the MTMB simulation data and provides an estimate for the LLCPP location (red open circle). These results are consistent with the existence of an LLT in this DP model, providing *ab-initio* evidence for this phenomenon.

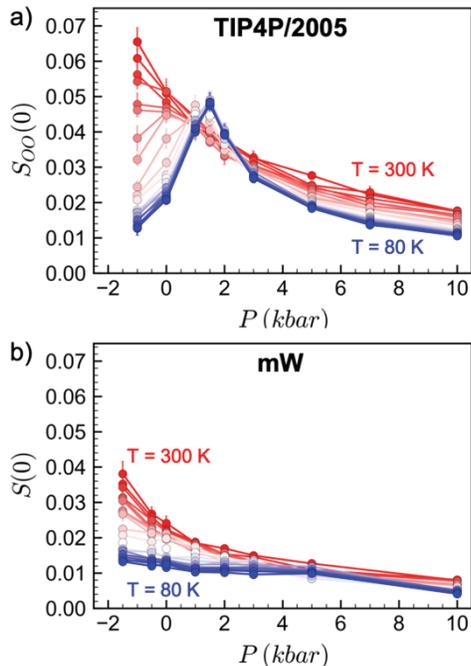
While the above results are strongly suggestive of the existence of the LLT, a definitive demonstration requires additional simulations. We plan to extend this work by using advanced sampling simulations to calculate the free energy surface of this DP model at temperatures and



**Figure 1:** MTMB simulation results (squares) for the density of supercooled liquid water as a function of temperature and pressure. Lines are the TSEOS fit to the simulation data. The liquid-liquid coexistence line and the LLCPP are denoted with the thick black line and open red circle, respectively. Isobars range from  $P = 1 \text{ bar}$  (blue) to  $P = 3000 \text{ bar}$  (dark blue) in steps of 250 bar.

pressures predicted by the TSEOS to exhibit liquid-liquid coexistence. Obtaining a free energy surface demonstrating liquid-liquid coexistence would be an unambiguous proof of the existence of an LLT in this DP model. In the longer term, we envision performing similar studies on DPs trained to even more accurate *ab-initio* functionals, sharpening our picture of supercooled water’s thermophysical anomalies and phase behavior.

In Project 2, motivated by the recent finding that long-range structural metrics (i.e., long-wavelength density fluctuations characterized by the low-wavenumber limit of the structure factor,



**Figure 2:** Low-wavenumber limit of the structure factor ( $S(0)$ ) during isobaric cooling simulations with the (a) TIP4P/2005 and (b) mW models of water. Different colors represent different temperatures along the cooling ramp, ranging from  $T = 300$  K (red) to  $T = 80$  K (blue) in steps of 10 K.

comprehensive characterization of the structure, dynamics, and mechanical properties of these systems as they are cooled near the LLC. Specifically, we aim to find a mechanistic explanation for the significant degree of structural relaxation observed in TIP4P/2005 at low and negative pressures, and to quantify the mechanical properties of water glasses prepared via these routes. Such a study would help clarify not only the relationship between polyamorphism and the LLC, but also contribute to our understanding of the physics of glasses.

In sum, our marriage of first-principles, classical molecular simulation, advanced sampling, and machine learning approaches have enabled us to rigorously explore the richly detailed phase behavior of supercooled and glassy water. Our preliminary results provide strong evidence for the existence of an LLT via *ab-initio* simulation techniques. Also, via classical MD simulations we uncovered a simple structural metric that suggests the possibility of identifying systems with an LLC. These findings help strengthen our understanding of the sources of water’s unusual properties, bolstering our ability to explain and/or harness water’s impacts on myriad natural, industrial, and energy-producing processes.

**Grant DE-SC001934: Chemistry in Solution and at Interfaces**

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**Students:** Linfeng Zhang

**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 potentials from correlated ab-initio ground-state densities. Thus, the overall direction of our effort is focused on developing systematically convergent, computationally efficient and scalable large-scale all-electron DFT calculation and employing these to address some of the outstanding issues in the field.

The recent progress in our effort over the past year is three-fold. Firstly, we have made significant progress in developing the enriched finite-element (FE) basis for all-electron calculations. The enriched FE basis is constructed from enriching the finite-element basis functions with compactly supported enrichment functions. Our previous work had demonstrated the utility of the approach in non-periodic systems [1]. In the last year, we have extended the capability to periodic systems. As part of this effort we have improved the computational approach and the algorithms, where the enrichment functions are orthogonalized with respect to the FE basis to improve the conditioning. Our benchmarking studies demonstrated systematic convergence of the ground-state energies using the enriched FE basis. Comparing the enriched FE basis with classical FE basis, we find an  $\sim 10$ -fold reduction in the degrees of freedom needed to converge the ground-state energies to chemical accuracy. We have benchmarked the calculations with Elk open source code, and for a system with 216 atoms of Si, the computational resources required for solving the problem are 3-fold lesser compared to Elk. Further, we have demonstrated the capability to perform all-electron periodic calculations on systems approaching 1000 atoms that have been out of reach for Elk. A second aspect of our work focused on using the recently released *open-source* DFT-FE code (<https://github.com/dftfeDevelopers/dftfe>) [2] to compute spin Hamiltonian parameters for systems comprising of di-vacancy in SiC and NV center in diamond. As these are defect systems that can have large cell-size effects, we developed and used a mixed all-electron pseudopotential approach, where the regions of interest are treated with all-electron accuracy and the other regions are treated with pseudopotential accuracy. We have verified that this approach provides the desired accuracy in the spin Hamiltonian parameters by comparing with full all-electron calculations. Using this approach, we have been able to compute the hyperfine and zero-field splitting tensor that are converged with respect to cell-sizes. Interestingly, cell-size effects are present up to  $\sim 800$  atoms on the divacancy system in SiC, cell-sizes that are only accessible via the mixed all-electron pseudopotential formulation. Finally, we have used the ability

to conduct accurate all-electron calculations to compute the exact exchange-correlation potentials using ab-initio correlated densities on a range of molecular systems that are both weakly and strongly-correlated. We have demonstrated that the solution obtained from our inverse DFT formulation provided chemical accuracy, and demonstrated the capability on polyatomic systems containing up to 56 electrons [3].

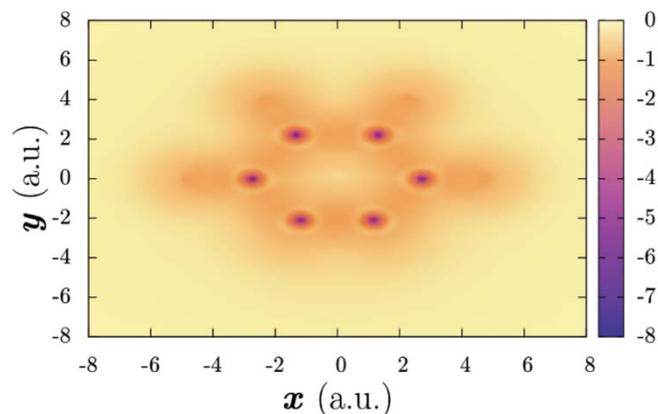


Figure: Exact exchange correlation potential of Benzene ( $C_6H_6$ ) computed using inverse DFT

Future plans continue to include the following aspects: (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 [1,4,5] 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.

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## 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):** Sambit Das

**Student(s):** Vishal Subramanian

## 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, *Comput. Phys. Commun.* **246**, 106853 (2020).
2. B. Kanungo, P. Zimmerman, V. Gavini, Exact exchange-correlation potentials from ground-state electron densities, *Nature Communications* **10**, 4497 (2019).
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Program Title: Theory and Code Developments and Applications to Surface Science, Heterogeneous Catalysis, and Intermolecular Interactions

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

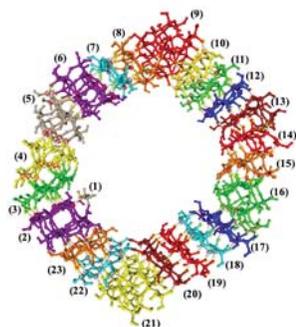
Recent Progress. A significant effort involves the development of efficient methods that can be applied to large systems, such as surfaces, nanoparticles and liquids. One such method is the effective fragment potential (EFP) method whose accuracy for intermolecular interactions rivals that of second 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 (SF) 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. More recently, we have developed a spin-flip approach (called SF ORMAS) that provides spin-correct wave functions, which most SF methods do not do. We now have fully analytic SF ORMAS gradients and, most recently, non-adiabatic coupling matrix elements (NACME). Related to this work, the derivation and coding of TDDFT NACME is almost completed.

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. A previous 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, thereby providing true linear scaling. 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 for most of the terms have been derived and implemented. The derivation and implementation of the remaining charge transfer (CT) term is in progress. The CT term is the most computationally demanding and the corresponding analytic gradient is the most complex component. However, CT can be very important when one is considering polar or ionic species.

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. Two papers on this work has been published, in collaboration with Professor Mel. Levy Tulane University), and another paper is in preparation.

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, Slowing and Windus groups. Electronic structure theory calculations have been combined with the non-equilibrium statistical mechanics methods of the Evans group, and with classical molecular dynamics simulations by the Evans and Windus groups, and also by EFP MD simulations, to provide insights about processes that occur within an MSN, as part of the CCS project. EFP MD simulations are being conducted on mixtures of reactants and solvents that might be found inside the pore. 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. The outcome of this study is that no alternative treatment of Coulomb effects that was considered 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.

Two of the CCS groups, those of Crawford (Virginia Tech) and Sherrill (Georgia Tech) have made excellent progress in the development of machine learning related to electronic structure theory. Crawford and his colleagues are about to submit a paper to a special issue of JPCA in which they demonstrate the efficacy of the density representation. The Sherrill group is applying machine learning to intermolecular interactions, starting with the multipole interactions that are important in the Coulomb term.

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.

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 and Theresa Windus, 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. We are also performing EFP MD simulations to predict diffusion constants inside the pore.

To obtain accurate potential energy surfaces, it is desirable to use coupled cluster (CC) theory, but CC theory is very time-consuming, scaling  $\sim N^7$ , where N is related to the size

of the system. To moderate the cost we are developing CC methods that apply the resolution of the identity (RI) to both CCSD(T) and CR-CC(2,3), as part of our CCS effort. The RI reduces 4-center 2-electron integrals to 3-center integrals, saving both computer time and memory costs. The code will be highly parallel and will ultimately be developed for GPU architectures. We (Sosonkina-ODU) are also assessing the impact of reducing the clock speed for EFMO calculations, in order to reduce the power consumption for large calculations. Power consumption can be a significant cost factor in modern computing. The group at EP Analytics (Leang, Tiwari, Carrington) and the group at UTK (Danalis, Jagode) are conducting performance analyses of the RI-MP2 code, with and without FMO, respectively. Access to high performance computing is necessary to determine scaling of the method.

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## Electrocatalysis at Liquid-Solid Interfaces: Principles and Reactivity-Stability Trends

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### Abstract

#### Program scope and definition

We continue to explore the fundamental principles of electrocatalysis and electrocatalytic reaction mechanisms at electrified solid/liquid interfaces using periodic Density Functional Theory methodologies. This effort seeks to identify and exploit efficient methods to elucidate complex electrocatalytic reaction mechanisms under realistic *in-situ* conditions, estimate the statistical thermodynamics and kinetics of charge transfer at interfaces, generate pH/potential-dependent phase diagrams of multifunctional interfaces in aqueous environments, and investigate new approaches for applying these fundamental insights to enhance the properties of electrocatalysts for energy-relevant chemistries.

#### Recent Progress

In this update, we describe work in two primary topic areas related to thermodynamic and mechanistic analyses of catalytic phenomena at liquid/solid interfaces (a few additional projects are not described herein). The first project combines applications with some methods development to probe the structure sensitivity of ethanol electrooxidation on platinum. This chemistry, which could in principle be used to power low temperature fuel cells as a highly convenient alternative to hydrogen, is among the most mechanistically complex electrocatalytic reactions ever to be studied. It has been the subject of numerous studies, and yet fundamental questions, such as which reaction intermediates are present on the catalyst surface and which elementary reaction steps limit performance, are still extensively debated. Answering these questions will provide opportunities for both fundamental development of strategies for modeling electrocatalysis at liquid/solid interfaces and, ultimately, making theory-guided suggestions for new strategies to optimize materials for ethanol-based fuel cells and related electrochemical devices. We have, in the past project year, initiated studies in this area by combining traditional Nernstian techniques, such as the standard hydrogen electrode formalism developed several years ago by Nørskov and coworkers, rigorous strategies for calculating true free energy barriers for electrocatalytic reactions at water-solid interfaces, and microkinetic modeling of extensive reaction networks to describe the ethanol electrochemistry at an unprecedented level of detail.

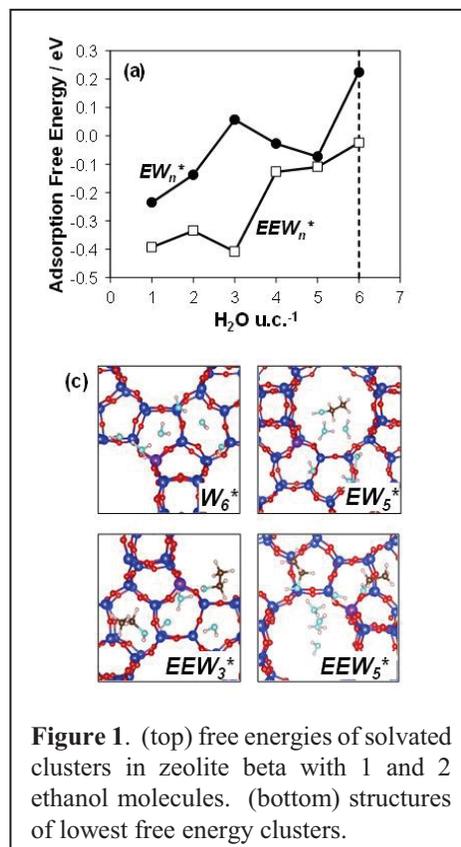
Our initial analysis has focused on the Pt(100) single crystal surface, as this facet is known to show some of the high activity characteristic of undercoordinated steps while preserving the structural simplicity that is invaluable for initial modeling analyses. In analyzing the various reaction steps, it is useful to recognize that there are three primary classes of elementary steps, each of which requires a different computational strategy: 1) traditional covalent bond-breaking reactions that do not involve explicit charge transfer, including C-C scission, 2) C-H and O-H bond breaking steps that may or may not involve direct formation of a proton/electron pair and, hence, charge transfer, and 3) adsorption/desorption steps that involve significant rearrangements of water molecules as species approach/desorb from the surface. We have introduced strategies for self-consistently dealing with each of these classes of steps. C-C bond activation and C-H bond activation, wherein the hydrogen

atom product proceeds directly to the surface, are found to be relatively standard covalent bond-breaking processes. Such reactions can be treated well with traditional (and inexpensive) saddle point search techniques. We have extensively verified this conclusion with rigorous thermodynamic integration analyses through potential of mean force (PMF) simulations. O—H bond activation, however, appears to routinely involve formation of proton-electron pairs, and to accurately model the potential dependence of these processes, we use a full double layer model in which the double layer is treated as a plate capacitor, permitting accurate extrapolation of the O—H scission barriers to conditions of constant potential. Adsorption/desorption steps, in contrast, involve significant reorganization of solvent species and so must be treated with rigorous potential mean force analyses. In addition to providing particular insights into ethanol electrochemistry (described further below), we expect that these general conclusions could accelerate future analyses of complex electrochemical hydrocarbon reaction networks.

One of the key mechanistic conclusions to date has been that the initial dissociative adsorption of ethanol via C-H bond scission is a crucial selectivity-determining step. Activation of an  $\alpha$  C—H bond results in selectivity towards partially oxidized products such as acetaldehyde and acetic acid (2 and 4 e- transfer per ethanol molecule, respectively). Conversely, the  $\beta$  C—H pathway leads to the formation of  $\text{CH}_2\text{CH}_2\text{OH}^*$  intermediate, which can undergo multiple facile C—H and O—H bond breaking reactions and ultimately C-C scission to yield  $\text{CH}^*$ ,  $\text{CH}_2^*$  and  $\text{CO}^*$ , which can then react with surface oxygenated species to form  $\text{CO}_2$  (12 e- transfer per ethanol molecule). Preliminary microkinetic treatments confirm these interpretations and suggest that finding catalysts to promote  $\alpha$  C-H activation could be a useful strategy to enhance the total oxidation of ethanol.

### Water structuring near catalytic active sites in confined geometries

A central theme of electrocatalysis is the impact of water on surface chemical reactions and on the structure of the electrochemical double layer. The structure of the aqueous solvent often differs dramatically from that of bulk water due to the combined effects of confined geometries near surfaces and disruption of the water structure from solvated cations and adsorbed surface species. Over the past two years, we have developed a strategy, based on the use of ab-initio molecular dynamics simulations, to estimate the entropy of water in such condensed phases by calculating the vibrational density of states of the water and decomposing this density into ideal gas, rotational, and vibrational contributions. The approach predicts the absolute entropy of bulk liquid water to within  $\sim 5\%$ , and when combined with average potential energies from the AIMD runs, can be used to compute Helmholtz free energies of water in different condensed geometries and at different densities. We have recently completed application of this approach to the study of water in a well-known zeolite class, called Beta, that is used for a



**Figure 1.** (top) free energies of solvated clusters in zeolite beta with 1 and 2 ethanol molecules. (bottom) structures of lowest free energy clusters.

variety of industrially-relevant energy conversion processes. This analysis, which was recently published in *Angewandte Chemie*, is a first step towards the application of similar techniques to the even richer environment of charged double layers near solid surfaces.

In addition, in the past project year, we have generalized this work to study the effects of Brønsted acid proton delocalization to water clusters surrounding the active site, and to understand how these confined solvated phases interact with reacting species. To this end, we have studied the ethanol dimerization to diethyl ether, a common probe reaction in the condensed phase zeolite literature. Building upon the recently published study in our team, we used an extensive series of AIMD simulations to study the dynamics of different sizes of water clusters in the pores of zeolite Beta, wherein one Si atom in the pore walls was replaced with aluminum and charge compensated with a proton to form the Brønsted site. For each such cluster size, the average energies were determined from the AIMD trajectories, and the entropies of the solvated water were determined using a quasi-harmonic frequency analysis wherein all changes in water and proton entropies were approximated by a combination of translational and vibrational modes. All water clusters were found to be electrostatically tethered to the Brønsted sites, and the protons were found to be largely delocalized throughout the clusters. For the ethanol dehydration chemistry, the full free energy analysis determined that minima in free energy can be found for a single ethanol molecule solvated by five water molecules and for an ethanol dimer solvated by three water molecules (Figure 1). A rigorous metadynamics simulation (which can be thought of as a generalization of potential of mean force integrations) found a free energy barrier for ethanol dimer conversion to diethyl ether of  $\sim 1.3$  eV. Both the ethanol dimeric reactants and the transition state for DEE formation were found to live on the *edges* of the water clusters, with the hydrophobic groups sticking out of the clusters. In close collaboration with the group of Rajamani Gounder at Purdue, we determined that this arrangement leads to relatively intuitive Langmuir-Hinshelwood kinetics for the ethanol dehydration reaction. In contrast, when the water partial pressure in the system is increased near the point of bulk liquid water formation, the zeolite Beta pores undergo a complete wetting transition, after which, as shown by the Gounder group's kinetic measurements, the kinetics become highly non-ideal. The simulations suggest that this non-ideality, in turn, is related to the greater difference in solvation free energies of the hydrophobic tails of the transition and initial states during DEE formation.

Taken together, these two studies establish a practical and accurate strategy for describing the effect of solvents in reduced dimensions on reaction chemistries. We are beginning to explore the impact of these differing local water structures on catalytic events that occur near the defects, and we are additionally starting to adapt these techniques to calculation of the entropy of local water structures in electrocatalytic double layers near smooth and nanoparticle metal surfaces.

## **Future Plans**

In addition to continuing the efforts described above, we will continue developing strategies for describing solvation effects on catalysis in reduced dimensions, including in microporous solids and at transition metal surfaces. We intend to extend our detailed kinetic work to evaluate the influence of solvation and microkinetic balances on oxygen evolution reaction (OER) electrocatalysis on base metal hydroxyoxides in alkaline solutions. We will also continue efforts to apply the metadynamics, potential of mean force, and quasi-harmonic strategies developed during the previous project year to provide enhanced descriptions of electrochemical double layer structure for complex reacting species.

If time permits, we would also like to extend these analyses beyond double layers in acidic solutions, which constitute the state of the art in computational analysis, to alkaline double layers, which have received no treatments in the literature and yet which may have important implications for the growing field of alkaline electrocatalysis.

### Grant Numbers and Grant Titles

DE-BES-CTC: Electrocatalysis at Liquid-Solid Interfaces: Principles and Reactivity-Stability Trends

**Postdoc(s):** Zhenhua Zeng

**Student(s):** Ankita Morankar, Joseph Kubal, Siddharth Deshpande

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

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## Nonadiabatic Photochemistry

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### 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 diabatic potential energy surfaces fit to accurate electronic structure data (ESD) generated from accurate, quantum mechanical wavefunctions.

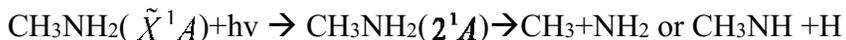
### Recent progress:

#### David R. Yarkony

During the present performance period we have addressed three aspects of conical intersections, a ubiquitous topographical feature of the potential energy landscape.

We have developed a completely new version of our algorithm (SURFGEN),<sup>1</sup> which simultaneously fits and diabaticizes *ab initio* adiabatic ESD. It replaces the molecular functions, bond angles and dihedral angles used in SURFGEN with feed forward Neural Network (NN) functions. This algorithm (NN-SURFGEN) employs permutation invariant polynomials (PIPs)<sup>2</sup> which unlike molecular functions can be symmetry equivalent atoms, in the CNPI group,<sup>3</sup> without treating multidimensional irreducible representations. Our previous representations of ESD have focused on the coupled potentials energy surfaces (PESs). Interactions with the electric field, dipole and transition dipole and the spin-orbit interaction were not considered. As part of other funded research, we have developed algorithms to fit dipole and transition dipole moments<sup>4</sup> and spin-orbit interaction.<sup>5</sup> This will allow us to handle problems not usually treated with the fit representation of ESD approach. In particular we hope to treat processes in which the electromagnetic fields shift the locus of the conical intersection seam<sup>6</sup> and in which intersystem crossing competes with internal conversion.<sup>7</sup>

We studied the photodissociation of methylamine,<sup>8</sup>



a deceptively simple methyl derivative of NH<sub>3</sub>. It might appear that both the methyl and hydrogen channels of the above photodissociation would be produced by a similar mechanism. But that is not the case, as the excited 2<sup>1</sup>A state barrier and 1-2<sup>1</sup>A conical intersection relevant to the methyl channel are sufficiently high in energy to preclude direct production of that channel. Rather, the methyl channel is produced indirectly via the 1<sup>1</sup>A state equilibrium structure. This required us to develop a representation of the ESD that could describe both direct and statistical, long time propagation, dissociation. Long time propagation dynamics requires fit ESD as opposed to on-the-fly ESD. In future work we will compare the long-lived trajectories with the predictions of statistical models.

With Guo we are studying the effects of the conical intersections on product energy disposal in the nonadiabatic photodissociation of phenol

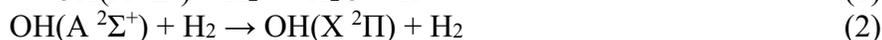


The primacy of the **g** and **h** modes,<sup>9</sup> defining the branching space in the vicinity of a conical intersection, is well established. Here **g** and **h** are 2 of the 3 disappearing modes. However, the

role of the remaining modes is less well studied/understood. A key question is: how is energy redistributed into and among these modes during photodissociation. The assignment of the line positions and intensities in the observed H-atom kinetic energy release (KER) spectrum<sup>10</sup> is computationally challenging since the process involves two nonadiabatic steps. Guo has carried out<sup>11</sup> a series of 1,2,3<sup>1</sup>A state reduced 4-internal coordinate (3 disappearing modes and one phenoxyl mode), coupled adiabatic state simulations of the measured KER spectrum. It is gratifying that the diabatic potential energy matrix (DPEM) used in these calculations is the one we determined over 4 years ago as part of a previous DoE BES grant.<sup>1, 12</sup> Guo's results challenged prior interpretations of the measured KER spectra. In the coming performance period, the dynamical model will be extended to incorporate additional degrees of freedom, yielding a more accurate representation/understanding of the photodissociation.

### Donald G. Truhlar

The reactions



provide enticing targets for theoretical study because of the detailed experimental data available, dating back to the pioneering experimental studies in the Lester, Crosley, and Heard laboratories. Upon the A <sup>2</sup>Σ<sup>+</sup>-X <sup>2</sup>Π excitation of isolated OH, only radiative decay is conceivable, but collisions with other molecules open nonradiative de-excitation pathways, such as reactions (1) and (2). Understanding these competitive pathways is necessary to fully interpret the LIF measurements. In addition, the OH<sub>3</sub> system has established itself as the four-body system most widely studied by quantum mechanical dynamics calculations; in particular, OH<sub>3</sub> is a prototype for four-body quantum dynamics in a similar way to how H<sub>3</sub> is a prototype for three-body quantum dynamics.

We have employed extended multi-configuration quasidegenerate perturbation theory, fourfold-way diabatic molecular orbitals, and configurational uniformity to develop a global three-state diabatic representation of the PESs and their couplings for the electronically nonadiabatic reaction (1).<sup>13</sup> To achieve sign consistency of the computed diabatic couplings, we developed a GPU-accelerated algorithm called the cluster-growing algorithm. Having obtained consistent signs of the diabatic couplings, we fit the diabatic matrix elements (which consist of the diabatic potentials and the diabatic couplings) to analytic representations. Adiabatic PESs are generated by diagonalizing the 3 × 3 DPEM. The comparisons between the fitted and computed DPEM elements and between the originally computed adiabatic PESs and those generated from the fits indicate that the fit is accurate enough for semiclassical dynamics calculations, although further adjustments are necessary for quantal dynamics calculations that require energies over a broader range of geometries than are accessed in the classical trajectories explored during the parametrization.

Photodissociation of thiophenol produces a phenylthiyl radical in which the singly occupied molecular orbitals (SOMOs) for the both the ground and first excited states are dominated by the occupied 3*p* orbital on sulfur. Photoinduced bond fission processes proceeding via an n<sub>π</sub>σ\* excited state are prototypes of electronically nonadiabatic reactions. The photodissociation of thiophenol is a representative of these n<sub>π</sub>σ\*-mediated reactions that has been extensively studied both experimentally and theoretically. The photo-induced S-H fission of thiophenol mainly involves the ground state and the first two excited singlet states; these singlet states are labeled as

${}^1\Pi\Pi$ ,  ${}^1\Pi\Pi^*$ , and  ${}^1n_\Pi\sigma^*$  in the diabatic representation and as  $S_0$ ,  $S_1$ , and  $S_2$  in the adiabatic representation. The  ${}^1n_\Pi\sigma^*$  state is repulsive along the S–H dissociation coordinates and intersects the  ${}^1\Pi\Pi^*$  and  ${}^1\Pi\Pi$  states; the conical intersections are  $(3N - 8)$ -dimensional subspaces of these  $(3N - 7)$ -dimensional diabatic crossings. We have constructed a set of full-dimensional PESs and state couplings for thiophenol in the diabatic representation.<sup>14</sup> The DPEMs are obtained by electronic structure calculations including dynamic correlation via excitations into the virtual space of a three-state multi-configuration self-consistent field calculation. The resulting DPEM is a function of all the internal coordinates of thiophenol. The DPEM as a function of the S–H bond stretch and C–C–S–H torsion and the diabatic couplings along two in-plane bend modes and nine out-of-plane distortion modes are computed using extended multi-configurational quasi-degenerate perturbation theory followed by the fourfold way determination of diabatic molecular orbitals and model space diabatization by configurational uniformity, and this dependence of the DPEM is represented by general functional forms. Potentials along 31 tertiary internal degrees of freedom are modeled with system-dependent, primary-coordinate-dependent nonreactive molecular mechanics-type force fields that are parametrized by Cartesian Hessians calculated by generalized Kohn-Sham density functional theory. These component fits are joined together by the anchor points reactive potential (APRP) scheme developed in our group. The resulting full-dimensional potentials and state couplings are functions of all 33 internal degrees of freedom of thiophenol. Adiabatic PESs and nonadiabatic couplings are obtained by a transformation of the DPEM. The topography of the APRP PESs is characterized by vertical excitation energies, equilibrium geometries, vibrational frequencies, and conical intersections, and we find good agreement with available reference data. This analytic DPEM is suitable for full-dimensional electronically nonadiabatic molecular dynamics calculations of the photodissociation of thiophenol with analytic gradients in either the adiabatic or diabatic representation.

We pointed out an angular momentum conservation problem that exists in widely used mixed quantum–classical nonadiabatic dynamics algorithms, including trajectory surface hopping (TSH), semiclassical Ehrenfest (SE), and coherent switching with decay of mixing (CSDM). We found that none of these dynamical methods conserve angular momentum when using the nonadiabatic coupling vectors (NAC) directly computed from the electronic structure theory codes usually employed in on-the-fly nonadiabatic dynamics. We proposed a projection operator to apply to the NAC to project out the translational and rotational contributions. We demonstrated that the projected NAC conserves angular momentum very well for TSH, SE, and CSDM dynamics.<sup>15</sup>

Electron momentum spectroscopy, scanning tunneling microscopy, and photoelectron spectroscopy provide unique information about electronic structure, but their interpretation has been controversial. We discussed a framework for interpretation stressing that these experiments provide information about how the electron distribution changes upon ionization, not how electrons behave in the pre-ionized state.<sup>16</sup>

We studied the effects of anharmonicity on reaction dynamics and reaction kinetics.<sup>17-25</sup>

## Hua Guo

Two invited reviews of our (Yarkony and Guo) recent work on geometric phase effects in nonadiabatic unimolecular reactions are published.<sup>26, 27</sup>

In collaboration with the Zhang (UCR), Dawes (MUST), and Xie (Nanjing) groups, we have investigated the nonadiabatic dynamics in photodissociation of HCO, in which the CO

product state distribution exhibits strong oscillation.<sup>28</sup> We have identified the origin of such oscillation as the interference between different reaction paths on the ground state PES. Furthermore, we have made significant progress in understanding the nonadiabatic photodissociation dynamics of hydroxymethyl using a full-dimensional quantum model on the global DPEM developed by Yarkony.<sup>29</sup> The quantum dynamical calculations revealed the initial dynamics in the Franck-Condon region and helps to assign the features in the absorption spectrum. In a more recent work with Yarkony, the energy disposal in phenol photodissociation was investigated using reduced dimensional models and the results challenged the original assignment of the KER.<sup>11</sup>

In collaboration with Yarkony, we have also explored various approaches to constructing high accuracy DPEM using NN approaches.<sup>8, 30, 31</sup>

We have been continuing our investigation of dynamics of bimolecular scattering and reactions. These studies include the  $O(^3P) + HCCH$  reaction,<sup>32</sup> the  $F + CH_3OH$  reaction,<sup>33, 34</sup> the nonadiabatic quenching of  $C(^1D)$  by  $N_2$ ,<sup>35</sup> the isomerization between  $HCCH$  and  $H_2CC$ ,<sup>36</sup> the  $NO + Ar$  scattering,<sup>37</sup> the  $OH + O_2$  scattering,<sup>38</sup> and  $HO + HO_2$  reaction.<sup>39</sup>

### **Future plans:**

#### **David R. Yarkony**

In the coming performance period, we will extend the current work as noted above, including using our emerging tools to study the competition between spin-conserving and spin-nonconserving nonadiabatic dynamics and energy transfer into and within the complement of the branching plane. With the growing importance of diabatic representations in nonadiabatic dynamics, it is important to juxtapose distinct approaches for constructing diabatic representations. Our tripartite collaboration provides just such an opportunity using the archetypical  $HO_3$  system. For reactive and nonreactive quenching processes reaction (1) and reaction (2) Truhlar's group has recently reported a 3 state diabatization based on his symmetry adapted 4-fold way. We are currently preparing for submission a four state representation constructed using our SURFGEN algorithm. This same ESD will be used to construct a 3-state coupled diabatic state representation using our NN-SURFGEN algorithm. The resulting DPEMs will be compared with the published results of Truhlar and used for quantum dynamics by Guo.

#### **Donald G. Truhlar**

In the coming period we will carry out dynamics calculations on  $OH(A) + H_2$  nonadiabatic collisions and photodissociation of  $C_6H_5SH$  – in both cases using PESs and couplings developed on this grant in 2019.

We will present a full-dimensional DPEM for photodissociation of the N–H bond in methylamine. The electronic state space will include the ground and first excited singlet state. Input for the fit will be calculated by extended multi-state complete active space second-order perturbation theory (XMS-CASPT2) with diabatization using the dipole–quadrupole (DQ) diabatization method into which we will incorporate a coordinate-dependent weighting scheme for the contribution of the quadrupole moments. To make the resulting potential energy surfaces semiglobal, we will extend the APRP method.

The  $OH_3$  and  $CH_3NH_2$  projects mentioned in the two previous paragraphs provide excellent opportunities for intraproject collaboration as they were chosen because they are well suited for study by the quantal wave packet methods developed by the Guo group.

A primary area of advance in methodology is development of improved methods and programs for semiclassical dynamics methods. We will put our coherent switching with decay-of-mixing method into the SHARC program developed by a team in the group of Prof. González at the Institute of Theoretical Chemistry at the University of Vienna, Austria. This program is not as general as our own ANT program, but it has advantages for direct dynamics. We are also developing a way to make the coherent switching with decay-of-mixing semiclassical algorithm much more efficient for direct dynamics by changing the approximation to the nonadiabatic coupling vector, and we will incorporate this into SHARC.

### Hua Guo

We will be focusing on the nonadiabatic dynamics for the OH(A) + H<sub>2</sub> reaction dynamics, which includes the reactive and nonreactive quenching channels, using the newly developed DPEMs from both the Yarkony and Truhlar groups. Both reduced dimensional quantum and full-dimensional trajectory surface hopping calculations will be carried out to explore the reactive and non-reactive quenching channels. Quantum dynamical calculations will also be carried out for several prototypical systems, such as methylamine, hydroxymethyl, and thiophenol, that DPEMs have been constructed. Particular attention will be paid to the use of the MCTDH approach. In addition, we will explore the possible impact of diabatic singularities on nonadiabatic dynamics.

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## A Practical Yet Accurate Fragmentation Method for Quantum Chemistry

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### Abstract

The goal of this project is to develop fragment-based quantum chemistry methods that are *accurate* (meaning  $\sim 1$  kcal/mol fidelity with respect to an electronic structure calculation performed on the same system without fragmentation) and also *robust* (meaning that they can be applied using essentially arbitrary levels of electronic structure theory and with flexible basis sets). Most existing fragment-based approaches fail to satisfy one or both of these criteria, *e.g.*, because they are unstable in extended basis sets and therefore cannot be applied using the highest levels of electronic structure theory, for which large basis sets are required. Furthermore, low-order many-body expansions that are not faithful to full-system calculations. We have demonstrated in previous work that four-body interactions are generally not negligible if kcal/mol accuracy is targeted, but full inclusion of four-body terms poses a catastrophic combinatorial problem for large systems. Absent additional approximations, widespread implementation of four-body methods remains prohibitively expensive even given the highly parallelizable nature of fragment-based methods.

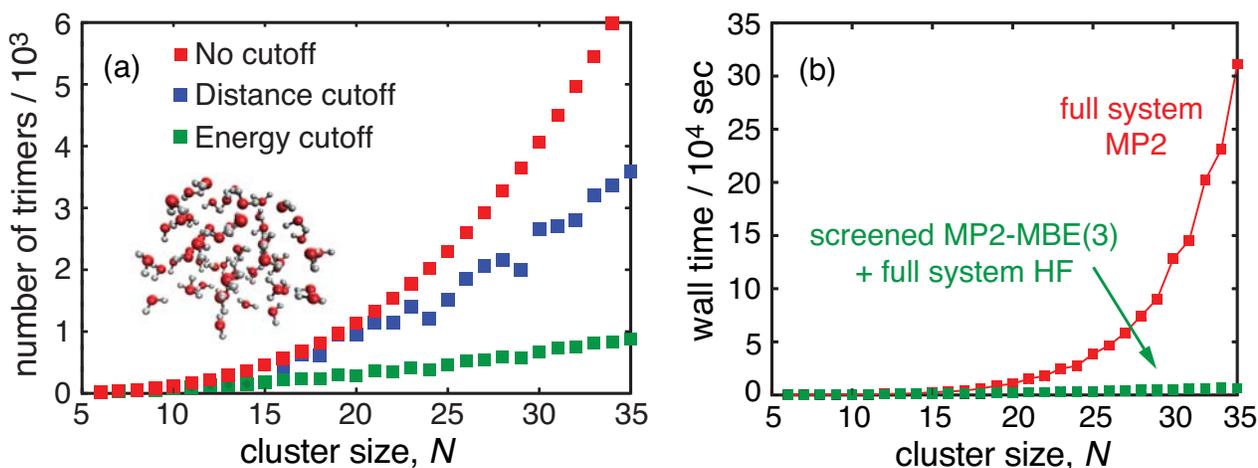
In recent work we have examined whether energy-based screening at a very low level of theory can be used to cull the very large number of subsystem electronic structure calculations that are required for three- and four-body expansions on large systems. For water clusters, we find that energy-based screening using the effective fragment potential (EFP, a polarizable force field derivable from first principles) is even more efficacious than distance-based screening at reducing the number of required electronic structure calculations. Using conservative thresholds that maintain the desired  $\sim 1$  kcal/mol accuracy, about 80% of the requisite three-body quantum chemistry calculations can be neglected *a priori* and replaced with EFP, which is essentially free. We find that energy-based screening is more efficient than distance-based screening even for water clusters, which likely represent a best-case scenario for the distance-based thresholding approach due to the small (and homogeneous) size of the fragments. For more heterogeneous systems, or those with larger fragments, the distance threshold would need to be increased in order to retain accuracy, thus sacrificing efficiency. In contrast, we expect that a conservative choice for the energy threshold (below which the many-body terms are described only with the low-level method) is likely independent of system composition and fragment size.

The energy-screened many-body expansion method has several important advantages:

- It can be used with arbitrary basis sets, including basis sets containing diffuse functions. Stability in large basis sets comes from iterating the subsystem calculations to convergence in the presence of exchange interactions, whereas methods that iterate only at the one-body level experience charge leakage problems in extended basis sets.
- Using a three-body MP2 calculation combined with Hartree-Fock theory as a low-level method for the whole system,  $\sim 1$  kcal/mol accuracy is achieved for the extremely challenging problem of predicting relative energies of different cluster isomers.
- The aforementioned method is more efficient than a supersystem MP2 calculation even

without significant parallelization, *e.g.*, running on a single 40-core node.

Preliminary results for  $(\text{H}_2\text{O})_N$  clusters of increasing size are shown in the figure below. The panel on the left demonstrates the reduction in the number of three-body terms that is achieved even relative to distance based screening, when both thresholding procedures are applied in a conservative way that maintains kcal/mol fidelity with respect to a calculation performed on the entire cluster at the same level of theory. The panel on the right shows that a three-body MP2 calculation, combined with a full-system Hartree-Fock calculation, remains dramatically less expensive as compared to MP2 on the full cluster. Notably, the timings shown are wall times on a single 40-core node, indicating that one does not need to resort to massively-parallel architectures in order to achieve dramatic speedup.



In future work, we will extend energy-based screening to four-body expansions. By making the four-body approach combinatorially (and therefore computationally) tractable, we hope to reduce the accuracy burden that is carried by the full-system part of the calculation such that the fully-system Hartree-Fock calculation (which is cubic scaling with respect to system size, even if the prefactor is small) can be replaced with a more affordable low-level method such as semi-empirical quantum chemistry or perhaps even the EFP force field itself, which was used to screen the interactions but proved inadequate as a supersystem correction when only three-body terms were included in the many-body expansion.

## Grant Numbers and Grant Titles

“Fragment-based quantum chemistry for intermolecular interactions and exciton transport in molecular liquids and solids” (Computational & Theoretical Chemistry, DE-SC000855)

**Postdoc(s):** None

**Student(s):** Bushra Alam, Kevin Carter-Fenk, Kuan-Yu Liu

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

1. K.-Y. Liu and J. M. Herbert. Energy-screened many-body expansion: A practical yet accurate fragmentation method for quantum chemistry. *J. Chem. Theory Comput.* **16**, 475 (2020).
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**Finite-temperature many-body perturbation theory for electrons &  
Grid-based diffusion Monte Carlo without fixed-node approximation &  
Monte Carlo Green's function methods**

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**Program Title:** Breakthrough Design and Implementations of Electronic and Vibrational Many-Body Theories (DE-SC0006028/0009)

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**Program Scope:** The overarching goal of the project is to bring the predictive capabilities of systematic *ab initio* many-body theories for electrons and vibrations to condensed matter. This is more than just exportation of existing theories, algorithms, or software to larger and larger systems using a more powerful computer. When there are Avogadro's number of particles in the system, (**Theory**) one must integrate quantum mechanics and statistical thermodynamics and adjust the mathematical theories to fully account for size-consistency as well as finite temperature, pressure, and chemical potential, so that they can describe uniquely condensed-matter properties or phase such as metals and superconductors, phase transitions, dispersion, and dynamics [the theory projects]. One must also address immense computational costs of these already expensive methods when they are applied to an infinitely extended system; one must often discard the existing matrix-algebra-based algorithm and come up with a completely new one that is scalable with system size and computer size [the algorithm projects]. One then applies these theories and algorithms to interesting and important condensed-phase systems such as liquid water, ice, and advanced materials [the application projects].

**Recent Progress:** On the theory front, we made major progress in finite-temperature many-body perturbation theory (MBPT) for electrons. On the algorithm front, we introduced grid-based diffusion Monte Carlo (DMC), finally removing the fixed-node approximation. We also fully developed a stochastic algorithm of *ab initio* Green's function theory.

- (1) **Finite-temperature MBPT.** Solids whose electronic properties can be modulated by temperature are of great interest. They include superconductors and optoelectronic materials. MBPT at a finite temperature that accounts for thermodynamics of electrons is described in many textbooks, which defines the theory by quantum field theory based on Matsubara finite-temperature Green's function or equivalent thermal Wick's theorem in the time-dependent diagrammatic language. In 1960, however, Kohn and Luttinger wrote a landmark paper questioning its correctness, showing that it does not reduce to the zero-temperature MBPT for a degenerate ground state as temperature tends to zero. This remains to be a fundamental theoretical physics mystery to this day.

Funded by DOE, we developed (Ref. 5) a numerical procedure to obtain the benchmark data for

several low-order perturbation corrections to any quantities including thermodynamic functions defined by the finite-temperature MBPT. We showed that the formulas in the textbooks do not reproduce these benchmark data and are, therefore, incorrect. We identified the source of this discrepancy to the inadequate treatment of chemical potential, and derived (Ref. 4) the correct finite-temperature MBPT formulas for the grand potential, internal energy, and chemical potential in the first-order perturbation theory. We introduced a transparent and general derivation method of these formulas that relies only on the sum rules of the Hirschfelder-Certain degenerate perturbation energies and elementary calculus and combinatorics, avoiding diagrammatic quantum field theoretic derivations altogether.

In this funding cycle, we derived the sum-over-states and sum-over-orbitals (reduced) analytical formulas for the second-order corrections to the grand potential, internal energy, and chemical potential (a manuscript under review). They differ from the formulas in the textbooks, while numerically exactly reproducing the benchmark data (Ref. 5), and are the correct analytical formulas of the finite-temperature MBPT. The internal energy formulas at the first and second orders can be used to once and for all settle the Kohn-Luttinger question. We found (a manuscript in preparation), both analytically and numerically in an application to a degenerate ground state of  $H_4$ , that these correct finite-temperature MBPT formulas do not reduce to the corresponding formulas of the zero-temperature MBPT as temperature tends to zero; the former are divergent at the second order, while the latter are non-divergent. We traced this shocking non-convergence to the non-analytic nature of the Boltzmann factor (which is, in fact, a textbook example of a smooth non-analytic function that cannot be expanded in a Taylor series), causing the finite-temperature MBPT to have the zero radius of convergence at zero temperature. Therefore, we concluded that Kohn and Luttinger were right: the finite-temperature MBPT is indeed incorrect, which echoes the long-standing similar failure of quantum field theory (which is perturbative) in its application to quantum electrodynamics. These studies were led by the PI.

- (2) **Grid-based DMC.** A DMC algorithm is introduced (Ref. 2) that can determine the correct nodal structure of the wave function of a few-fermion system and its ground-state energy without an uncontrolled bias. This is achieved by confining signed random walkers to the points of a uniform infinite spatial grid, allowing them to meet and annihilate one another to establish the nodal structure without the fixed-node approximation. An imaginary-time propagator is derived rigorously from a discretized Hamiltonian, governing a non-Gaussian, sign-flipping, branching, and mutually annihilating random walk of particles. The accuracy of the resulting stochastic representations of a fermion wave function is limited only by the grid and imaginary-time resolutions and can be improved in a controlled manner. The method is tested for a series of model problems including fermions in a harmonic trap as well as the He atom in its singlet or triplet ground state. For the latter case, the energies approach from above with increasing grid resolution and converge within  $0.015 E_h$  of the exact basis-set-limit value for the grid spacing of 0.08 a.u. with a statistical uncertainty of  $10^{-5} E_h$  without an importance sampling or Jastrow factor. This work was led by Dr. Alexander Kunitsa.
- (3) **MC-GF2/GF3.** We fully develop the Monte Carlo many-body Green's function (MC-GF) method with the following enhancements: (1) The truncation order of the perturbation expansion of the Dyson self-energy is raised from the second order (MC-GF2) to the third order (MC-GF3) with the aid of a computerized procedure to enumerate and transform all 84 third-order Goldstone diagrams into Monte Carlo integrable expressions and then into central processing

unit (CPU)/graphical processing unit (GPU)-parallel computer codes. (2) An efficient algorithm is proposed that computes all off-diagonal and diagonal elements of the MC-GF2 and MC-GF3 self-energy matrices by common subexpression elimination. (3) The frequency-independent approximation is lifted by introducing a method that computes frequency derivatives of the MC-GF2 and MC-GF3 self-energies up to any arbitrarily high order at nearly no additional computational cost. (4) The imaginary-time integration in the Laplace-transformed expressions of the self-energy is carried out stochastically (instead of using a quadrature), resulting in a 50- to 200-fold speedup. (5) The efficiency of the redundant-walker convergence acceleration scheme is analyzed numerically, and the guidelines are established to select an optimal number of walkers for maximal efficiency. When such an optimal number is used, the cost per sample is constant of molecular size on either many CPUs or many GPUs. (6) The computational cost to obtain a binding energy within a given statistical uncertainty is observed to increase as (tentatively)  $O(n^4)$  and  $O(n^5)$  of molecular size ( $n$  is the number of electrons) with and without the diagonal approximation, respectively, as opposed to  $O(n^5)$  and  $O(n^6)$  of the corresponding deterministic algorithms. With this method applied to the electron binding energies of  $C_{60}$ , we show that the third-order corrections to the self-energies are much greater in electron binding energies than in ground-state energies. They display a sign of oscillatory convergence toward experimental results, not necessarily improving the agreement with increasing perturbation order, justifying MC-GF3 and motivating even higher-order methods. This work was led by Dr. Alexander Doran.

#### Future Plan:

- (1) **Kohn-Luttinger conundrum redux.** As described above, we have established the non-convergence of the finite-temperature MBPT internal energy to the zero-temperature MBPT energy for degenerate ground state. We are analyzing each term of the first- and second-order formulas to understand the precise origin of the non-convergence in relation to the so-called Kohn-Luttinger anomalous diagram contributions, which were implicated in it. A manuscript is in preparation by the PI.
- (2) **MC-MP4.** The fourth-order MBPT or MP4 is roughly equivalent in cost-accuracy balance to the gold-standard CCSD(T). We, therefore, set the development of a scalable Monte Carlo algorithm of MP4 as the holy grail of the MC project; MP4, when feasible, will be the “answer” to nearly all chemical problems, and its MC algorithm should vastly broaden the feasibility. We introduced three speedup measures to make MC-MP4 viable. They are: the Monte Carlo integration in the imaginary-time domains; the direct sampling (as opposed to the Metropolis sampling); the control variate method. This work was spearheaded by Dr. Alexander Doran.
- (3) **Anharmonic phonon dispersion.** Quasi-particle (i.e., correlated) energy bands for lattice vibrations amount to the anharmonic phonon dispersion curves, obtainable by Green’s function theory. We applied diagrammatic size-extensive vibrational second-order Møller-Plesset (XVMP2) method to an infinite polyethylene (most thoroughly characterized experimentally) to obtain self-energies and pole strengths in the second-order Green’s function theory. We showed that, in a frequency-independent approximation, phonon dispersion curves are plagued with divergences almost everywhere. In a self-consistent solution of the Dyson equation, phonon dispersion curves reproduce extensive resonance structures in the CH stretching region and band widths (thus phonon lifetime). This work was done by Mr. Xiuyi (Terry) Qin.

### Computational Chemical Sciences (2017-)

Scalable Predictive methods for Excitations and Correlated phenomena (led by PNNL)

**Postdocs:** Alexander E. Doran

**Students:** Edwin Alvarado-Rodriguez; Aidan Beckley; Punit K. Jha; Xiuyi (Terry) Qin

### DE-SC0006028/0009 (2018-)

Breakthrough Design and Implementation of Electronic and Vibrational Many-Body Theories

**Postdocs:** Alexander E. Doran; Alexander Kunitsa

**Students:** Edwin Alvarado-Rodriguez; Aidan Beckley; Punit K. Jha; Xiuyi (Terry) Qin

### Ten Publications Acknowledging these Grants in the Last 3 Years

1. P. K. Jha and S. Hirata,  
*Physical Review E* **101**, 022106 (2020) (8 pages), arXiv:1910.07628,  
“Finite-temperature many-body perturbation theory in the canonical ensemble.”
2. A. A. Kunitsa and S. Hirata,  
*Physical Review E* **101**, 013311 (2020) (8 pages), arXiv:1811:03000,  
“Grid-based diffusion Monte Carlo for fermions without the fixed-node approximation.”
3. A. E. Doran and S. Hirata,  
*Journal of Chemical Theory and Computation* **15**, 6097-6110 (2019),  
“Monte Carlo second- and third-order many-body Green's function methods with frequency-dependent, nondiagonal self-energy.”
4. S. Hirata and P. K. Jha,  
*Annual Reports in Computational Chemistry* **15**, 17-37 (2019), arXiv:1812:07088,  
“Converging finite-temperature many-body perturbation theory in the grand canonical ensemble that conserves the average number of electrons.”
5. P. K. Jha and S. Hirata,  
*Annual Reports in Computational Chemistry* **15**, 3-15 (2019), arXiv:1809.10316,  
“Numerical evidence invalidating finite-temperature many-body perturbation theory.”
6. P. Rai, K. Sargsyan, H. Najm, and S. Hirata,  
*Journal of Mathematical Chemistry* **57**, 1732-1754 (2019),  
“Sparse low rank approximation of potential energy surfaces with applications in estimation of anharmonic zero point energies and frequencies.”
7. C. M. Johnson, A. E. Doran, S. L. Ten-no, and S. Hirata,  
*The Journal of Chemical Physics* **149**, 174112 (2018) (9 pages),  
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*The Journal of Chemical Physics* **147**, 044108 (2017) (31 pages),  
“One-particle many-body Green's function theory: Algebraic recursive definitions, linked-diagram theorem, irreducible-diagram theorem, and general-order algorithms.”
10. C. M. Johnson, S. Hirata, and S. Ten-no,  
*Chemical Physics Letters* **683**, 247-252 (2017) (Ahmed Zewail Commemoration Issue),  
“Explicit correlation factors.”

# Space-Time Quantum Information from the Entangled States of Magnetic Molecules

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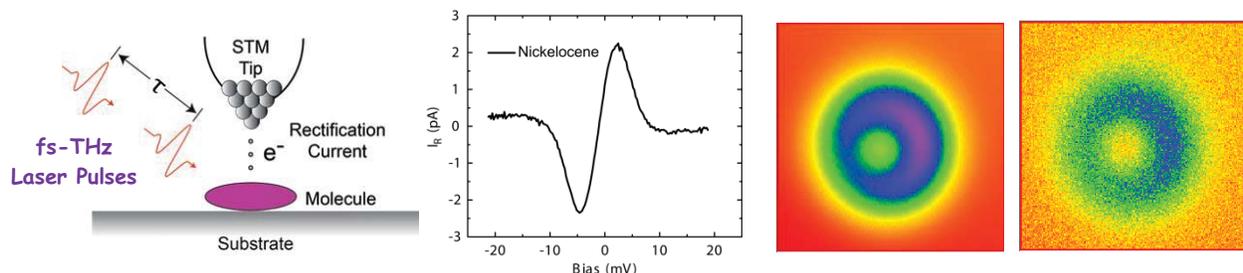
## Program Scope

The ability to vary and control the quantum properties of single magnetic molecules arises from the large variations that are possible in the elemental composition and structure of organometallic molecules. These variations include choices in the transition and rare earth metal atoms and the attached organic framework that isolate the magnetic centers from the environment but also couple to them. Because the electron spins can form two-level systems and have long coherence times, they are potential candidates for quantum information processing as qubits. Furthermore, the sensitivity of the electron spin to the magnetic field and other nearby spins enables it to be configured for sensing and imaging. This collaborative project combines synthesis, measurement, and theory of magnetic molecules as qubits, sensors, and imaging agents by studying the energies and spatial distributions of quantized excitations, the length of time the quantum states remain superposed and entangled, and the different factors that cause dephasing and degradation of coherence.

## Recent Progress

### Femtosecond THz Rectification Spectroscopy and Microscopy of Single Magnetic Molecules:

One of the focused efforts led to the completion of the design and construction of a high repetition rate (1 GHz), femtosecond THz laser interfaced to a low temperature (9 K) STM in ultrahigh vacuum. Time domain THz spectroscopy has been obtained from ambient water molecules, showing absorption frequencies and intensities in excellent agreement with calculations. Time domain spectroscopy was also obtained from gaseous carbon monoxide and methanol. These results on an ensemble of gaseous molecules validated the design and methodology of time domain THz spectroscopy using the highest repetition laser to date.



**Fig. 1:** Schematic diagram of a femtosecond THz laser combined with a low temperature scanning tunneling microscope probing a single nickelocene molecule adsorbed on Cu(001) surface at 9 K; rectification spectrum induced by the laser; topographic image of the molecule; laser induced rectification current image of the same molecule.

It was also demonstrated that single molecule spectroscopy and microscopy can be achieved with the combination of a femtosecond THz laser and the STM. Specifically, the magnetic excitations in molecular systems, from a single molecule to molecular lattices, have been measured by inelastic electron tunneling spectroscopy (IETS) and microscopy and femtosecond THz laser induced rectification current spectroscopy and microscopy with the laser scanning tunneling microscope (laser-STM), as shown in Fig. 1. The rectification peak at 3.9 meV (0.94 THz) corresponds to the  $m = 0$  to the  $m = \pm 1$  states of the triplet state of the nickelocene molecule, i.e. the magnetic anisotropy energy. These results revealed the fundamental mechanism of the rectification signal, arising from the nonlinearity of the I-V curve associated with an excitation of the molecule. For the first time, it has been possible to obtain rectification spectroscopy and microscopy from a single molecule.

Uranium Adatoms on Defect Aluminum Oxide for Qubits: Nanomagnets with giant magnetic anisotropy energy and long coherence time are desired for various technological innovations such as quantum information procession and storage. Based on the first-principles calculations and model analyses, we demonstrate that a single uranium atom that substitutes Al on the  $\text{Al}_2\text{O}_3$  (0001) surface may have high structural stability and large magnetic anisotropy energy up to 48 meV per magnetic atom. As the magnetization resides in the localized f-shell, which is not much involved in chemical bonding with neighbors, long coherence time ( $\sim 32 \mu\text{s}$ ) for the quantum spin states can be achieved. These results suggest a new strategy for the search of ultrasmall magnetic units for diverse applications in the quantum information era.

The Effect of Spin-Vibration Coupling on the Lifetime of Quantum States of Magnetic Molecules: While exponential and power law dependence of the relaxation time on temperature are widely used to fit experimental data, these rules have not been validated in the context of single-molecule magnets. Based on the phonon spectrum and spin-phonon coupling strength, we derived a theory showing how these dependences arise and how transitions among them occur with temperature variation. The theory also solves the puzzle of lower-than-expected Orbach barrier and multiple barriers found in recent experiments, and elucidates the Orbach process as Raman process in disguise. Our results suggest that the ground state tunneling is the dominant relaxation channel for the magnetization. This implies a call for shifting our attention from achieving super large Orbach barriers to magnetic engineering that diminishes the transverse and high order magnetic anisotropies, and also to dynamic engineering that lifts vibration modes that strongly couple to the spin.

Synthesis of Rare Earth Magnetic Molecules: A new method for introducing samples into the STM chamber has been developed. A device called a “doser” has been built that can be loaded in the Evans group inert atmosphere glovebox under rigorously air and water free conditions and then attached to the Ho group instrument for dosing onto the surface. The doser has a stage that can be heated and provides a better way to get the volatile compounds into the system faster with minimal decomposition. The doser has been used with several compounds prepared in the Evans lab: the actinide, uranocene, bis(cyclooctatetraenyl) uranium,  $\text{U}(\text{C}_8\text{H}_8)_2$ , and the transition metal complexes, dinickelocene,  $(\text{C}_{10}\text{H}_8)_2\text{Ni}_2$  and dicobaltocene for comparison with the earlier nickelocene and cobaltocene studies. The rare earth complexes praseodymium hexafluoroacetylacetonate,  $\text{Pr}(\text{hfac})_3$  ( $\text{hfac} = \text{CF}_3\text{C}(=\text{O})\text{CHC}(=\text{O})\text{CF}_3$ ), the tris(cyclopentadienyl) praseodymium complex,  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Pr}$ , and the cyclooctatetraenyl cyclopentadienyl mixed

sandwich erbium complex,  $(C_8H_8)Er[C_5H(CHMe_2)_4]$  were also prepared for studies of single molecules and assemblies by STM combined with femtosecond terahertz radiation.

### **Future Plans**

The coherent superposition and entanglement of the magnetic states are created and tracked in time by terahertz (THz) and near-IR femtosecond laser pulses coupled with the STM. Measurement with simultaneous spatial and temporal resolution enables a basic understanding and system control at the atomic scale. A variety of molecular complexes that have a magnetic atom sandwiched between two rings of carbon atoms will be synthesized, measured, and calculated. The two rings isolate the central magnetic atom from its environment, which would increase the length of time the spin quantum states remain superposed and entangled. An important goal of the planned research is to maximize this time for information processing based on the quantum states by optimizing the composition and structure of molecules. The sandwiched metal atom in these molecules can be a transition metal, a rare earth metal, or uranium to provide rich spin correlation effects. The possibility of ligand substitution allows alterations of the molecular motions that affect the strength of the spin-vibration coupling and the time duration of the spin coherence in molecular qubit states. Reversible electron transfer from the STM tip to the bridging molecule in bimetallic rare earth magnetic molecules allows electrical control of the spin correlation between the two magnetic atoms within the complex. This research lays the foundation for optimizing the composition, structure, and interaction of magnetic molecules as carriers of quantum information by combining chemical synthesis, measurement in space-time, and ab-initio theory.

**Grant Number:** DE-SC0019448

**Grant Title:** Space-Time Quantum Information from the Entangled States of Magnetic Molecules

**Postdocs:** Lei Gu, Jie Li, Song Xu

**Students:** Siyu Chen, Wenlu Shi, Yunpeng Xia, Likun Wang, Justin Wedal

### **Publications**

1. "Stable Giant Magnetic Anisotropy Energy and Long Coherence Time of Uranium Adatoms on Defect Aluminum Oxide", Jie Li, Lei Gu, and Ruqian Wu, Phys. Rev. B, submitted (2020).
2. "Theory of Spin-Lattice Relaxation in Single-Molecule Magnets: Reasons of Long Lifetimes", Lei Gu and Ruqian Wu, Phys. Rev. Lett, submitted (2020).

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

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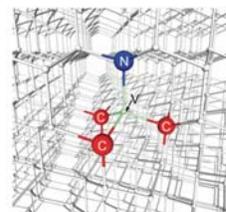
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### Abstract

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 the spin-flip (SF) Bethe-Salpeter Equation (BSE) method, developing and assessing the use of an improved  $\Delta$ SCF approach for studying photochemistry and excited state vibrational frequencies, and developing models for predicting electronic-vibrational coupling and nonlinear spectroscopy in complex systems.

### Ground and excited states for open-shell systems:

Open-shell systems, including molecules and defects, are interesting platforms for spin physics, quantum information, and magnetic applications. Their multi-determinantal states are difficult to handle with conventional first-principles calculations. A practical solution is the spin-flip approach: the ground and excited states are considered as spin-flipping excitations of a single-determinant high-spin reference state. The SF approach was originally used with wave function approaches such as configuration interaction and was later extended to time-dependent density-functional theory (TDDFT), with notable



Method / Energy (eV)	$E(^1E) - E(^3A_2)$	$E(^1A_2) - E(^3A_2)$	$E(^3E) - E(^3A_2)$
SF-BSE (present)	0.45	1.93	2.04
CI [A]	0.68	2.11	2.24
CI Cluster [B]	0.64	2.02	2.00
Extended Hubbard, fit to GW [C]	0.48	1.45	2.13
Experiment	0.2 [D]	1.39 [D]	2.15 [E]

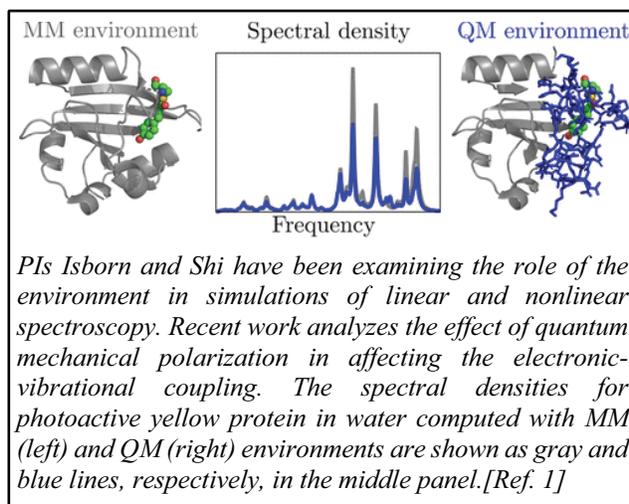
PI Strubbe has developed a spin-flip Bethe-Salpeter (SF-BSE) model showing excellent progress for complex systems. Shown here are calculated energies of the lowest-lying states of the well-studied NV<sup>-</sup> defect in diamond, with promising results against computational and experimental literature.

success. Standard TDDFT approximations, however, have well-known deficiencies including treatment of charge-transfer excitations and condensed phases. Therefore, we have developed a spin-flip approach to the GW/Bethe-Salpeter approach, taking advantage of a similar structure of the equations to TDDFT. GW/BSE is a many-body perturbation theory method commonly used in condensed-matter physics for solids and nanostructures, which has an ab initio long-ranged and non-local interaction kernel enabling more accurate excited state calculations. We have developed a spin-flip BSE theory and implementation. Critical issues of spin contamination and convergence with number of states in BSE have been assessed. We have demonstrated success of SF-BSE on some classic problems, including ethylene C–C rotation, which transitions between singlet and triplet ground states. Interestingly, there seems to be lower spin contamination than in SF-TDDFT cases. Given these successes in small systems, we performed a calculation on the well-studied NV<sup>-</sup> defect center in diamond, which is of interest for quantum information applications (see Figure, above). The ground state is a triplet  $^3A_2$  state, making ordinary DFT calculations unable to describe that state and its energy relative to the other states. We have obtained promising preliminary results for the low-lying states of the NV<sup>-</sup> center relative to other theoretical and experimental results and will explore this and other exciting applications in future work.

Another approach for studying excited states being explored by our team builds on the  $\Delta$ SCF model. Such methods have a rich history in the computational study of electronic excited states. However,  $\Delta$ SCF calculations often suffer from a number of challenges including convergence difficulties and variational collapse. We have developed a projection-operator based approach that significantly improves the robustness of the associated SCF optimization process. We are currently assessing the accuracy of  $\Delta$ SCF for optimizing minimum energy structures and carrying out vibrational analysis of excited state species. Preliminary results are quite promising. As might be expected, many open shell species and one-electron excitations of closed shell ground states result in significant spin contamination in SCF determinants. In future work, we will explore the use of spin projection models – originally developed for use in ground state applications – with  $\Delta$ SCF and examine the use of a spin projected  $\Delta$ SCF model for studying photochemistry and response properties of systems in excited electronic states using well established and robust ground state schemes.

**Nonlinear spectroscopy:** Accurate spectral densities are necessary for computing realistic exciton dynamics and nonlinear optical spectra of chromophores in condensed-phase environments, including multichromophore pigment–protein systems. However, due to the significant computational cost of computing spectral densities from first principles, requiring many thousands of excited-state calculations, most simulations of realistic systems rely on treating the environment as fixed point charges. Using a number of representative systems ranging from solvated chromophores to the photoactive yellow protein (PYP), we demonstrated that the quantum mechanical (QM) electronic polarization of the environment is key to obtaining accurate spectral densities and line shapes within the cumulant framework (see Figure, below). We have shown that the QM environment can enhance or depress coupling of fast chromophore degrees of freedom

to the energy gap, altering the electronic–vibrational coupling and the resulting vibronic progressions in the absorption spectrum. In analyzing the physical origin of peaks in the spectral density, we identified vibrational modes that couple the electron and the hole as being particularly sensitive to the QM screening of the environment. For PYP, we revealed the need for careful determination of the appropriate QM region to obtain reliable spectral densities. Our results indicate that the QM polarization of the environment can be crucial not just for excitation energies but also for electronic–vibrational coupling in complex systems with implications for the correct modeling of linear and nonlinear optical spectroscopy in the condensed phase as well as energy transfer in pigment–protein complexes.



In the next year, our team will continue advances in the development and application of new approaches for studying electronic excited states, exploring photochemistry, and simulating nonlinear optical spectroscopy. We will also begin developing synergistic applications of our recently developed and implemented models to novel transition metal-containing materials and chemistries.

### Grant Number and Title

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

**Ph.D. Students:** Bowen Han, Vincent Martinetto, and Ali Abou-Taka

**Postdocs:** Bradford Barker, Hector Corzo, Shao-Yu Lu, and Tim Zuehlsdorff

### Publications

1. T. J. Zuehlsdorff, H. Hong, L. Shi, and C. M. Isborn, “Influence of Electronic Polarization on the Spectral Density”, *J. Phys. Chem. B* **124**, 531–543 (2020). DOI: 10.1021/acs.jpccb.9b10250.

2. M. Long, S. Alland, M. Martin, and C. Isborn, “Molecular Dynamics Simulations of Alkaline Earth Metal Ions Binding to DNA Reveal Ion Size and Hydration Effects”, *Phys. Chem. Chem. Phys.* **22**, 5584–5596 (2020). DOI: 10.1039/C9CP06844A

## Genetic Algorithms for Rapid Molecular Materials Screening

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### Abstract

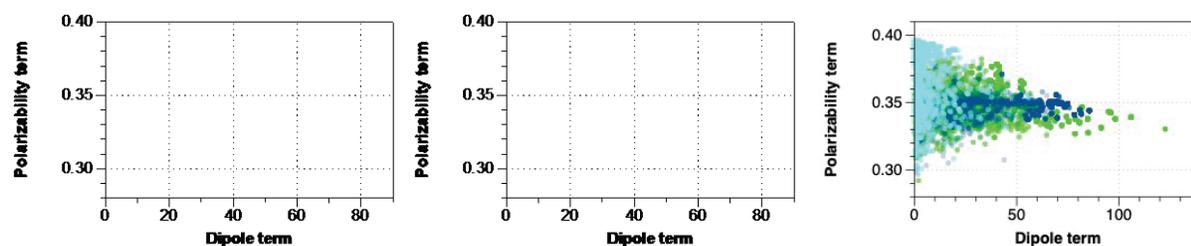
#### Program Scope

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.

#### 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.

*Highly Polarizable  $\pi$ -Conjugated Molecules*: 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. Using our genetic algorithm, we have uncovered a Pareto trade-off between polarizability and dipole moment, when normalized by the molecular volume (**Fig. 1**). The resulting molecules yield a diverse set for machine learning training, as discussed below, but also reveal challenges to current electronic structure methods. For example, we find large differences between static polarizabilities calculated with B3LYP or wB97X and the D3 and D4 dispersion models, resulting in incorrect dispersion interaction energies.



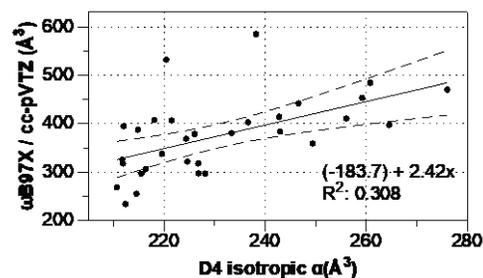
**Figure 1.** Genetic algorithm searches for  $\pi$ -conjugated chromophores with (left) large dipole moments per unit volume, (middle) large polarizability per unit volume, and (right) composite of multiple runs reflecting Pareto trade-off.

We have generated a large ( $\sim 3.4$  million compounds) diverse data set of molecular static polarizabilities for atomistic machine learning methods, collaborating with the Swamidass group at Wash. U. St. Louis, to develop methods with state-of-the-art accuracy on polarizabilities. The results are therefore useful for improving empirical dispersion corrections for density functional methods, but also property predictions for machine learning. The GA search has also revealed unexpected structure/property correlations for increasing dielectric constants in  $\pi$ -conjugated materials.

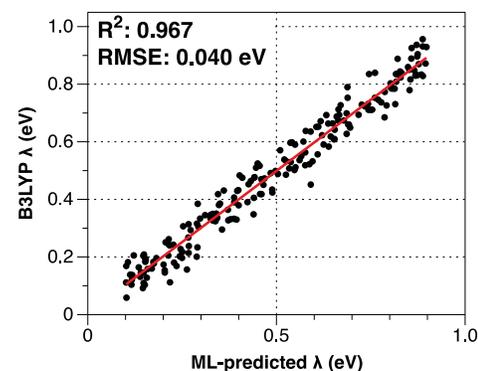
**Marcus Reorganization Energies:** The Marcus reorganization energy is a measure of geometric distortion during charge transfer, and thus influences hopping-style charge transport common in organic materials. Using our GA, combined with an active-learning approach, we are presently training a deep neural network to rapidly predict reorganization energies. Figure 3 illustrates that after two rounds on small molecules (10-25 atoms), the ML predictions are already highly correlated with B3LYP calculations on much larger molecules.

### 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 efficient non-fullerene acceptors for multi-chromophore organic photovoltaics, and  $\pi$ -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.



**Figure 2.** Poor correlation and large discrepancies between isotropic static polarizabilities from the D4 dispersion model (x-axis) and  $\omega$ B97X density functional.



**Figure 3.** Neural network prediction of B3LYP-predicted Marcus reorganization energies after two rounds of active learning.

**Grant Numbers and Grant Titles**

DE-SC0019335 Genetic Algorithms for Rapid Molecular Materials Screening

**Student(s):** Dakota Folmsbee, Danielle Heiner

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

Matthew K Matlock, Max Hoffman, Na Le Dang, Dakota L. Folmsbee, Luke A. Langkamp, Geoffrey R. Hutchison, Neeraj Kumar, and S. Joshua Swamidass. “Deep learning coordinate-free quantum chemistry.” Submitted to *Nature Machine Intelligence*.

# APPLYING DEEP LEARNING METHODS TO DEVELOP NEW MODELS OF MOLECULAR CHARGE TRANSFER, NONADIABATIC DYNAMICS, AND NONLINEAR SPECTROSCOPY IN THE CONDENSED PHASE

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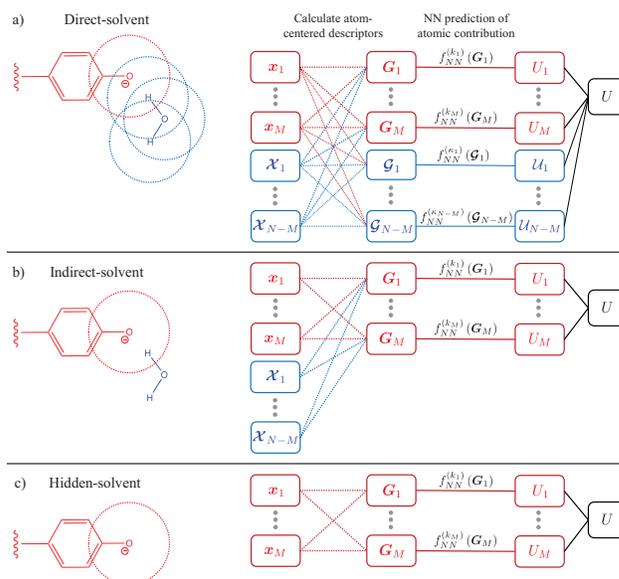
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Photon- and field-induced charge transfer has central importance in the generation and storage of electricity, the novel properties of materials, photo-induced catalysis, and electro-optic activity (e.g., photovoltaic cells, fuel cells, and organic chromophores for use in optical fibers and light-emission diodes). These non-equilibrium electronic and chemical transformations are probed by ultrafast, nonlinear spectroscopies. Accurate simulations play a crucial role in our ability to understand, optimize, and control these transformations. This project aims to apply modern deep learning methods to dramatically improve models of electronic dynamics, electronic-nuclear dynamics, and spectroscopic measurements. This will yield improved simulations of chemistry in complex environments, far from equilibrium phenomena, and processes in extreme environments, such as materials exposed to strong or resonant fields. This project seeks accurate neural net models that go beyond predictive capability to also yield interpretable approximations of electron potentials and memory kernels, providing new insight into the fundamental physics underlying electron and nuclear dynamics. To achieve its objectives, this project will explore and develop customized versions of high-capacity deep learning algorithms/models such as recurrent neural networks and autoencoders. These techniques will be developed with an emphasis on fundamental chemical insight, not just predictive accuracy, to assist development of the next generation of quantum simulation methods.

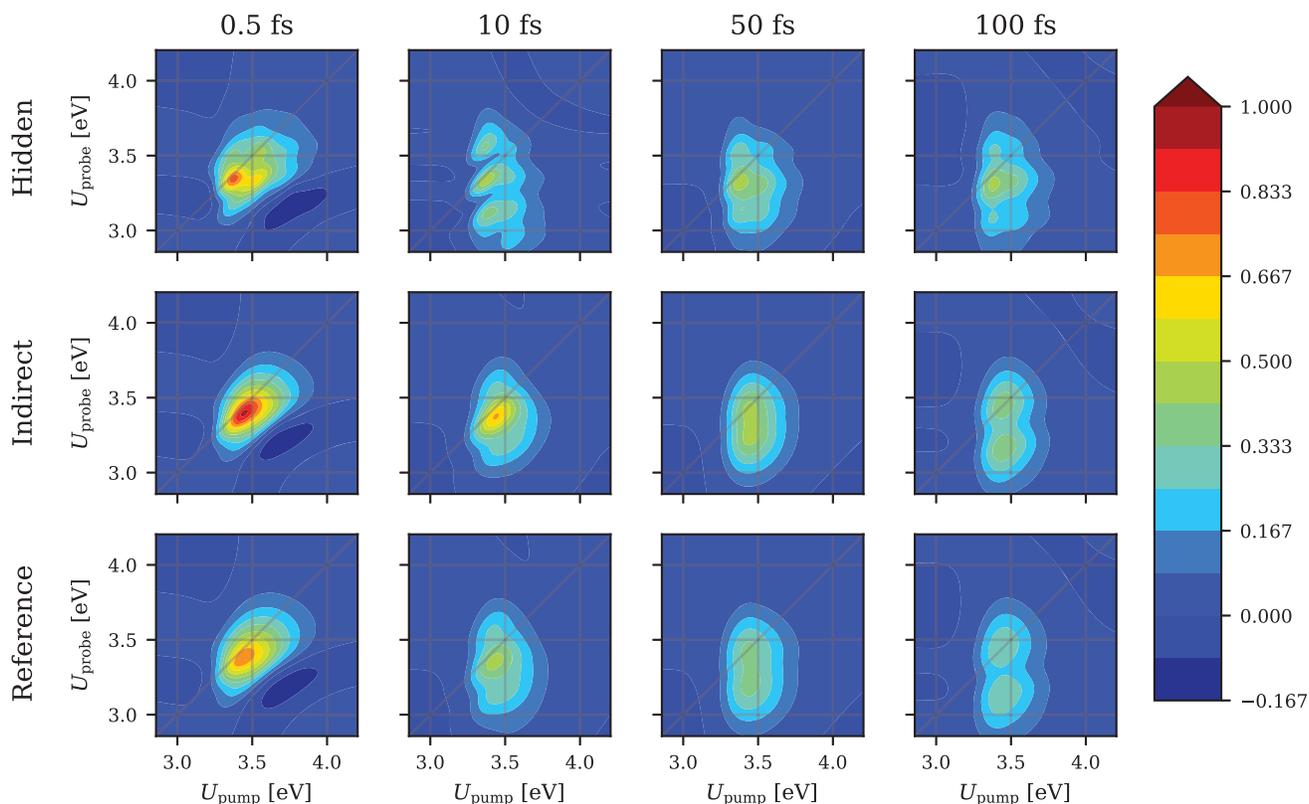
**MACHINE LEARNING FOR NONLINEAR SPECTROSCOPY IN THE CONDENSED PHASE:** The excited state dynamics of chromophores in complex environments determine a range of vital biological and energy capture processes. Time-resolved, multidimensional optical spectroscopies provide a key tool to investigate these processes. Although theory has the potential to decode these spectra in terms of the electronic and atomistic dynamics, the need for large numbers of excited state electronic structure calculations severely limits first principles predictions of multidimensional optical spectra for chromophores in the condensed phase. *One of the first areas we've focused on in the early stages of this grant is developing a machine learning model for condensed phase energy gaps which can be used to calculate linear and multidimensional optical spectra (Figure 1).* Here, we leverage the locality of chromophore excitations to develop machine learning models to



**Figure 1:** Schematic depictions of three approaches to incorporating a chromophore's environment in the ML model. By analyzing the performance of these models, which span a hierarchy of physical approximations, across a range of chromophore-environment interaction strengths, we provide strategies for the construction of ML models that greatly accelerate the calculation of multidimensional optical spectra from first principles.

predict the excited state energy gap of chromophores in complex environments for efficiently constructing linear and multidimensional optical spectra.

By introducing and analyzing the performance of three ways to incorporate the solvent environment in the ML model, which span a hierarchy of physical approximations, across a range of chromophore-environment interaction strengths, we provide strategies for the construction of ML models that greatly accelerate the calculation of multidimensional optical spectra from first principles. We have analyzed how different solvent representations in ML models can be more data efficient and accurate depending on the strength of the chromophore-solvent coupling. For weakly coupled systems, we were able to completely ignore solvent positions in the ML model and trained a model which gave accurate linear and 2D electronic spectra with as few as 2000 training points. For systems with stronger and more site specific chromophore-solvent interactions, the simplified hidden-solvent approach did not suffice. However, by accounting for solvent atoms located close to the chromophore, we were able to train an accurate indirect-solvent model with 2000 training points (Figure 2). Our work therefore provides a highly efficient scheme to generate accurate multidimensional optical spectra for chromophores in condensed phase environments.



**Figure 2:** Two-dimensional electronic spectra for an anionic chromophore in water. The hidden solvent and indirect solvent ML models are trained on 2000 energy gaps and then used to predict the 32,000 excitation energies used to compute these spectra. The corresponding reference results are computed using 32,000 energy gaps from electronic structure calculations.

### Award Number DE-SC0020203:

Exploiting Machine Learning to Efficiently Predict Multidimensional Optical Spectra in Complex Environments. *M. S. Chen, T. J. Zuehlsdorff, T. Morawietz, C. M. Isborn, T. E. Markland.*  
Submitted.

**Koblar A. Jackson**

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

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**Abstract**

**Overview**

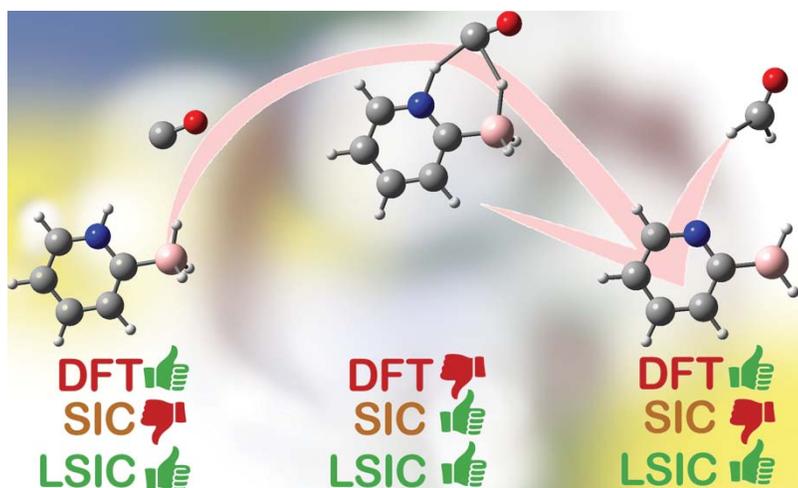
The goal of the FLO-SIC Center is to enable accurate and efficient density functional theory (DFT) calculations that are free of unphysical electron self-interaction error (SIE), a problem that plagues essentially all DFT methods. Reaching this goal requires developing an improved theoretical approach for removing SIE and implementing it in efficient, highly parallel software. The framework for the research is the Fermi-Löwdin orbital self-interaction correction method (FLO-SIC), a size-consistent and unitarily invariant alternative to the Perdew-Zunger self-interaction correction (PZ-SIC). The work of the Center also includes experimental and theoretical research into metal organic framework (MOF)-based catalysis and molecular magnets. These initiatives are ultimately aimed at validating new methods developed in the Center, but also target technologically important problems relevant to the wider mission of the Department of Energy.

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 list of personnel is given below.

**Recent results** ([1] indicates a paper in the list of publications included below.)

A discovery made [1] in the Center is helping to explain the paradoxical performance of PZ-SIC when combined with sophisticated density functional approximations (DFAs). PZ-SIC succeeds in removing SIE in situations where it is pronounced, most remarkably when electrons are shared over stretched bonds. But its use degrades the excellent performance of DFAs such as the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) and the strongly constrained and appropriately normed (SCAN) meta-GGA when atoms are near equilibrium positions. By systematically computing errors in the exchange-correlation energy ( $E_{xc}$ ) for rare gas atoms and carefully extrapolating the results to the infinite size limit, Santra and Perdew proved[1] that self-interaction corrections made in the PZ-SIC way cause significant errors in  $E_{xc}$  in the limit of a slowly-varying density. DFAs such as the local density approximation (LDA), PBE, and SCAN are constructed to be exact in this limit. The work establishes that the PZ-SIC approach must be modified in order to maintain correct behavior of  $E_{xc}$  for slowly-varying densities. Based on this discovery, Zope *et al.* [2] proposed a local scaling approach to the SIC.

This LSIC method uses an iso-orbital indicator,  $z_{\sigma}(\vec{r}) = \tau_{\sigma}^W / \tau_{\sigma}$ , where  $\tau_{\sigma}^W$  is the von-Weizacker kinetic energy density and  $\tau_{\sigma}$  is the normal kinetic energy density, to scale the self-interaction energy density.  $z_{\sigma}$  varies from 1 for a one-electron density to 0 for a uniform density. The scaling therefore recovers



The LSIC method [1] removes self-interaction errors in DFT without sacrificing accuracy, allowing accurate predictions for molecules in equilibrium (left and right) and in transition states (center).

full PZ-SIC when the density is one-electron-like, but reduces the correction to near zero when the density varies slowly. Stated differently, LSIC recovers the exact behavior of PZ-SIC for a single electron system and the exact behavior of uncorrected DFAs for uniform densities. A non-self-consistent version of LSIC was tested using densities obtained from PZ-SIC-LSDA calculations. The results show that LSIC-LDA preserves the good performance of PZ-SIC for stretched-bond properties like reaction barriers, but also gives strikingly good performance for equilibrium properties like atomization energies. The paper describing LSIC [2] was selected by the Editors of the Journal of Chemical

Physics as one of the journal's top papers of 2019 and put in a special online highlights collection.

The code development team recently modified the FLOSIC code to enable accurate FLOSIC-SCAN calculations. [3] The SCAN meta-GGA method is known to be numerically demanding, requiring very dense integration grids to accurately compute the SCAN total energies and matrix elements. The demands become more acute in SIC calculations where the SCAN functional is applied to rapidly-varying orbital densities. The UTEP group developed and tested a scheme to overcome these numerical challenges and obtain reliable SCAN results in FLOSIC calculations. This is a critical accomplishment. Since SCAN is the arguably the most accurate DFA, yielding excellent predictions of most properties of materials in near-equilibrium situations, building a successful self-interaction correction on top of SCAN is likely the best route to a method that is accurate in all settings.

Another achievement of the development team was the release of FLOSIC0.1, made available on github in August, 2019. The distribution includes the source code, as well as a simple user manual and data for sample calculations.

Proof-of-principle FLOSIC-DFT calculations of dipole moments for a diverse set of around 50 molecules confirmed [4] that SIE worsens predictions of charge separation in heteronuclear molecules. The anionic part of an ionic molecule is relatively destabilized by SIE, leading to too little charge transfer and an under-estimated dipole moment. We found [4] that removing self-interaction generally leads to larger dipole moments, but the details of the correction are functional-dependent. For LDA and PBE, the correction results in better agreement with accurate reference values, though the corrected values somewhat overestimate these. SCAN also gives dipole moments that are too small, but closer to the reference values than for LDA and PBE. The FLOSIC-SCAN corrections, though smaller than those for FLOSIC-LDA or FLOSIC-PBE, result in over-correcting the dipoles and somewhat worse agreement with the reference values. Removing self-interaction also improves the description of the dipole moment as the atomic separation in a diatomic molecule is increased and gives the proper separated atom limit of neutral atoms, whereas the uncorrected DFA's generally predict non-zero charge transfer between the separated atoms.

Self-interaction leaves the electrons in an atom too weakly bound in DFA calculations, leading to an exaggerated predicted response to external electric fields compared to accurate reference values. In [5]

we show that removing self-interaction via FLOSIC-DFA calculations results in smaller polarizabilities for the atoms from H to Ar and their cations and anions. As in the dipole study, the corrections generally overshoot, leading to values that are smaller than reference values. For LDA and PBE, the corrections lead to improved predictions, but not for SCAN.

In [6] and [7] we used FLO-SIC calculations to study the effect of electron self-interaction on the description of clusters of water molecules. In [6] the focus is on vertical detachment energies (VDE) of the excess electron in water cluster anions. Removing self-interaction significantly improves the orbital energy of the extra electron, making it an excellent predictor of the VDE. In [7] we investigated the effect of self-interaction on the strength of water-water hydrogen bonds and on cluster structures. Removing self-interaction eliminates the over-binding of the clusters predicted by DFAs. In particular, FLO-SIC-SCAN gives binding energies nearly as accurate as reference values without altering the correct structural ordering of water hexamers predicted by SCAN.

To understand the reactivity at open Cu sites in a novel MOF material, adsorption energies of several molecules were determined both experimentally and computationally. The results in [8] indicate systematic over-binding of adsorbate molecules by uncorrected DFAs. The over-binding is reduced by decreasing self-interaction error using hybrid DFA methods that include a fraction of exact Hartree-Fock exchange. An important by-product of this work is the prediction that olefinic and paraffinic hydrocarbons have substantially different adsorption energies in the MOF. This prediction was the basis for a successful scheme, described in [9], to separate ethylene from ethane in column breakthrough experiments. The method yields ethylene purities in excess of 99.999% from an evenly mixed feed gas.

Work on magnetic molecules included a computational study [10] of a large set of di-nuclear Fe compounds. The study compared the performance of a number of DFAs including popular hybrid, range-separated hybrid, and meta-GGA hybrid functionals for predicting magnetic exchange couplings and produced benchmark comparison data for future FLOSIC calculations.

## Future directions

We continue to seek alternatives to PZ-SIC that reproduce the known behavior of  $E_{xc}$  in the one-electron and the slowly-varying density limits. One line of research is to further test LSIC and to develop a variational and self-consistent implementation of the method. Another is to investigate why LSIC yields remarkably good results when used in conjunction with LDA, but not with more sophisticated functionals like SCAN. One hypothesis is that local scaling encounters a gauge problem when used with these functionals. Alternative versions of the local scaling approach are also being studied.

Code and method development initiatives include algorithmic changes intended to increase the efficiency of FLOSIC calculations. Many of these are aimed at improving how the Fermi-Löwdin orbitals are optimized. Improving the scalability of the FLOSIC code is also on-going, as is an effort to create a periodic version of FLOSIC. Progress in these areas will allow applications of the method to more complex systems like molecular magnets. Another area of study is the treatment of virtual orbitals in FLOSIC. Because the PZ-SIC energy functional is orbital dependent, each occupied orbital “sees” a different one electron Hamiltonian, improving the orbital energies and charge densities for these states. But the virtual orbitals are not directly affected by self-interaction corrections, leaving their energies and densities similar to their uncorrected DFT counterparts. We are investigating approaches in which virtual orbitals also “see” an SIC potential. Virtual orbitals obtained in this way can be useful in time dependent versions of the theory.

## Grant Number and Title

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

## Project Personnel

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**Students:** Kushantha Withanage, Duyen Nguyen, Nageeb Zaman, and Alex Johnson (CMU); Sharmin Akther, Alan Salcedo, Prakash Mishra, and Carlos Diaz (UTEP); Kamal Wagle, Puskar Bhattarai, Niri Nepal, and Santosh Adhikari (UT); Alok Singh and Khalil Abboud (UF).

## Publications (Total of 23 published journal articles since the project started in Oct. 2017)

1. *Perdew-Zunger self-interaction correction: How wrong for uniform densities and large-Z atoms?*, B. Santra and J. P. Perdew, *J. Chem. Phys.* **150**, 174106 (2019). doi:10.1063/1.5090534
2. *A step in the direction of resolving the paradox of the Perdew-Zunger self-interaction correction.* Rajendra R. Zope, Yoh Yamamoto, Carlos Diaz, Tunna Baruah, Juan E. Peralta, Koblar A. Jackson, Biswajit Santra, and John P. Perdew, *J. Chem. Phys.* **151**, 214108 (2019) (**Featured article; Editor's Highlight Selection**) DOI: 10.1063/1.5129533
3. *Fermi-Löwdin orbital self-interaction correction using the strongly constrained and appropriately normed meta-GGA functional.* Yoh Yamamoto, Carlos M. Diaz, Luis Basurto, Koblar A. Jackson, Tunna Baruah, and Rajendra R. Zope, *J. Chem. Phys.* **151**, 154105 (2019). DOI: 10.1063/1.5120532
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5. *Self-interaction-free electric dipole polarizabilities for atoms and their ions using the Fermi-Löwdin self-interaction correction (FLO-SIC)*, K. P. K. Withanage, S. Akter, C. Shahi, R. P. Joshi, C. Diaz, Y. Yamamoto, R. Zope, T. Baruah, J. P. Perdew, J. E. Peralta, and K. A. Jackson, *Phys. Rev. A* **100**, 012505 (2019). <https://doi.org/10.1103/PhysRevA.100.012505>
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7. *Self-interaction error overbinds water clusters, but cancels out structural energy differences.* Kamal Sharkas, Kamal Wagle, Biswajit Santra, Sharmin Akter, Rajendra R. Zope, Tunna Baruah, Koblar A. Jackson, John P. Perdew, and Juan E. Peralta, *Proceedings of the National Academy of Sciences*, to appear (March 2020).
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10. *Accuracy of Density Functional Theory Methods for the Calculation of Magnetic Exchange Couplings in Binuclear Iron(III) Complexes.* Rajendra Joshi, Jordan Phillips, Kylie Mitchell, George Christou, Koblar A. Jackson, and Juan E. Peralta. *Polyhedron* **176**, 114194 (2020). DOI: 10.1016/j.poly.2019.114194

## Computational Investigation of Exciton Spectroscopy and Charge Transport Dynamics

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### Abstract

#### Program Scope:

Two major objectives of this research project have been (i) to identify and confirm novel design principles for *efficient* and *robust* exciton migration from natural light harvesting complexes and (ii) to develop computational methods for reliable modeling and theoretical analysis of exciton and charge migration processes that have significant implications for improving photovoltaic devices based on organic materials. The objective (i) has mostly been accomplished to the extent that was proposed in the original proposal. The effort for the objective (ii) has been continuing, for which significant progress has been made during the past year. In particular, we developed and tested theories and computational methods that can be applied to reliable and efficient computational modeling of exciton and charge migration dynamics in systems such as organic photovoltaic devices. Particular focus of the project has been to quantitatively understand and assess various quantum effects on the dynamics of exciton and charge transport dynamics.

While continuing this work, in the coming years, we plan to intensify our effort to find ways to exploit molecular excitons positively for more efficient solar light harvesting, quantum information processing, and sensing. This will be achieved through combination of five complementary projects. The first is focused on establishing a more general understanding of the spectroscopy of molecular excitons of medium to large sizes, through theoretically investigating the spectroscopy and the long range exciton dynamics for well-defined models that can serve as the most common building blocks of solar light harvesting systems. The second project aims to identify and model important physical effects due to the coupling of electronic and nuclear degrees of freedom, which are ignored by standard models for excitons. The third project is to develop theories and computational methods for controlling the dynamics of excitons through the application of time dependent fields, outcomes of which will help develop new ways to utilize molecular excitons for quantum information processing and quantum sensing. The fourth project is to theoretically characterize and determine the stability of excitons at larger length scales where they can be viewed as bound electron-hole pairs to investigate the effects of confinement and medium response on the binding/dissociation energies and kinetics of excitons. The fifth project is to make a recently developed coarse-grained exciton dynamics

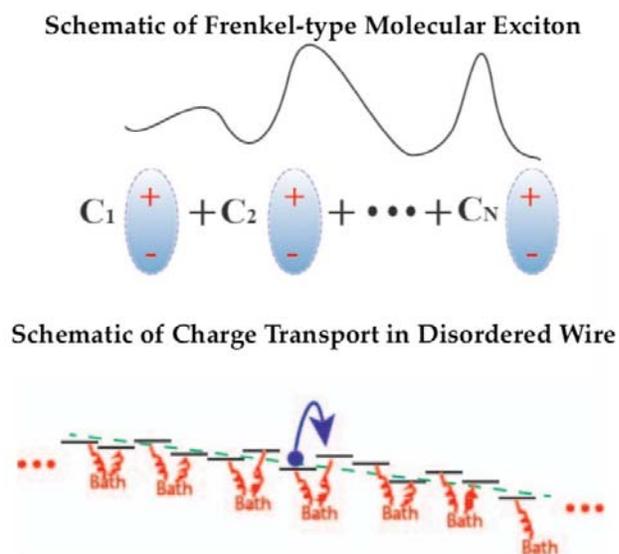


Figure 1. Schematic of a molecular exciton for which the spectroscopic lineshape is developed and schematic of a one dimensional wire for which charge transport calculation is conducted.

method much more versatile so that it can be applied to larger and complex systems more efficiently. The five projects described above will collectively contribute to a better understanding of how to prepare the right environment for optimal exciton dynamics and also to identify novel mechanisms to actively control the dynamics of excitons through intervention by external fields. Pursuing both passive and active control mechanisms of excitons as proposed in this research can lead to new holistic approaches serving as both precise and efficient control methods for novel energy conversion and quantum sensing techniques in the future.

### **Recent Progress:**

*Fourth order expressions for the electronic absorption lineshape of molecular excitons:* The lineshape of electronic absorption spectroscopy reflects the information on quantum dynamical processes accompanying the electronic excitation, and its accurate description is an important component for validating theoretical models and assumptions. This theoretical work provided detailed expressions for the absorption lineshape of molecular excitons that are valid up to the fourth order of exciton-bath interactions within the quantum master equation approach. These expressions can serve as the basis for developing general and systematic methods to model the lineshape for a broad class of molecular excitons. The theoretical expressions were tested for simple models, which demonstrated the feasibility of calculations and offered insights for the development even more accurate theories in the future.

*Simulation of charge transport in quantum environments:* This project investigated the effects of energy gradients on charge hopping dynamics along a one-dimensional chain of discrete sites coupled to quantum bath. Three different numerical/simulation methods of solving the master equation for the charge transport dynamics were tested to produce virtually identical values of time-dependent mean square displacement, diffusion constant, and mobility. Five different rate expressions including exact numerical evaluation of Fermi's Golden Rule (FGR) rate were all tested in order to understand the effects of approximations in representing quantum environments in the presence of energy gradients. The results based on direct numerical evaluation of FGR rate exhibited transition from diffusive to non-diffusive behavior with the increase of the gradient, and showed that the charge transport in the quantum bath is more sensitive to the magnitude of the gradient and the disorder than in the classical bath. Among all the four approximations for the hopping rates, we confirmed that a stationary phase interpolation approximation that was previously developed by Jang and Newton worked best. Two different methods of calculating mobility constant were tested, which provided quantitative information on how quantum effects of the bath influence the charge mobility and confirmed that the drift motion of the population distribution is the source of apparent non-diffusive behavior.

### **Future Plans:**

- **Comprehensive modeling of the spectroscopy and long range dynamics of excitons:** For a well-defined class of Frenkel-type models representing lines, rings, and tubes of chromophores, we will conduct comprehensive computational modeling of the spectroscopy and the quantum dynamics of excitons. These will mostly employ existing theories or their improved versions that will also be developed throughout this project. Particular focus of the study will be systems of nanometer scale sizes with 10-1000 chromophore units and with intermediate magnitudes of the inter-chromophore electronic and exciton-bath couplings that are comparable to thermal fluctuations, for which there is little understanding of how such details influence key spectroscopic features and exciton dynamics.

Establishing these details will help experimentalists' effort to engineer synthetic supramolecular systems to produce desired spectroscopic and dynamical features of excitons. These model systems will also serve as prototypes with respect to which many of current quantum dynamics methods can be compared and validated.

- **Development and validation of new exciton-bath models:** We will extend standard exciton-bath models so as to include non-adiabatic and non-Condon effects, through combination of careful theoretical analysis and validation through quantum dynamical calculations. Accordingly, we will pursue further improvement and generalization of existing quantum dynamics methods so that they can be applicable to new types of models being developed.
- **Quantum control of exciton dynamics:** We will formulate new theoretical approaches and conduct proof-of-concept computational studies for controlling the energetics, details of coherence, and lifetimes of excitons. The major objective of this effort is to establish reliable and practical computational tools that can guide quantum control of various spatio-temporal features of excitons.
- **Path integral simulation of electron-hole pair models for excitons:** We will employ imaginary time path integral simulation and related dynamics theory for excitons modeled by pairs of electron and hole with respective effective masses that are bound by screened Coulomb interactions. This work will help elucidate the effects of interfaces, boundaries, and thermal fluctuations on the extent of delocalization and dissociation kinetics of excitons.
- **Improvement/Application of the GME-MED method and KMC simulation:** We will develop a coarse-grained simulation method accounting for both the variability of the exciton delocalization length and the accompanying fluctuations of lifetime decay rate. Such a method will play an important role for quantitative modeling of long range exciton dynamics in photosynthetic light harvesting complexes and organic photovoltaic materials. This will be pursued through devising a scheme to define effective modules in the generalized master equation method and also developing a corresponding kinetic Monte Carlo simulation method.

**DE-SC0001393: Molecular Level Characterization of Quantum Design Principles for Efficient and Robust Exciton and Charge Migration & Integrative Computational Investigation of the Spectroscopy, Dynamics, and Controlling of Molecular Excitons in Complex Environments**

**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 and Gregory A. Voth, "Can quantum transition state theory be defined as an exact  $t=0+$  limit?," *Journal of Chemical Physics* **144**, 084110 (2016)
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5. Seogjoo J. Jang and Benedetta Mennucci, "Delocalized excitons in natural light harvesting complexes," *Reviews of Modern Physics* **90**, 035003 (2018)
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7. 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)
8. Marta Kowalczyk, Ning Chen, and Seogjoo J. Jang, "Comparative computational study of electronic excitations of neutral and charged small oligothiophenes and their extrapolations based on simple models," *ACS Omega* **4**, 5758-5767 (2019)
9. Seogjoo J. Jang, "Fourth order expressions for the electronic absorption lineshape of molecular excitons," *Journal of Chemical Physics* **151**, 044110 (2019)
10. Ning Chen, Murali Devi, and Seogjoo J. Jang, "Computational modeling of charge hopping dynamics along a disordered one-dimensional wire with energy gradients in quantum environments," *Journal of Chemical Physics*, Submitted (2020)

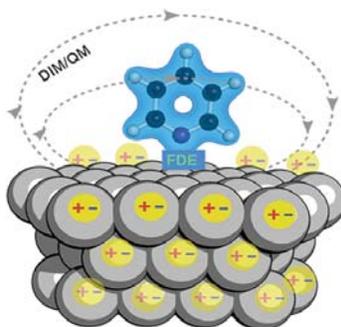
## A Polarizable Frozen-Density Embedding Method

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### 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:** The FDE-pol method combines a frozen density embedding methods with the polarizable DIM/QM model.

### Recent progress

We have extended the FDE-pol method to include an automatic determination of the polarization parameters. The FDE-pol method combines a frozen density embedding methods with the polarizable DIM/QM model. 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. Using a Hirshfeld partitioning we have implemented an automatic determination of the polarization parameter needed for the frozen environment. Benchmark test of molecular polarizabilities obtained from the Hirshfeld parameters is shown to reproduce DFT results within a 10% error. The results are

also consistent with general parameters fitted to a large databased of polarizability data obtained at the CCSD level of theory. Therefore, the Hirshfeld based approach enables fully polarizable FDE-pol simulations without the need to fit the polarization parameters.

The FDE-pol method has also been extended to TDDFT so that excitation energies and polarizabilities can be calculated. We have included local-field effects in the FDE-pol method so that the response of the environment can be captured. The quality of different polarization embedding models in FDE-pol has been benchmarked by comparing with supermolecular DFT calculations of polarizabilities provides. This shows that the inclusion of local field effects is essential for reproducing the results from super-molecular DFT simulations. Comparison of FDE-pol with an exact FDE-EO embedding method for calculation of polarizabilities is underway. Current efforts are focused on extending the FDE-pol method to include larger metal substrates. We are also examining the coupling between excited states in photoactive molecules (azobenzenes, photoswitches) and the metal surface using the FDE-pol method.

### **Grant Numbers and Grant Titles**

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

**Postdoc:** Aparna Harshan

**Students:** Pengchong Liu, Gaohe Hu

### **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, *J. Chem. Theory. Comp.*, **15**, 6588-6596, 2019.
2. A Hirshfeld-based Polarizable Frozen Density Embedding Model, Aparna Harshan, and Lasse Jensen, In preparation, 2020

# Quantum Computing Algorithms and Applications for Coherent and Strongly Correlated Chemical Systems

Sponsor Institution: Purdue University

Award number DE-SC0019215

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## DOE Quantum Computing in Chemical and Materials Sciences

(DE-FOA-0001909) Topical Area: Quantum Computing in Chemical and Materials Sciences.

**PROJECT SUMMARY:** A central challenge of science is the design and synthesis of “efficient” molecules and materials, that is molecules and materials that can efficiently transfer and store energy and/or information or generate new molecules through chemical reactions. The appearance of these desirable properties in molecules and materials, however, frequently coincides with the emergence of exponential complexity in their many-electron wave functions, known as strong electron correlation. The advent of publicly available quantum computing hardware with programmable interfaces has led to an explosion of interest in developing and applying quantum algorithms to chemistry problems. We aim specifically to develop and apply quantum computing algorithms to (a) describing strongly correlated “efficient” molecules and materials at a computational cost that scales non-exponentially with the number of atoms and electrons and (b) elucidating reaction mechanisms in complex chemical systems through Markovian and non-Markovian open quantum systems techniques. For transition-metal coordination polymers we will use quantum-computing algorithms, synthesis, and experimental measurements to develop modular materials with novel catalytic, magnetic, and spin-related properties. For molecular aggregates we will through a combination of quantum computing algorithms and experiment exploit the analogy between the Holstein polaron in superconducting circuits and vibronic coupling in molecular aggregates to gain insights into designing molecular systems with longer coherence lifetime or greater exciton and charge-transfer rate.



## ACCOMPLISHMENTS:

- (1) Designing quantum algorithms for simulating quantum systems has seen enormous progress, yet few studies have been done to develop quantum algorithms for open quantum dynamics despite its importance in modeling the system-environment interaction found in most realistic physical models. Kais and his group have developed and demonstrated a general quantum algorithm to evolve open quantum dynamics on quantum computing devices. The Kraus operators governing the time evolution can be converted into unitary matrices with minimal dilation guaranteed by the Sz.-Nagy theorem. This allows the evolution of the initial state through unitary quantum gates, while using significantly less resource than required by the conventional Stinespring dilation. We have demonstrated the algorithm on an amplitude damping channel using the IBM Qiskit quantum simulator and the IBM Q 5 Tenerife quantum device. The proposed algorithm does not require particular models of dynamics or decomposition of the quantum channel, and thus can be easily generalized to other open quantum dynamical models.
- (2) We have introduced an auxiliary function to simplify the complicated measurement results and develop a generalized Bell-type inequality for continuous measurements. We have also proposed an experimental design to test the method in scattering of chemical reactions. The ability to measure entanglement in chemical reactions can further our understandings about the reaction processes and products, which may lead to better design of materials and systems such as those used in light harvesting systems.
- (3) The accurate computation of ground and excited states of many-fermion quantum systems is one of the most consequential and contemporary challenges in the physical and computational sciences whose solution stands to benefit significantly from the advent of quantum computing devices. Mazziotti and his research group at the University of Chicago has made four significant advances towards quantum chemistry on quantum computers: (1) experimental verification of a generalization of Pauli's exclusion principle on a quantum computer, (2) accurate computation of a Mott metal-to-insulator in a strongly correlated hydrogen chain from error-mitigating conditions on the two-electron reduced density matrix, (3) benchmarking of quantum devices for quantum chemistry through an efficient two-electron ansatz, and (4) computations of strongly correlated molecules from a new quantum solver of the eigenvalue equation that addresses the disadvantages of both quantum phase estimation and variational solvers. In collaboration with Anderson and his research group Mazziotti and his group have investigated strong electron correlation in novel materials including tetrathiafulvalene-2,3,6,7-tetrathiolate bridged tin, nickel, and palladium compounds and a bi-cobalt complex. These molecules and materials have potential applications as superconductors or spin- and/or magnetic materials.
- (4) Anderson and his research group have been focused on developing new molecules and molecular materials that either model quantum phenomena or can be used for potential molecular qubit candidates. We have been doing this work in close collaboration with the theory component of our group, Mazziotti and Kais, as well as with assistance with advanced characterization from the Huang group. We have primarily focused on two areas: making model molecules whose quantum character can only be properly modeled with advanced computation, and making new molecules and materials which could be molecular qubit candidates. In the first area, we have focused on molecular materials with sulfur-based compounds including iron-sulfur clusters. We have also

made a series of tetrathiafulvalene (TTF) complexes which are highly conjugated and redox-active. We have collaborated closely with the Mazziotti group to an accurate picture of the electronic structure of these systems. Furthermore, we have sent samples to Purdue and the Huang group to examine how charge and excitation can be transported along the molecular stacks in these materials. Furthermore, we have also synthesized a well-defined dicobalt complex that serves as a model for the role that pi-conjugation plays in mediating magnetic exchange over long distances. Surprisingly, the Mazziotti group has shown that the coupling in this molecule arises not from canonical superexchange mechanisms, but instead from through-space entanglement. While this serves as a model where theory explains the observed experimental phenomena, we have also used experiment to validate theoretical phenomena as well. Mazziotti recently reported that the assignment of a V(III) oxo complex was incorrect, and that in fact this was a V(IV) complex with the reducing electron entangled across multiple orthogonal pyridine ligands. We have recently experimentally probed this theory with X-ray spectroscopy and validated this proposed electronic structure. Finally, we have also discovered a new class of iron-sulfide materials serendipitously, which have exciting potential applications in battery technology.

- (5) Controlling energy transport between complex quantum states over long distance and across interfaces remains a central challenge for designing new quantum computing materials from molecular components. Addressing this challenge requires developing new experimental strategies for quantifying energy transport dynamics in both temporal and spatial domains to probe dynamics ideally to single molecule level while able to address the whole system. Despite the extraordinary expansion of ultrafast spectroscopic tool kits, existing techniques do not allow a detailed investigation of such quantum energy transfer processes. To address this challenge, Libai group are developing ultrafast microscopy with entangle photon pairs to map out coherent energy transport pathways. As a model system, we have performed measurements on perylene diimides (PDI) aggregates, demonstrating the quantum interference between long-range dipole coupling and short-range charge transfer coupling in energy transport. We compare two contrasting PDI  $\pi$ -stacked aggregates, N-Phenyl PDI and Tetra-Phenyl PDI which is assigned as H<sub>j</sub> (stronger long-range dipole coupling) and h<sub>j</sub> aggregates (stronger short-range charge-transfer coupling) respectively. These measurements provide experimental evidence for a strong dependence of exciton-exciton annihilation on the sign of coulombic coupling and annihilation rate is significantly suppressed for N-Phenyl PDIs. As exciton-exciton annihilation is a major dynamical channel in optoelectronic materials these findings have important implications on designing molecular materials for optoelectronic applications.
- (6) Chen and Zemlyanov are developing a new synthesis method of supper heterostructures of transition metal dichalcogenides (TMDC) (Pt and Pd selenides and tellurides) and another TMDC or topological insulators (TIs), such as Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub>. We use the surface characterization techniques such scanning probe microscopy (SPM), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and high-resolution energy electron loss spectroscopy (HREELS). So far, we synthesized 2D TMDC/TI superposed heterostructures of PtSe<sub>2</sub>/Bi<sub>2</sub>Se<sub>3</sub> and PdSe<sub>2</sub>/Bi<sub>2</sub>Se<sub>3</sub>. The examples of the STM images and the XPS spectra are shown in the Figure below. We also investigated growth of Pt and Pd selenides and tellurides on the different surfaces of Pd and Pt single crystals. Stacking of 2D TMDCs with TIs will greatly broaden the 2D family and result in novel applications. The overlapped crystalline orientations and coupling of different electronic states open up an unprecedented way for bandgap engineering and controlling.
- (7) Chen group have made a significant progress in interferometrically controlling photo-chemical reactions with Rb Bose-Einstein condensates. To change the rate of photoassociation (PA) continuously, we proposed and experimentally demonstrated controlling the relative phase between different scattering channels and photoassociating optically-trapped ultracold Rb atoms into Rb

molecules. We first create the condensates in superposition of different spin components in the  $F=1$  hyperfine state of Rb atoms using RF coupling. Then, we select a spin-sensitive PA line such that there are only two allowed scattering channels, namely, between two atoms with  $m_f=0$  spin or between atoms with  $m_f=+1$  and  $m_f=-1$  spins. To control the relative phase between the two scattering channels (quantum pathways), we rely on the quadratic Zeeman shift at low bias magnetic field strengths. One of the scattering channels acquires no phase because linear Zeeman splittings with opposite signs cancel regardless of the bias field strength. The other channel acquires a phase due to quadratic Zeeman shift. This shift, then, results in a slowly varying phase between the two quantum pathways. As a result, with a Ramsey-like pulse sequence, we control the chemical reactions as the quadratic phase results in destructive or constructive quantum pathway interferences based on the wait time between the two pulses.

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## Interface characteristics of organic molecules on metal surfaces

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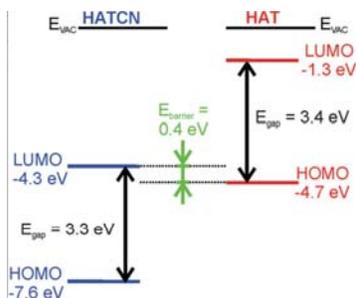
### Abstract

We have investigated extensively the role of van der Waals (vdWs) interactions, when incorporated self-consistently into density functional theory (DFT). Our investigations follow two avenues: i) screening of several vdWs schemes at the generalized gradient approximation (GGA), using adsorption of small organic molecules on a variety of metal surfaces; and ii) simulating the adsorption of large organic molecules, which were subject of experimental investigations. These investigations led us to the conclusion that, if the inclusion of the vdWs interactions improved the nature of the adsorption and brought some excellent agreements with the experimental observations of the adsorption geometries, there is still a lot to do when it comes to the changes to the electronic structure upon adsorption. We have targeted the charge transfer and change in the workfunction as electronic properties to be studied both at the GGA and meta-GGA levels, for a few cases. We found that for the adsorption of thiophene on Ir(100) and Rh(100), OptB88-vdW give results very different from SCAN+rVV10. SCAN+rVV10 predicts large charge transfer as compared to OptB88-vdW, which predicts almost no charge transfer. The large charge transfer may indicate the presence of self-interaction error, which needs further investigation.

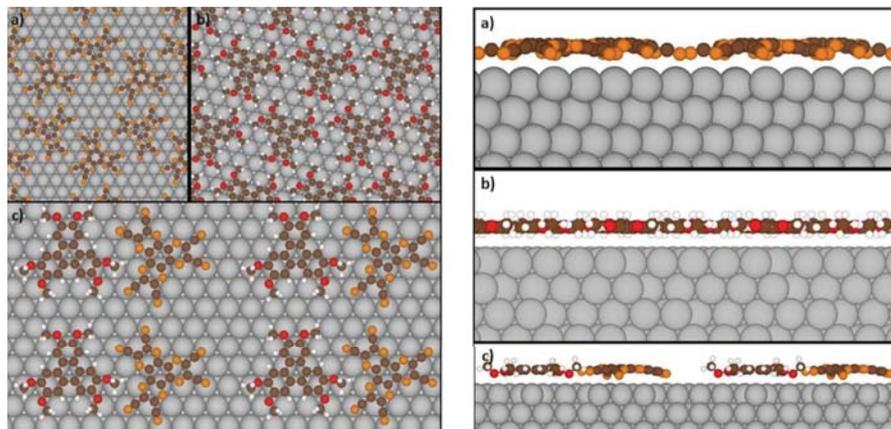
Let us bring here a couple of examples where the inclusion of vdWs interactions brought the simulated structures close to the experimental observations.

### 1) Triphenylene-Derived Electron Acceptors and Donors on Ag (111): Formation of Intermolecular Charge-Transfer Complexes with Common Unoccupied Molecular States

Over the past years, ultrathin films consisting of electron donating and accepting molecules have attracted increasing attention due to their potential usage in optoelectronic devices. Key parameters for understanding and tuning their performance are intermolecular and molecule–substrate interactions. Here, the formation of a monolayer thick blend of triphenylene-based organic donor and acceptor molecules from hexamethoxytriphenylene (HAT) and hexaazatriphenylenehexacarbonitrile (HATCN), respectively, on a silver (111) surface is reported. Scanning tunneling microscopy and spectroscopy, valence and core level photoelectron spectroscopy, as well as low-energy electron diffraction measurements are used, complemented by density functional theory calculations, to investigate both the electronic and structural properties of the homomolecular as well as the intermixed layers. The donor molecules are weakly interacting with the Ag(111) surface, while the acceptor molecules show a strong interaction with the substrate leading to charge transfer and substantial buckling of the top silver layer and of the adsorbates. Upon mixing acceptor and donor molecules, strong hybridization occurs between the two different molecules leading to the emergence of a common unoccupied molecular orbital located at both the donor and acceptor molecules. The donor acceptor blend studied here is, therefore, a compelling candidate for organic electronics based on self-assembled charge-transfer complexes.



Schematic view of the energy levels of HATCN (left) and HAT (right). The bandgaps are taken from the UV-vis data, the LUMO of HATCN was derived from the CV curves and the HOMO and LUMO of HAT



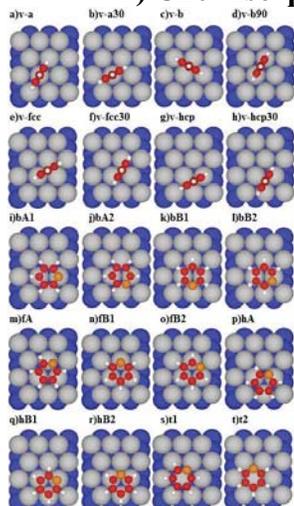
Calculated superstructures of HATCN, HAT and the intermixed layer on Ag(111). Top (left) and side (right) views of (a) HATCN in the  $(7 \times 7)$  structure; (b) HAT in the  $(\sqrt{21} \times \sqrt{21})R10.9^\circ$  structure and (c) the mixed structure. Color code: brown: carbon, orange: nitrogen, red: oxygen, white: hydrogen, grey: silver.

Workfunction Changes Comparison

	HATCN	HAT	HAT+HATCN
Work function changes [eV] from UPS	0.0	-0.9	-0.4
Work function changes [eV] from DFT	+0.1	-0.9	-0.3

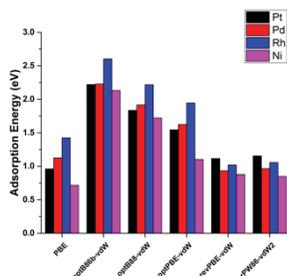
Comparison between experimental and calculated changes in workfunction.

## 2) Chemisorption characteristics of pyridine on Rh, Pd, Pt and Ni(1 1 1)



Adsorption of pyridine on Rh, Pd, Pt, and Ni(1 1 1) is investigated using density functional theory with five van der Waals inclusive functionals (optB86-vdW, optB88-vdW, optPBE-vdW, revPBE-vdW, and the rPW86-vdW2), and PBE. The two most energetically favorable configurations were either a vertical configuration with the molecule's N atom bonded to a metal atom or a flat configuration with center of the molecule's ring over a bridge site with the N atom close to a metal atom. We find that whether the equilibrium adsorption configuration is a flat or vertical depends strongly on the choice of functional and metal. This sharp contrast in final adsorption configurations demonstrates the difficulty current methods have in calculating the adsorption of pyridine on transition metal surfaces, especially Ni(1 1 1). Along with the final adsorption configurations, we present various geometric and electronic properties of the equilibrium adsorption configurations including adsorption heights, buckling of

the first layer of the substrate, tilt angle of the molecule, charge transfer to/from the molecule, change in the surface's work function, and change in the surface's d-band upon the adsorption of pyridine.



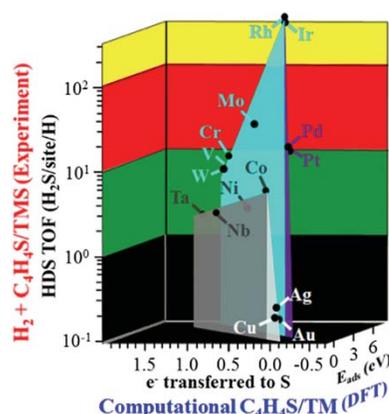
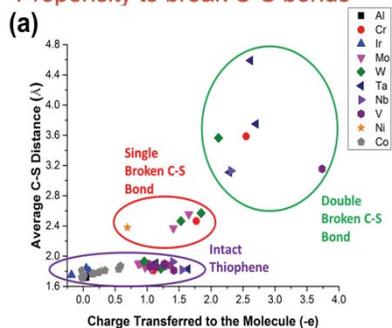
Adsorption Energy for the highest adsorption energy configuration for each metal/functional combination.

### 3) Using DFT Models (Charge Transfer) of Thiophene Adsorption at Transition Metal Interfaces to Interpret Periodic Trends in Thiophene Hydrodesulfurization on Transition Metal Sulfides

We study the adsorption of thiophene on Al(100), Ir(100), W(100), Mo(100), Cr(100), Ta(100), Nb(100), V(100), and Co(10–10) surfaces using density functional theory specifically the van der Waals inclusive optB88-vdW functional. We present a thorough report detailing the geometric and electronic structure of the adsorbate/substrate systems including adsorption heights, adsorption energies, buckling of the first layer of the substrate, C–S bond distances, modification of the surface's d-band, change in the surface's work function, and charge transfer to the thiophene molecule. Altogether, we observe a breaking of a single C–S bond when thiophene adsorbs over Mo(100), and the breaking of up to two C–S bonds when thiophene adsorbs over Cr, Ta, Nb, and V (100). We note a direct correlation between the charge transferred to the thiophene molecule, specifically thiophene's S atom, and thiophene's propensity to break C–S bonds over these surfaces, leading us to frame the desulfurization of thiophene as a process governed by charge transfer.

Charge-transfer and molecular adsorption energy have been modeled by density functional theory with the optB88-vdw functional for a large series of thiophene/transition-metal (TM) combinations. We note an offset in a direct scaling relationship exhibited between these properties sufficient to separate the TMs into two distinct groups. The difference in relationship is shown to correlate strongly with different trends in thiophene hydrodesulfurization when catalyzed by corresponding monometallic transition-metal-sulfides.

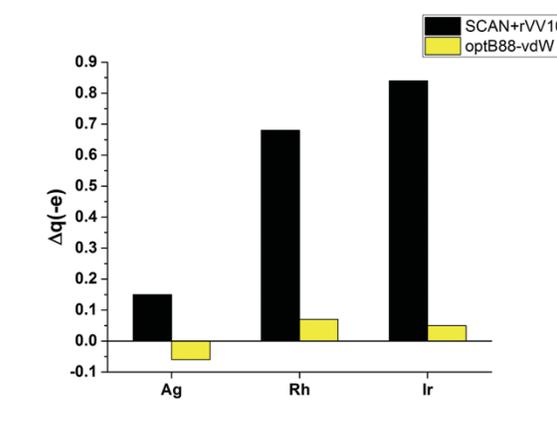
#### Charge Transfer and Thiophene's Propensity to break C-S bonds



#### 4) Going beyond GGA

After completing an extensive study of the self-consistent inclusion of vdWs interactions for the adsorption of benzene on several metal surfaces, with varying chemistry and orientation, we embarked in the same detailed study for other types of prototype small molecules such as thiophene and pyridine. The detailed studies show again an overall good performance by the optB88 functionals, which is now routinely used when simulating experimentally studied large molecules. The natural next step consists in going beyond the GGA level of accuracy, namely invoking the meta-GGA, where the laplacian of the density is included in the calculations. To our knowledge, there is no extensive and detailed study of the performance of the meta-GGA, and meta-GGA+vdWs, on the adsorption characteristics of organic molecules on metal surfaces. Recently, the SCAN (meta-GGA) and the SCAN+rVV10 (Meta-GGA+vdWs) have been developed and implemented in VASP. We have explored the adsorption of benzene, thiophene and pyridine (only for the –optB88- most stable configurations) on Au, Ag, Cu, Ni, Pd, and Pt (111) surfaces.

Metal/Site	Method	$\Delta\Phi$ (eV)	Charge Transfer (-e)
Ag(100)/hollow45	SCAN+rVV10	<b>-0.59</b>	<b>0.15</b>
Ag(100)/hollow45	optB88-vdW	<b>-0.53</b>	<b>-0.06</b>
Ir(100)/bridge45	SCAN+rVV10	<b>0.07</b>	<b>0.84</b>
Ir(100)/hollow45	SCAN+rVV10	<b>-0.13</b>	<b>0.69</b>
Ir(100)/hollow45	optB88-vdW	<b>-1.23</b>	<b>0.05</b>
Rh(100)/hollow45	SCAN+rVV10	<b>-1.02</b>	<b>0.68</b>
Rh(100)/hollow45	optB88-vdW	<b>-1.02</b>	<b>0.07</b>



Charge transfer and change in workfunction for Thiophene on Ag, Rh and Ir (100).

Our preliminary results show a substantial difference between SCAN+rVV10 and OptB88-vdW pointing to the need for further investigation of the role of Meta-GGA in describing the electronic properties of molecules on metal surfaces, especially when the molecules are chemisorbed, exploring the rapidly changing electronic densities near the metallic surfaces.

## Grant Numbers and Grant Titles

DE-FG02-11ER16243: Adsorption and Growth of Organic Materials on Metal Surfaces

**Student(s):** PhD: Walter Malone, Nusaiba Zamane; Undergraduate: Johnathan Von Der Heyde, Isabella Kastor.

### Recent Publications acknowledging DE-FG02-11ER16243:

1. W. Malone and A. Kara, Chemisorption characteristics of pyridine on Rh, Pd, Pt and Ni(111), *Elec. Stru.* **2**, 015001 (2020).
2. W. Malone and A. Kara, A coverage dependent study of the adsorption of pyridine on the (111) coinage metal surfaces, *Surf. Sci.* **693**, 121525 (2020).
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7. W. Malone, J. von der Heyde and A. Kara, Competing Adsorption Mechanisms of Pyridine on Cu, Ag, Au, and Pt(110) Surfaces, *J. Chem. Phys.*, in press (2018).
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# 2020 CTC PI MEETING

## 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](mailto: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.

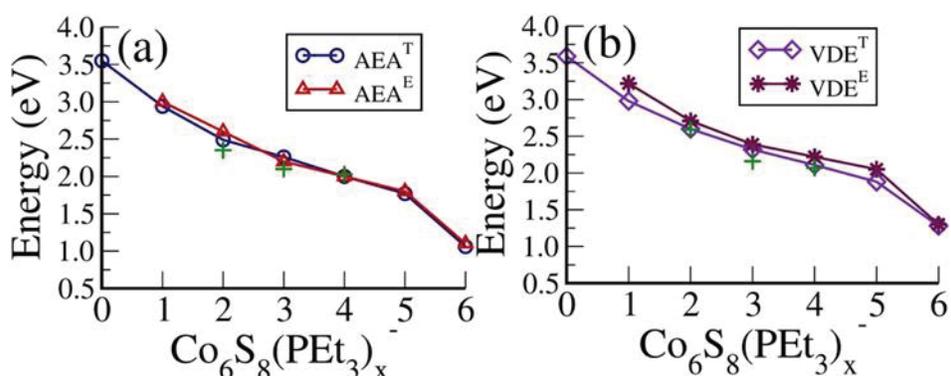
We propose to undertake a comprehensive program starting from electronic structure, stability, and magnetic properties of various classes of clusters including mixed transition metal clusters, chalcogenide superatoms, and silicon transition metal clusters. Our objective is to propose novel materials 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  $TM_{1n}TM_{2m}C_l$  (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. Developing Super Donors and Acceptors by Adding Organic Ligands to Clusters.

We have developed a novel approach that allows designer clusters and nanoparticles with tunable band gaps and location of energy levels controlling donor or acceptor characteristics. Electronic states in a confined nearly free electron gas are grouped into shells due to quantum confinement. Depending on the nature of metal, small compact clusters of metals therefore have electronic structure marked by gaps between filled and unfilled states. These features allow classification of clusters with well-defined valence as superatoms as originally proposed by us. We have now shown that by attaching charge transfer organic ligands to the surface atoms, the electronic spectrum of the cluster can be raised or lowered without affecting the occupation of the levels. We proposed that the effect is fairly general and can be applied to clusters of metallic and semiconducting elements and even compound clusters offering a novel approach to controlling redox character.

We recently collaborated with experimental groups of Prof. Kit Bowen at Johns Hopkins University and Prof. Xavier Roy at Columbia University to confirm the theoretical predictions that the ionization energy (I.E.) and electron affinity (EA) are reduced as  $\text{PET}_3$  ligands are added. We used anion photoelectron spectroscopy to probe the EA and peaks in photo-detachment spectra of a series of cobalt sulfide clusters, whose ligand shells consist of differing number of  $\text{PET}_3$  ligands. In these experiments, the cluster  $\text{Co}_6\text{S}_8(\text{PET}_3)_6$  is synthesized and then brought into the gas phase, where ligands are sequentially dissociated and electrons are attached to form anions, using the IR/PE source. Mass spectrometry confirms the existence of  $\text{Co}_6\text{S}_8(\text{PET}_3)_x^-$  with  $x$  ranging from 0 to 6. The theoretical studies predict that the addition of charge donating  $\text{PET}_3$



**Figure 1.** The experimental and theoretical adiabatic and vertical detachment energy of anionic  $\text{Co}_6\text{S}_8(\text{PET}_3)_x^-$  ( $x = 0 - 6$ ) clusters. The plus symbol (+) indicates the  $\text{AEA}^T$  and  $\text{VDE}^T$  values of cluster's isomers at  $x=2, 3,$  and  $5$ .

ligands decreases the ionization energy (I.E.) and the electron affinity (E. A.) of clusters. The photoelectron spectroscopy only provided measurements of the vertical detachment energy (VDE) and the adiabatic electron affinity (AEA) of anionic clusters. VDE represents the energy required to remove an electron in a vertical process that generates a neutral cluster in the same geometry as the anion while the AEA represents the energy difference between the ground state of the anion and the neutral species. Fig. 1 compares the experimental findings and the theoretical calculations

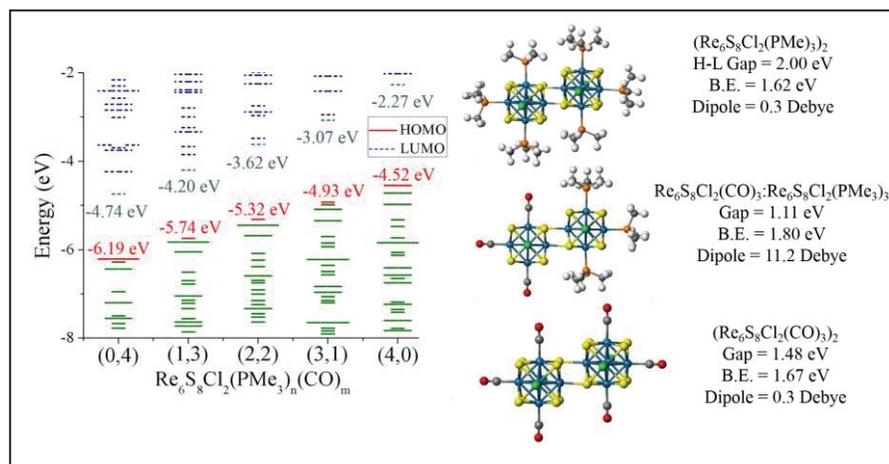
The close agreement between theory and experiment validates the theoretical prediction that the addition of  $\text{PET}_3$  ligands indeed reduces the E.A. consistent with a lifting of the LUMO of the cluster. As the lifting of LUMO is accompanied by lifting of HUMO, these findings also imply that it is possible to generate

super donors (clusters that can donate multiple electrons with low I.E.) by adding charge transfer ligands to the clusters.

## 2. Using Donor/Acceptor Clusters to form Molecules/chains resembling Nano p-n junctions

Having formed clusters with controlled redox properties, we investigated if it was possible to form dimers or longer chains of ligated superatoms that are marked by large internal fields and could be used to separate electron-hole pairs as well as directed electrical transport. In a typical p-n junctions, n- and p- type semiconductors are joined together, and the chemical potential imbalance leads to a flow of charge across the junction boundary resulting in the formation of a depletion layer and an internal electric field. The internal electric field can separate electron-hole pairs or provide diode character as the width of the depletion layer can change with the direction of the applied voltage. To construct a p-n junction at the cluster level, one would need to join two clusters with different chemical potentials, however, in most fused clusters, where two superatomic clusters are strongly bound to each other, the clusters are identical. A dimer of two identical clusters will not generally exhibit a large internal electric field or dipole moment, and the binding of two different atom precise clusters requires exquisite chemical control. A distinct possibility for such systems are metal chalcogenide clusters with large HOMO-LUMO gaps whose chemical potential could be controlled by selecting the appropriate ligands.

In a recent work, we demonstrated this intriguing possibility by considering a  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{L})_4$  clusters whose chemical potential was adjusted using different ligands without appreciable change in the HOMO-LUMO gap. The electron affinity for  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_4$  is 3.21 eV, making it an excellent electron acceptor despite its large gap, and the cluster's electron affinity is much larger than the 0.96 eV electron affinity of  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_4$ .  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_4$  has an ionization energy of 6.00 eV, lower than the 7.78 eV of  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_4$ , making the phosphine ligated cluster a significantly better electron donor. Irrespective of the combination of ligands, the ligated species always have a closed shell electronic configuration with a high HOMO-LUMO gap. More detailed studies showed that the change in donor/acceptor characteristics is due to a shift in the electronic spectrum that can be rationalized as ligands forming a coulomb well that surrounds the cluster and may raise or lower the energy of the states depending on the ligand. This can be clearly seen in Figure 2, in which the absolute HOMO and LUMO of the ligated clusters are graphed.



**Fig. 2.** One electron levels in  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_n(\text{CO})_m$  clusters. Also shown are the gap, binding energy and dipole moment in dimers.

### 3. Superatomic Molecules/chains with Internal Electric Fields for Light Harvesting.

It is known that an interface between p- and n- type semiconductors marked by an electric field allows the separation of electron-hole pairs as well as directed electrical transport. To demonstrate this possibility using clusters, we decorated the stable  $\text{Re}_6\text{S}_8\text{Cl}_2$  cluster with 3 CO and 3  $\text{PMe}_3$  ligands to form  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$  and  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$  motifs that could be joined with S of one cluster bonding to the Re of the other cluster. We then formed homocluster and heterocluster combinations. Fig. 2 shows the structure of the three fused clusters or superatomic molecules with two  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$  motifs, B) the mixed  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3:\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$  clusters, and C) two  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$  clusters. The mixed cluster molecule had the highest binding energy. More importantly, this fused cluster was found to be marked by an intense internal electric field as evidenced by its large dipole moment of 11.2 Debye (Fig. 2). The internal electric field in the mixed cluster causes a redistribution of charge consistent with our donor-acceptor hypothesis.

Next, we investigated the optical spectra of the mixed cluster, using Time Dependent-Density Functional Theory (TD-DFT). We found that an excitation of the CO side of cluster may strongly absorb light, however the lower energy excitations that the cluster will decay to are optically weak which should inhibit electron-hole pair recombination. Our studies also confirmed that the mixed cluster was a genuine superatomic model of a p-n junctions, and will be ideal to separate electron-hole pairs. There is a net charge flow from the  $\text{PMe}_3$  donor side to CO acceptor side. In an anionic cluster (Figure 3A), the excess charge is localized

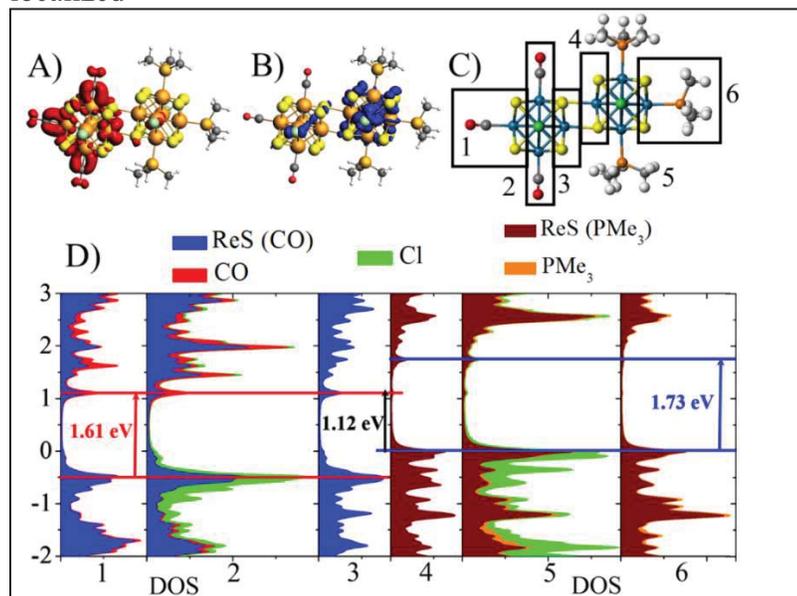


Fig. 3. The structure of the A) Anionic, B) Cationic, and C) Neutral  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ . The isosurfaces indicate the location of an extra electron, and electron-hole. D) The density of states at different locations in the fused cluster. The position is indicated in part C.

on the CO side of the cluster, while in Figure 3B (cationic cluster) the hole is localized on the  $\text{PMe}_3$  side of the cluster. This demonstrates that the electron-hole pair are well-separated on the different sides of the fused cluster. We also found (Fig. 3C and D) that the molecule is marked by band bending at the interface, one of the hallmark characteristics of any p-n junction. Figure 3D shows the local density of states as a function of the position. The acceptor, CO, side of the cluster has effectively no density at the HOMO energy level, and the valence band energy is at -0.49 eV. The conduction band energy of the CO side is at 1.12 eV, with the gap on the CO side of the cluster being effectively 1.61 eV. On the  $\text{PMe}_3$  side of the cluster, the valence band is at 0 energy, and the conduction band is at 1.73 eV. Thus the valence band of the  $\text{PMe}_3$  side is 0.49 eV higher than the CO side, and the conduction band is 0.61 eV higher in energy. While both sides of the cluster molecule have local density of states with gaps of 1.61 and 1.73 eV, the states of  $\text{PMe}_3$  side are raised with

respect to the CO side, a clear analog of band bending. We also found that the application of an external electric field changed the relative splitting between the left and right hand bands thus offering the possibility of controlling the band mismatch through application of an electric field. Because of this strong internal electric field, the electron and hole are separated, inhibiting recombination. The fused clusters behave much like a cluster p-n junction, with the ligands acting as charge transfer dopants. Our preliminary studies also show that an external electric field can change the shift and may even align the levels suggesting that these fused clusters may act like a diode.

- **Future Plans:**

We are proceeding along several directions. We are working with experimental groups at Johns Hopkins and Columbia University to explore the formation of magnetic species with controlled redox properties and to see if such clusters can be used as dopants on two dimensional semiconductors to form magnetic species. We are also planning to extend our studies to phosphorene nanoribbons.

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**Metal-Chalcogenide Superatomic Molecules/Chains: Unusual Nano p- n- junctions with tunable Band gap, Adjustable Band Alignment, and Effective Electron Hole separation**

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 Abstract

The poster will present our recent efforts in laying the foundation for developing nano p-n junctions by combining metal-chalcogenide clusters with controlled redox properties to form molecules and extended chains. As we show, an unusual feature of such chains is that one can control three most significant requirements for the photovoltaic and other applications namely (1) Controllable band gap, (2) adjustable band alignment required to transfer electron and hole from the nano device, and (3) effective electron hole separation needed to reduce recombination of electron and hole generated upon absorption of the photon.

The presentation will begin with first outlining how the band gap in metal-chalcogenide clusters can be controlled by adding alkali or halogen atoms to attain closed shells with large gaps between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). Depending on the nature of metal and chalcogenide atoms, such a combinations can offer units which are stable and have large variations in HOMO-LUMO gaps needed for various applications.

The next step is to develop a procedure that can allow overall placement of levels so that bands can be aligned with host for an effective transfer of electrons and holes. As I will show, this can be accomplished

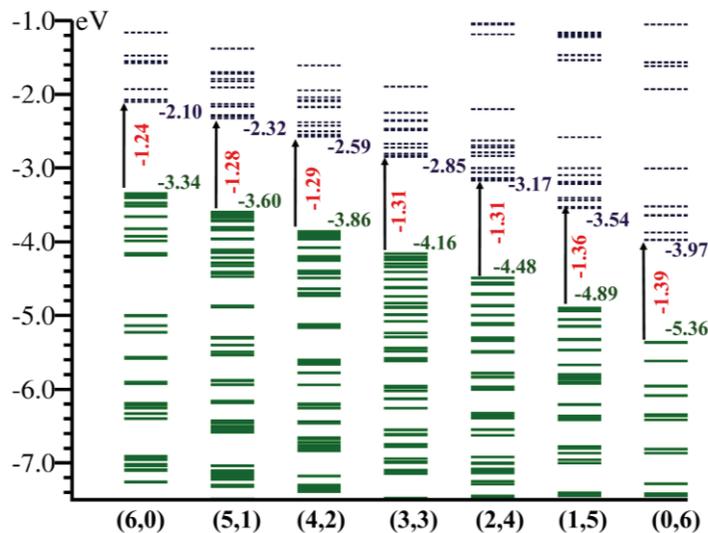


Fig. 1 The electronic structure of  $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_n(\text{CO})_m$ .

by adding charge transfer ligands including donor ligands like trimethyl phosphine or acceptor ligands like CO. The above figure shows how the addition of ligands can shift the electronic spectrum without changing the filling of the bands. We have also shown that the effect is fairly general and can be applied to a wide variety of clusters.

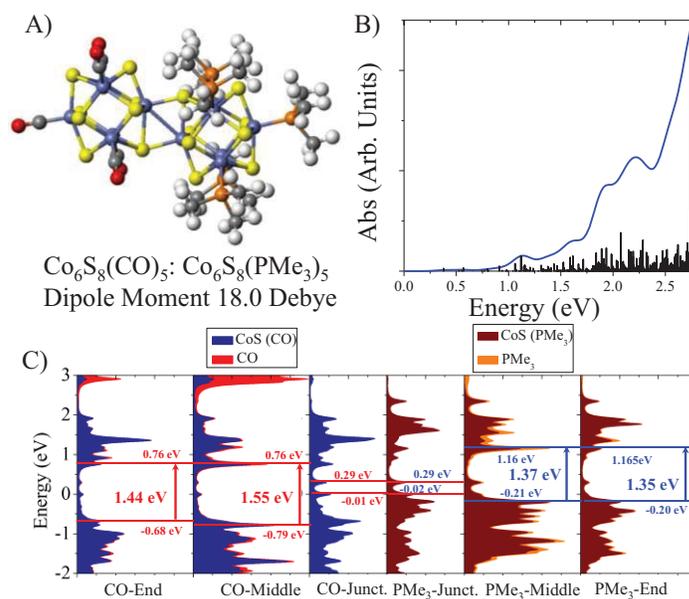


Fig. 2 The structure of  $\text{Co}_6\text{S}_8(\text{CO})_5: \text{Co}_6\text{S}_8(\text{PMe}_3)_5$ , the optical absorption spectra, and the density of states as a function of position.

In Fig. 2 we demonstrate a p-n junction formed by joining an electron donor and acceptor clusters. First, a  $\text{Co}_6\text{S}_8(\text{CO})_5$  acceptor cluster was formed by adding CO ligands to the  $\text{Co}_6\text{S}_8$  cluster. A corresponding donor cluster was then formed by adding donor ligands  $\text{PMe}_3$  to the  $\text{Co}_6\text{S}_8$  cluster. The two clusters were then joined by linking the unligated Co and S atoms to form the  $\text{Co}_6\text{S}_8(\text{CO})_5: \text{Co}_6\text{S}_8(\text{PMe}_3)_5$  molecule. We found that the clusters bind by 2.45 eV, and that the cluster has a dipole moment of 18.0 Debye, a larger dipole moment. The HOMO-LUMO gap is only 0.29 eV with the frontier orbitals being localized in the p-n junction. The optical absorption is shown in Figure 2B, and there is a weak absorption corresponding to the excitation in the junction, however the absorption at the individual cluster's HOMO-LUMO gap is much stronger. In Figure 2C, we see the band bending in the  $\text{Co}_6\text{S}_8(\text{CO})_5: \text{Co}_6\text{S}_8(\text{PMe}_3)_5$  fused cluster. While the frontier orbitals are in the gap, the valence band in the CO side is found to be at -0.68 eV, while the valence band on the  $\text{PMe}_3$  side is -0.21 eV. This shows that the use of donor/acceptor ligands on opposite sides of the cluster will induce a large internal electric field in different clusters. While the Cobalt cluster is not the ideal case to work for electron-hole pair excitation due to the presence of the defect states in the junction, the concept can be applied to other ligated clusters. We are currently investigating other cluster pairs to find the best candidate.

Our further investigations indicated that an external electric field may realign the levels, and the response suggests that these fused clusters may behave much like a diode. The fused clusters may be extended into nanowires, opening the possibility of more complicated pnp and npn type junctions using this strategy. Further, this concept may be applied to other ligated clusters, although the presence of defect states in the cluster junction may prevent electron-hole separation, so the choice of cluster requires care for light harvesting. Our results thus reveal an alternative strategy for forming and engineering internal electric fields at the scale of a single nanometer.

## 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  
Turbasu Sengupta  
Arthur Reber Research associate Professor (Partially)

**Student:**  
Dinesh Bista Graduate Student (partially)  
Abraham Palma Undergraduate Student (partially)  
Alain Ward Undergraduate Student (partially)

### Selected Publications:

- (1) Liu, G. Chauhan, V., Aydt, A.P. Ciborowski, S.M., Pinkard, A, Zhu, Z. Roy, X., Khanna, S.N., and Bowen, K.H. Ligand Effect on the Electronic Structure of Cobalt Sulfide Clusters: A Combined Experimental and Theoretical Study. *J. Phys. Chem. C* **123**, 25121–25127 (2019). DOI: 10.1021/acs.jpcc.9b04153
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- (3) 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>.
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## Data-Directed Synthesis of Multicomponent Materials for Light-Driven Hydrogen Production from Oxygenates

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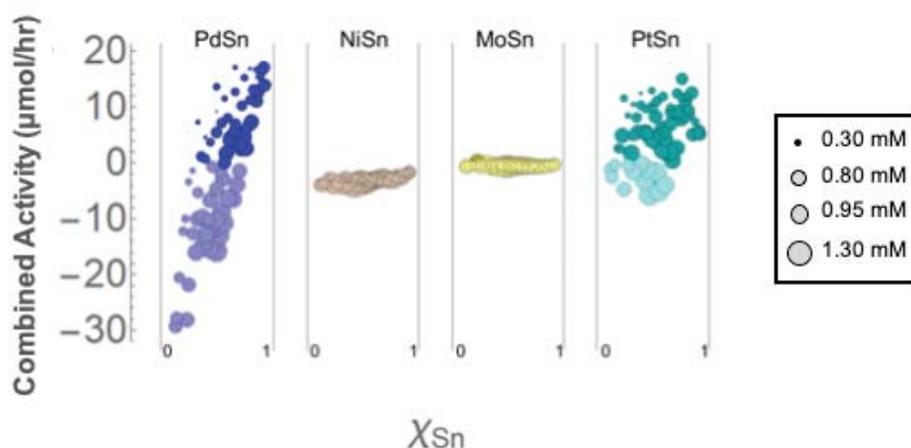
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### Abstract

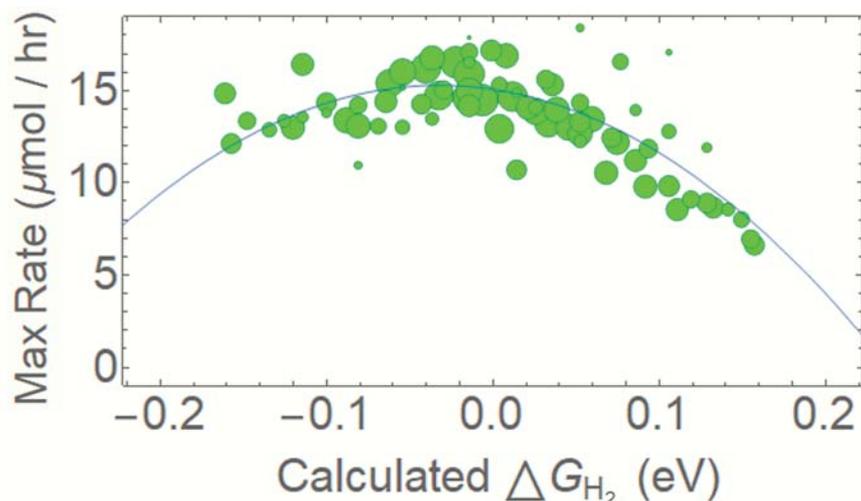
The renewable production of hydrogen is an important technology. Current approaches to catalyst discovery for thermo/electro and photochemical methods for hydrogen production have been difficult to optimize. This difficulty arises in part because of the separation of the synthesis and characterization of catalysts from their performance under operating conditions. It is challenging to build models that relate catalyst performance to synthesis conditions. We have taken a different approach to this problem. We use a photo-driven process that couples a photoabsorber with the synthesis of multi-component metal particles and hydrogen production. This approach is readily parallelized in a multi-well plate, enabling us to explore a wide range of synthesis conditions that are directly connected to catalyst performance measurements. We will show how we used this approach to screen thousands of possible catalyst synthesis conditions to identify promising combinations (Fig. 1).



**Figure 1. Some examples of ~400 Sn containing bimetallic catalysts for hydrogen production. Each circle represents a hydrogen production from one well with different compositions. Sn shows promoting activity for Pd and Pt, but not for Ni or Mo. Adapted from Ref 1.**

The high-throughput experiments alone, however, do not tell us what metals to test, or why one might be good. For this we augment the approach with a parallel high-throughput computation approach where thousands of DFT calculations are performed on multi-component alloy surfaces to screen for promising candidates with desired hydrogen and CO adsorption energies. For example, in Figure 2, we show estimated hydrogen adsorption energies on Pd-Sn bimetallic surfaces and compare them to experimentally measured rates from experiments with the same compositions. We find that the highest rates coincide with surfaces

that have a free energy of adsorption near 0 eV, consistent with our understanding of the electrochemical hydrogen evolution reaction.



**Figure 2. Integrated computational and experimental data for Pd-Sn bimetallic alloys. The x-axis shows the estimated hydrogen adsorption energy for the composition corresponding to the experimental maximum rate of hydrogen evolution at that composition.**

We currently have over 4000 bimetallic compositions in our data set from over 40 plates. We are building a Python based data structure that can be used through Jupyter notebooks for analysis of this data. We are working towards using Jupyter notebooks to setup the experiments, perform the analysis of each experiment, aggregate data across experiments, and to integrate machine learning into the design of the experiments. These notebooks utilize shared data from the project at NERSC.

Our future plans will focus on the photodriven generation of hydrogen from methanol. We were in the process of installing a robotic dispenser to facilitate automated plate filling when research was interrupted by COVID-19. When we return to the labs, we will complete this task so we can more directly couple the machine learning models with the design of the experiments.

### **Grant Numbers and Grant Titles**

DE-SC0020392 Data-Directed Synthesis of Multicomponent Materials for Light-Driven Hydrogen Production from Oxygenates

**Postdoc(s):** N/A

**Student(s):** Maya Bhat, Eric Lopato, Kirby Broderick, Zoe Simon, Emily Eikey

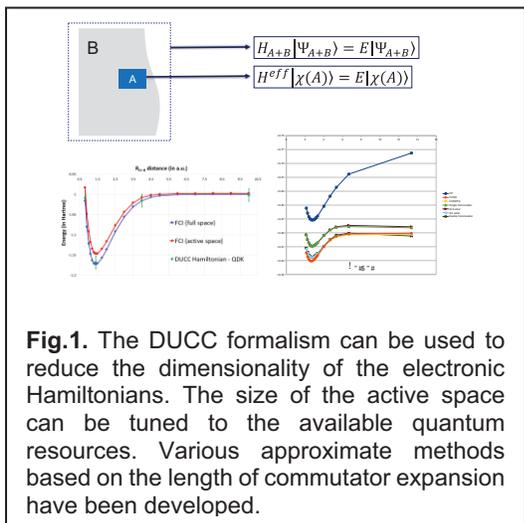
### **Up to Ten Publications Acknowledging these Grants in the last 3-4 years**

1. Parallelized Screening of Characterized and DFT-Modeled Bimetallic Colloidal Cocatalysts for Photocatalytic Hydrogen Evolution, Eric M. Lopato, Emily A. Eikey, Zoe C. Simon, Seoin Back, Kevin Tran, Jacqueline Lewis, Jakub F. Kowalewski, Sadeq Yazdi, John R. Kitchin, Zachary W. Ulissi, Jill E. Millstone, Stefan Bernhard, ACS Catal. 2020, 10, 7, 4244-4252, <https://doi.org/10.1021/acscatal.9b05404>.

# Embedding Quantum Computing into Many-body Frameworks for Strongly Correlated Molecular and Materials Systems

Nicholas Bauman, Eric Bylaska, Wibe A. de Jong, Travis Humble, Karol Kowalski, Sriram Krishnamoorthy, Mekena Metcalf, Duo Song, Nathan Wiebe, Dominika Zgid

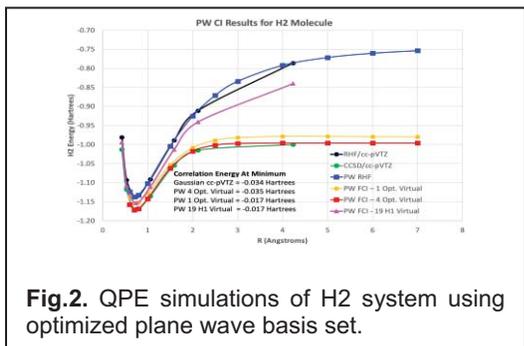
To take advantage of existing and soon-to-be quantum computing resources a balanced development of novel quantum simulation algorithms, applied math tools, and many-body quantum formulations amenable for quantum computing is needed. Of special interest is to enable accurate quantum chemical formulations that (1) can be used to reduce the dimensionality of many-body problems, (2) utilize various types of basis sets (Gaussian and plane waves basis sets), and (3) provide computational components of various embedding methods that require the inclusion of complex electron correlation effects. These formulations should also be flexible enough to utilize existing models for quantum computing including Quantum Phase Estimators (QPE) and Variational Quantum Eigensolvers (VQE). Building a mature quantum computational infrastructure will also initially require a coexistence of flexible computational frameworks that can be tuned to the available classical and quantum computing resources.



To address the problem of dimensionality reduction of many-body problems we have developed unitary coupled-cluster downfolding (DUCC) techniques that provide a mathematical background for reducing the dimensionality of many-body Hamiltonians and for integrating classical and quantum types of computing [1]. This active-space driven formalism can be used to integrate out a large class of fermionic degrees of freedom and as such is amenable for quantum computing on existing and soon to be quantum devices. An important aspect of CC downfolding methods is the existence of hierarchical structure of approximations associated with the size of the active space, accuracy of non-active-space (dynamical) correlation effects, and the length of commutator

expansion. It has already been shown that these techniques can be applied to describe ground and excited states of molecular systems [1-2] (Fig.2). Additionally, classical codes for calculating downfolded Hamiltonians have already been integrated with the QPE [3] and VQE[4] quantum solvers to evaluate the performance of these algorithms and determine the importance of various

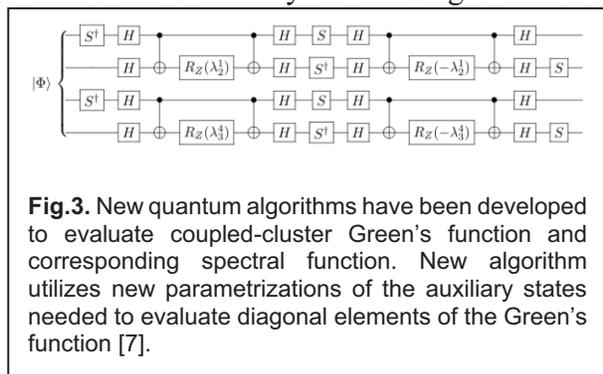
classes of excitations in strongly correlated regime. In these studies several benchmark systems have been used including: H<sub>2</sub>, H<sub>4</sub>, Be, Li<sub>2</sub>, H<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub> models.



For many-body methods such as MSCF and CASSCF, in which the number of one-electron orbitals are optimized and independent of basis set used, there are no problems with using plane-wave basis sets. However, for methods currently used in quantum computing such as select configuration interaction (CI)

and CC methods, it is necessary to have a virtual space that is able to capture a significant amount of electron-electron correlation in the system. The virtual orbitals in a plane-wave Hartree-Fock calculation, because of Coulomb repulsion, are often scattering states that interact very weakly with the filled orbitals. As a result, very little correlation energy is captured from them. The use of virtual spaces derived from the one-electron operators have also been tried, and while some correlation is captured, the amount is quite low even when 19 orbitals are used (magenta curve in Fig.2). To overcome these limitations, we have been developing new classes of algorithms to define virtual spaces by optimizing orbitals from small pairwise CI Hamiltonians. With these procedures we have been able to derive virtual spaces, containing only a few orbitals, that are able to capture a significant amount of correlation. For the H<sub>2</sub> molecule, we were able to get good agreement with cc-pVTZ basis set results with just 4 virtual orbitals (red line in Fig.2). Besides, using these derived basis sets for full CI quantum computing calculations, they can also be used in other many-body approaches, including coupled-cluster and Moller-Pleset perturbation theories, and open up the door to many-body calculations for plane-wave basis set methods.

The team has also developed Green's function method based on the downfolded Hamiltonians to evaluate the feasibility of utilizing reduced-dimensionality Hamiltonians in Green's function



simulations of spectral functions and binding energies in various energy regimes. The obtained results indicated that active-space representation provides an efficient way of encapsulating correlation effects needed for determination of satellite states.[4] These ideas have been further extended to calculate CC Green's functions using overlap-type quantum algorithms and new unitary-coupled-cluster based parametrization of intermediate states in  $N-1$  electron Hilbert space. These algorithms are

currently being tested for Hubbard model [7] (see Fig.3). An interesting feature of this approach is its hybrid character which can utilize classical and quantum resources.

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# Quantum Monte Carlo Calculations for Single-Molecule/Atom Magnets

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## Abstract

The development of quantum computers for information processing is currently the focus of intense investigation. Future quantum computers will be based on entangled two-state qubits (or higher), replacing the binary bits of classical computers. Theoretically they could deliver

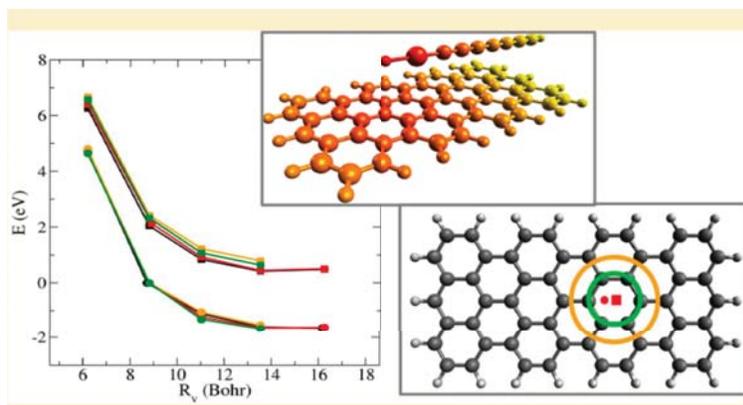
computational speeds far greater than those possible in classical computing. A challenge for any qubit physical implementation is maintaining entanglement in the presence of decoherence-inducing interactions.

Spin-based systems have long been considered, since they can be relatively well isolated, which is conducive to long coherence times. Single-atom and single-

molecule magnets have atoms with localized d and/or f electrons, where two-body Coulomb repulsion entangles the electrons and leads to a rich interplay among charge, lattice, orbital, and spin degrees of freedom, and sensitivity to external fields, strain, and temperature. This interplay supports rich functionalities for novel device applications.

The complexity of the materials, however, presents great challenges to the best theoretical many-body methods in guiding the design of new materials. The exponential growth of the many-electron Hilbert space is the main challenge in describing the properties of these systems. The key challenges are: i) reducing the exponential scaling of direct brute force approaches, and ii) delivering high predictive accuracy for strongly correlated electron systems. The auxiliary-field quantum Monte Carlo (AFQMC) method, developed by the PIs, has been shown to provide highly accurate description of strongly correlated electronic systems, from molecules to solids, while maintaining better computational scaling with systems size,  $N$  [ $O(N^3 - N^4)$ ], than most quantum chemistry many-body methods.

A specific objective of this proposal is to guide the design of single-atom and single-molecule magnets for applications in quantum information systems (QIS) and spintronics, by deploying AFQMC based computational methods for transition metal and



*Embedding and downfolding approach in AFQMC* will be used to model the local active environment of single-atom magnets/molecules. A local cluster in which electrons are fully correlated is defined, and the frozen orbital method is used on the remainder of the system to construct an effective Hamiltonian, which operates within the local cluster. [Eskridge, Krakauer, and Zhang, J. Chem. Theory Comput, 15, 3949–3959 (2019).]

f-orbital systems. To achieve this, a second objective is to further develop the state-of-start AFQMC method, adding new functionalities and efficiencies to address this challenging problem. In addition, it is important to improve the accuracy of standard density functional theory (DFT). We will benchmark DFT and quantum-chemistry methodologies against highly accurate AFQMC calculations.

Recent progress:

i) Local Embedding and Effective Downfolding in the Auxiliary-Field Quantum Monte Carlo Method:

A local embedding and effective downfolding scheme has been developed and implemented in the auxiliary-field quantum Monte Carlo (AFQMC) method. A local cluster in which electrons are fully correlated is defined, and the frozen orbital method is used on the remainder of the system to construct an effective Hamiltonian, which operates within the local cluster. The system size, which can be feasibly treated with AFQMC, is therefore greatly extended as only a single local cluster is explicitly correlated at the AFQMC level of theory. The approximation is controlled by the separate choice of the spatial size of the active occupied region and active virtual region. The systematic dependence of the AFQMC energy on the size of these regions was investigated, and it is found that relative AFQMC energies of physical and chemical interest converge rapidly to the full AFQMC treatment (i.e., using no embedding or downfolding). [Eskridge, B., Krakauer, H., & Zhang, S. Local Embedding and Effective Downfolding in the Auxiliary-Field Quantum Monte Carlo Method. *Journal of Chemical Theory and Computation*, 15(7), 3949–3959, July 9, 2019. <https://doi.org/10.1021/acs.jctc.8b01244>]

ii) Predicting Ligand-Dissociation Energies of 3d Coordination Complexes with Auxiliary-Field Quantum Monte Carlo:

Transition metal complexes are ubiquitous in biology and chemical catalysis, yet they remain difficult to accurately describe with ab initio methods due to the presence of a large degree of dynamic electron correlation, and, in some cases, strong static correlation which results from a manifold of low-lying states. Progress has been hindered by a scarcity of high quality gas-phase experimental data, while exact ab initio predictions are usually computationally unaffordable due to the large size of the relevant complexes. Calculations were presented for a data set of 34 tetrahedral, square planar, and octahedral 3d metal-containing complexes with gas-phase ligand-dissociation energies that have reported uncertainties of  $\leq 2$  kcal/mol. We performed all-electron phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) calculations utilizing multi-determinant trial wavefunctions selected by a black box procedure. We compare the results with those from density functional theory (DFT) with the B3LYP, B97, M06, PBE0,  $\omega$ B97X-V, and DSD-PBEP86/2013 functionals, and a localized orbital variant of coupled cluster theory with single, double, and perturbative triple excitations (DLPNO-CCSD(T)). We find mean averaged errors of  $1.09 \pm 0.28$  kcal/mol for our best ph-AFQMC method, vs 2.89 kcal/mol for DLPNO-CCSD(T) and 1.57 - 3.87 kcal/mol for DFT. We find maximum errors of  $2.96 \pm 1.71$  kcal/mol for our best ph-AFQMC method, vs 9.15 kcal/mol for DLPNO-CCSD(T) and 5.98 - 13.69 kcal/mol for DFT. The reasonable performance of a number of DFT functionals is in stark contrast to the much poorer accuracy previously demonstrated for diatomic species, suggesting a moderation in electron correlation due to ligand coordination. However, the unpredictably large errors for a small subset of cases

with both DFT and DLPNO-CCSD(T) methods leave cause for concern, especially in light of the unreliability of common multi-reference indicators. In contrast, the robust and, in principle, systematically improvable results of ph-AFQMC for these realistic complexes establish the method as a useful tool for elucidating the electronic structure of transition metal-containing complexes and predicting their gas-phase properties.[Rudshiteyn, B., Coskun, D., Weber, J. L., Arthur, E. J., Zhang, S., Reichman, D. R., Friesner, R. A., and Shee, J. (2020). “Predicting Ligand-Dissociation Energies of 3d Coordination Complexes with Auxiliary-Field Quantum Monte Carlo,” submitted 2020, <http://arxiv.org/abs/2001.07261>.]

#### Future Plans:

We will begin implementation and testing of spin-orbit interactions into AFQMC. Continue AFQMC calculations for small but realistic embedding models for the single-atom magnets.

### Grant Numbers and Grant Titles

DE-SC0001303: Quantum Monte Carlo Calculations to Guide the Design Of Single-Molecule/Atom Magnets

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**Student(s):** Brandon Eskridge

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

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

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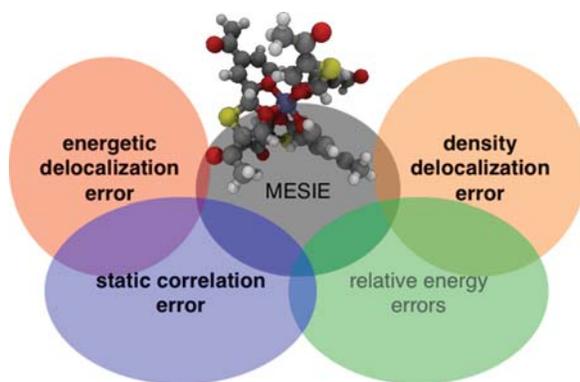
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### Abstract

**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. Not only do methods need to be accurate but they need to be efficient to enable large-scale screening of materials spaces, and their errors need to be balanced throughout the space to avoid introducing unsystematic biases towards specific lead compounds. 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 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) and then apply these methods to materials discovery (Figure 1). We work to understand how recovering piecewise linearity (i.e., eliminating energetic delocalization error) impacts density delocalization error with respect to accurate correlated wavefunction theory references. We define relative energy errors as residual errors in semi-local functionals that remain, even when other errors are eliminated. We develop models that eliminate these errors without increasing cost, and we use a combination of analytical and data-driven models to increase the accuracy of high-throughput screening and training of machine learning models for the discovery of transition metal redox couples.

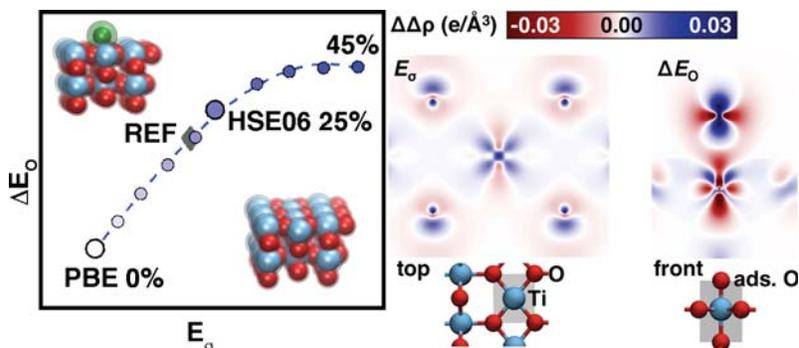
**Recent Progress:** In the past year, we have worked to both understand and correct approximate DFT errors for predictive modeling of transition metal chemistry through the following:

i) We have examined how common approximations to recover the derivative discontinuity (e.g., hybrid functionals and DFT+U) can improve properties of surfaces relevant to catalysis. Specifically, we focused on correlated rutile transition metal dioxide  $\text{MO}_2(110)$  surfaces ( $M = \text{Ti to Pt}$ ), several of which are known for their ability to act as water splitting catalysts. It has been known for some time that errors in semi-local DFT counterintuitively both overstabilize surfaces (i.e., as judged through surface formation energies) and make them too reactive (i.e., bind adsorbates too tightly). This is counterintuitive because in surface science, a surface's stability should be directly related to its reactivity. It has been argued that within conventional DFT (e.g., applied to metals), both cannot be improved at the same time. We studied a range of semi-local functionals, global and range-separated hybrids, and DFT+U corrections on  $\text{MO}_2(110)$  surfaces. We observed that DFT+U could improve either surface energies in early transition metals or adsorption energies only in late transition metals. Conversely, local range-separated hybrids could improve both simultaneously (Figure 2). These improvements were judged with respect to coupled-cluster-corrected references. Analyzing properties of the density revealed why hybrids could improve



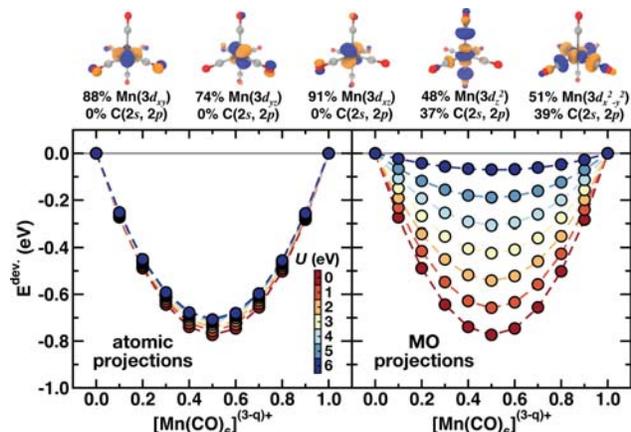
**Figure 1.** Range of coupled errors present in approximate density functional theory studied in this work relevant to a transition metal complex redox couple (top).

both properties simultaneously while DFT+U could improve only one property at once: namely, density delocalization errors could not be detected by DFT+U in select cases, whereas hybrids uniformly localized the density to destabilize surfaces and adsorbates in a manner that improved both of these quantities. Thus these observations suggest that further improvements are needed to DFT+U for the treatment of transition metal oxide surfaces, despite the fact that DFT+U remains one of the most widely used methods in this area of heterogeneous catalysis due to the sharp computational cost requirements for larger super cells. Our observations in solids are consistent with our recent observations on improved descriptions of M-O bonding in transition metal diatomic molecules as well, although there we observed that while hybrids could improve the description of the potential energy curve and of bonding, they worsened semi-local DFT descriptions of spin state ordering.



**Figure 2.** (Left) Observation of improved surface formation energy and adsorbate energy simultaneously for local hybrids in  $\text{TiO}_2(110)$ . (Right) Effect of increasing Hartree-Fock exchange on the density in the plane of a cleaved surface for surface formation energies or at the adsorbate for  $\text{TiO}_2(110)$ .

ii) We have extended 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 accomplished 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. We recently introduced fully



**Figure 3.** Fractional charge line analysis for high-spin  $\text{Mn}(\text{CO})_6$  between +2 and +3 charge states. (top) Wannier orbitals studied and their relative contribution of 3d and 2p occupations. The phase is shown in blue and orange. (bottom) Atomic projections recovering delocalization error (left) and MO projections (right) using the orbitals at top evaluated up to the global curvature  $U$  of 6 eV. Only the deviation from piecewise linearity is shown.

non-empirical coefficients, making the approach a parameter-free method to recover piecewise linearity. This year, we are improving the projection approach. We have recently shown that for transition metal complexes where DFT+U or jmDFT would have failed due to strong hybridization of the molecular orbitals, we can improve the efficiency of these methods significantly by altering the projections used in the formalism. Typically, occupations are evaluated on atomic projections, but we showed that incorporating hybridized orbitals can enable these methods to eliminate delocalization error where they would have otherwise had no positive effect or been efficient (Figure 3). Our new approach employs Foster-Boys localized orbitals for the projection scheme. We are currently testing whether this approach can improve the description of the solids described in progress point (i) as well.

iii) We have developed and demonstrated a range of data-driven methods for improving accuracy in high-throughput screening of transition metal complexes relevant as redox couples in redox flow batteries. We developed a structure-based approach to ground state spin assignment. Because structures are far less sensitive to DFT method accuracy than spin state energetics, this method is far less sensitive to the exchange-correlation approximation employed. We were able to reclassify several spin states where we had previously assigned them incorrectly or would not have been able to identify the experimental

spin state otherwise. Specifically, we look at the neural-network based bond lengths predicted for a complex, and we classify the experimental spin state based on which spin state its bond lengths are closer to. This allows us to classify spin states in spin crossover (SCO) complexes that change their spin state in response to temperature or light. Based on a dataset of text mined and sentiment analysis complexes, we are able to correctly identify 96% of Fe(II) SCO ground states in their low or high spin state (Figure 4). We are now extending this combined machine learning and sentiment-based text mining approach to curating experimental data sets of other properties for method assessment. We have also paired these method advances to guide the large-scale screening of candidate redox flow battery redox couples, arriving at design principles that are relatively method-insensitive by focusing on a single, high-spin state that is likely to be well-characterized by DFT (Figure 4). By pairing machine learning and high-throughput DFT with efficient global optimization, we arrived at design principles at least 500x faster than random search. Even after accounting for parallelization, this means we arrived at solutions in weeks instead of decades. We are now pairing these approaches with multi-objective efforts to improve calculation success and accuracy as well as methods to detect strong correlation in high-throughput screening.

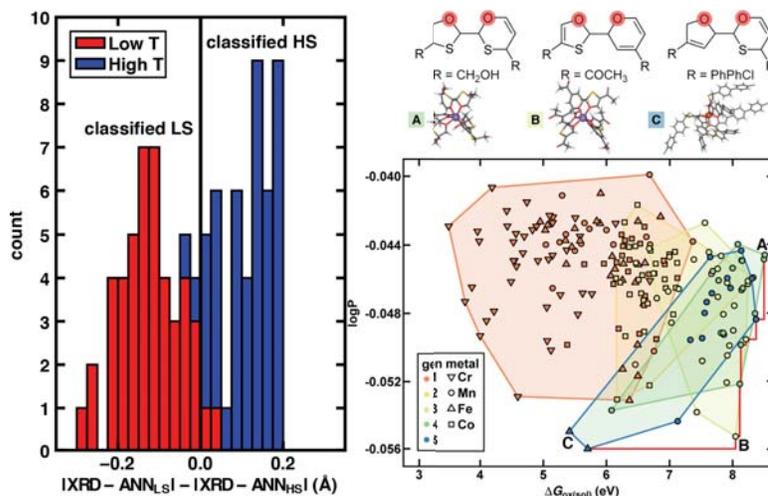


Figure 4. (Left) Classification of spin states from experimental bond lengths using our ANN approach in a stacked bar chart. Any red bars that are to the right of the vertical black line or blue bars to the left of the vertical black line are misclassified (4% overall). (Right) Pareto optimization of RFB redox couples using this approach reveals essential Mn high-spin complexes on the Pareto front.

**Future Plans:** We continue to advance the demonstration of how altering projections and functional forms can improve low-cost approaches to more accurate condensed phase systems (e.g., transition metal oxides). We also are working to understand how our automated tools can be used to improve the accuracy of high-throughput screening workflows by detecting strong correlation and adapting the methodology appropriately on the fly.

**DE-SC-0018096:** “Simultaneous mitigation of density and energy errors in approximate DFT for transition metal chemistry”

**Postdoc:** Fang Liu (NSF MolSSI fellow 2019-, supported by DOE 2017-2018)

**Ph.D. Students:** Akash Bajaj (65%), Vyshnavi Vennelakanti (35%), Qing Zhao (Ph.D. 2018)

**High school and undergraduate/masters students:** S. Lin, S. Ramesh (co-supervised Oxford M.S. ‘19)

**Ten recent publications acknowledging this grant (10 of 13 total 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*

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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. 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>

7. Q. Zhao and H. J. Kulik “Stable Surfaces that Bind too Tightly: Can Range Separated Hybrids or DFT+U Improve Paradoxical Descriptions of Surface Chemistry?” *The Journal of Physical Chemistry Letters*, **10**, 5090-5098 (2019). <https://doi.org/10.1021/acs.jpcllett.9b01650>

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9. J. P. Janet, S. Ramesh, C. Duan, and H. J. Kulik “Accurate Multiobjective Design in a Space of Millions of Transition Metal Complexes with Neural-Network-Driven Efficient Global Optimization” *ACS Central Science*, **Ahead of Print** (2020). <https://doi.org/10.1021/acscentsci.0c00026>

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10. M. G. Taylor, T. Yang, S. Lin, A. Nandy, J. P. Janet, C. Duan, and H. J. Kulik “Seeing is Believing: Experimental Spin States from Machine Learning Model Structure Predictions” *The Journal of Physical Chemistry A*, **ASAP** (2020). <https://doi.org/10.1021/acs.jpca.0c01458>

**Invited article for “Machine Learning” Virtual Special Issue**

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

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**ABSTRACT**

The research projects have 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 focus on examining a variety of factors impinging short-circuit current density ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ) 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. Based on the above scope, we have designed and screened potential lead organic dye-sensitizers for DSSCs with higher photo-conversion efficiency.

For polymer solar cell (PSC), ten novel fullerene-derivatives (FDs) of C60 and C70 had been designed as acceptor by employing quantitative structure-property relationship (QSPR) model which was developed strategically with reasonably big pool of experimental power conversion efficiency (PCE) data. The QSPR model was checked and validated with stringent parameter and reliability of predicted PCE values of all designed FDs. The predicted PCE of FDs range from 7.96 to 23.01. The obtained encouraging results led us to do the additional theoretical analysis of the energetics and UV-Vis spectra of isolated dyes employing DFT and TD-DFT calculations using PBE/6-31G(d,p) and CAM-B3LYP/6-311G(d,p) level calculations, respectively. Frontier orbital energies and UV-Vis absorption spectra of the isolated P3HT oligomer, PCBM and FDs were analyzed to estimate the optoelectronic properties of four FDs as an acceptor in future PSCs. Exciton binding energy plays the pivot role at interface when excitons to diffuse and dissociated in to electrons on LUMO level of the acceptor. The big off-set of LUMO energy levels will hinders this process. FD4 is the best C60-derivatives candidates for PSCs as it has the lowest exciton binding energy, up-shifted LUMO energy level that assist to increase  $V_{oc}$  and strong absorption in the UV region. The FD4 is the best C60-derivatives candidates for PSCs as it has the lowest exciton binding energy, up-shifted LUMO energy level to increase  $V_{oc}$  and strong absorption in the UV region. In case of C70-derivatives, FD7 is potential candidate for future PSCs due to its strong absorption in UV-Vis region and lower exciton binding energy with higher  $V_{oc}$ . The rational molecular modeling, designing, and prediction followed by quantum study offers valued reasoning for the synthesis of lead FDs with

higher power conversion efficiency. The structural analysis concluded the following points: (1) Ortho directing groups in the benzene rings and aromatic rings like phenyl, thiophene, pyrrole attached to the fullerene are significant features for better PCE of PSCs. and (2) Saturated carbon chains, (3) or higher –ortho substituents in benzene rings and a higher number of attachments in the parent fullerene core need to be avoided for higher PCE along with structural fragments with a lower solvent accessible surface area of polar atoms. The outcomes of tactical molecular design followed by the investigation of optoelectronic features are suggested to be employed as a significant resource for the synthesis of FDs as an acceptor of PSCs.[1]

We have performed chemometric modeling of power conversion efficiency (PCE) data of dye sensitized solar cells (DSSCs) using the biggest available data set till date. It comprises around 1200 dyes covering 7 chemical classes. To extract the best structural features required for higher PCE, we have developed multiple quantitative structure-property relationship (QSPR) models. Only 2D-descriptors were used during modeling for their easy computability and reproducibility, avoiding conformational complexity and computational expenses of 3D descriptors, still providing definite mechanistic interpretations. The partial least squares (PLS) models for the Triphenylamine, Phenothiazine, Indoline, Porphyrin, Coumarin, Carbazole and Diphenylamine datasets have been developed using descriptors derived from the best subset selection method. Among the models obtained from the best subset selection, we have selected five models in each dataset based on the Mean Absolute Error (MAE) values. The models were validated both internally and externally followed by the consensus predictions (separately for all seven datasets) using the developed PLS models employing “Intelligent Consensus Predictor” tool to examine whether the quality of predictions of the test set compounds can be improved with the “intelligent” selection of multiple PLS models (consensus model CM vs individual models IM). From the insights of the developed models, we concluded that attributes like a packed structure toward higher conductivity of electrons, auxiliary donor fragment of aromatic tertiary amines, number of thiophenes inducing the bathochromic shift and augmenting the absorption, presence of additional electron donors, enhancement of electron-donating abilities, number of non-aromatic conjugated C(sp<sup>2</sup>) which helps as conjugation extension units to broaden the absorption and highly conjugated  $\pi$ -systems exert positive contributions to the PCE. On the contrary, features negatively contributing to PCE are the followings: fragments which lower the tendency of localized  $\pi$ - $\pi^*$  transition, fragments related to larger volume and surface area of dyes along with hydrophobicity resulting in poor adhesion, fragment RC=N causing dye hydrolysis, steric hindrance for  $\pi$  electronic mobility, fragments enhancing polarity, *etc.* The developed models are useful for quick prediction of PCE of new/untested dyes along with designing of new dyes employing the deep mechanistic structural insights identified from individual and global models.[2]

We have assessed the competence of inclusion of spacer units in the metal-free D- $\pi$ -A organic dyes concerning the augmentation of dye-sensitized solar cell (DSSC) efficiency through the excited state simulations of the charge injection and recombination processes at the dye-semiconductor interface. We selected five recently synthesized DSSC photosensitizers, which were proposed to exhibit higher short-circuit current densities and power conversion efficiencies compared to earlier metal-free organic dyes using iodine as redox shuttle. These D- $\pi$ -A dyes comprise triphenylamine (TPA) as donor (D) unit, cyanoacrylic acid (CAA) as acceptor (A) unit, and highly planar tetrathienoacene (TTA) core as  $\pi$ -bridge unit. The TTA core of these dyes

contain a long alkyl substituent ( $R=n-C_{15}H_{31}$ ) to suppress dye aggregation and charge recombination on  $TiO_2$  surface. All these dyes contain thiophen (T) as spacer unit between the  $\pi$ -bridge and the D/A units so that the orientation effect of thiophene on the performance of DSSC could be monitored. Within the framework of time-dependent density functional theory, we have estimated the crucial factors controlling the rates of photoinduced charge-transfer and energy-transfer processes, including electronic coupling, reorganization energy, and threshold energy barrier in semi-classical Marcus formalism. The evaluation of fluorescent state appeared to be the crucial step while explaining the ultrafast electron injection process and the charge recombination at the Marcus inverted region, as revealed by the obtained results. The electron- and hole-hopping mechanisms were critically analyzed through the estimations of electronic coupling between the dye's excited state and the conduction band of the semiconductor employing different computational strategies such as Generalized Mulliken-Hush method, Förster-Dexter formalism, and semi-classical Marcus theory. The time scales for electron injection between the dye and the  $TiO_2$  surface were further computed by accounting the effect of adsorption on the relative alignment of electronic states of the photosensitizers and the lifetime broadening using the Newns-Anderson model. The retardation of charge recombination has been revealed to be assisted by the insertion of thiophene moiety between the  $\pi$ -bridge and the acceptor units. The estimated cold electron injection efficiencies deploying Onsagar-Braun theory, that rely on the computations of cold electron injection lifetime and cold electron lifetime, showed linear correlation with the experimental photovoltaic parameters of the DSSC comprising short-circuit current density, open-circuit voltage, and power conversion efficiency. The outcomes of the latest work establish a basis for unravelling the mechanism of intricate dynamical processes upon photoexcitation of the sensitizers, as well as devising plausible routes for functional DSSC materials.[3]

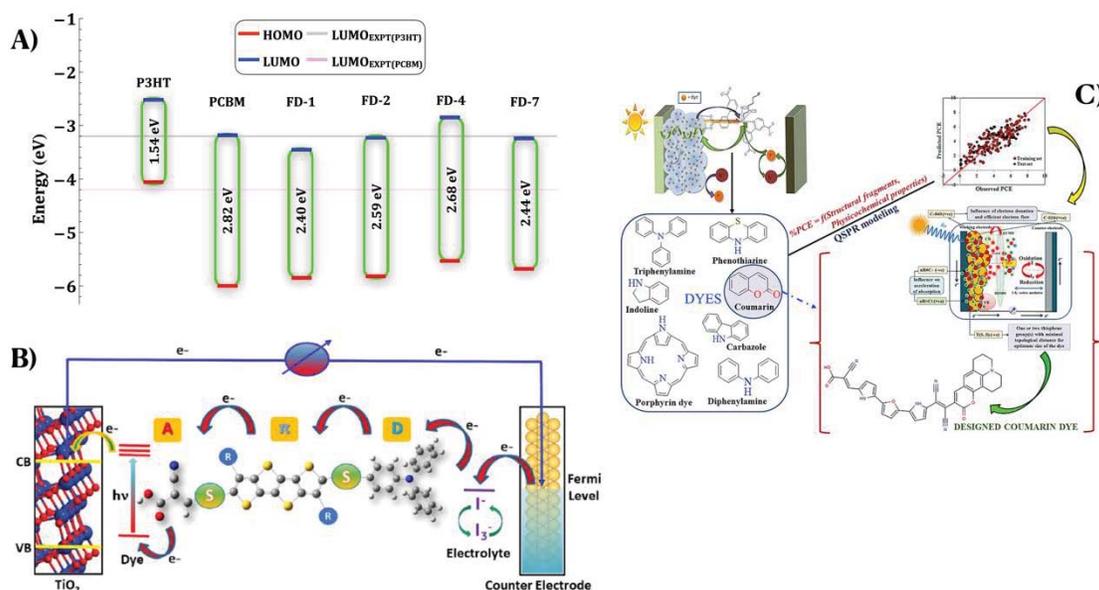


Figure : Energy profile of the designed FDs for PSC (A), Highly planer tetrathienoacene dye in DSSCs (B), and schematic of the QSPR modelling for DSSCs (C).

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 first 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. By employing Marcus electron transfer theory, 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.

### Grant Numbers and Grand Title

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

**Postdoc(s):** Juganta Roy and Pabitra Samanta

**Student(s):** Taylor Dorlus

### Publications Acknowledging this Grant

- (1) Roy, J. K.; Kar, S.; Leszczynski, J.; Roy, J. K.; Kar, S.; Leszczynski, J. *Materials* **2019**, *12* (14), 2282.
- (2) Krishna, J. G.; Ojha, P. K.; Kar, S.; Roy, K.; Leszczynski, J. *Nano Energy* **2020**, *70*, 104537.
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## Toward Ab Initio Quantum Molecular Dynamics on Many Electronic States

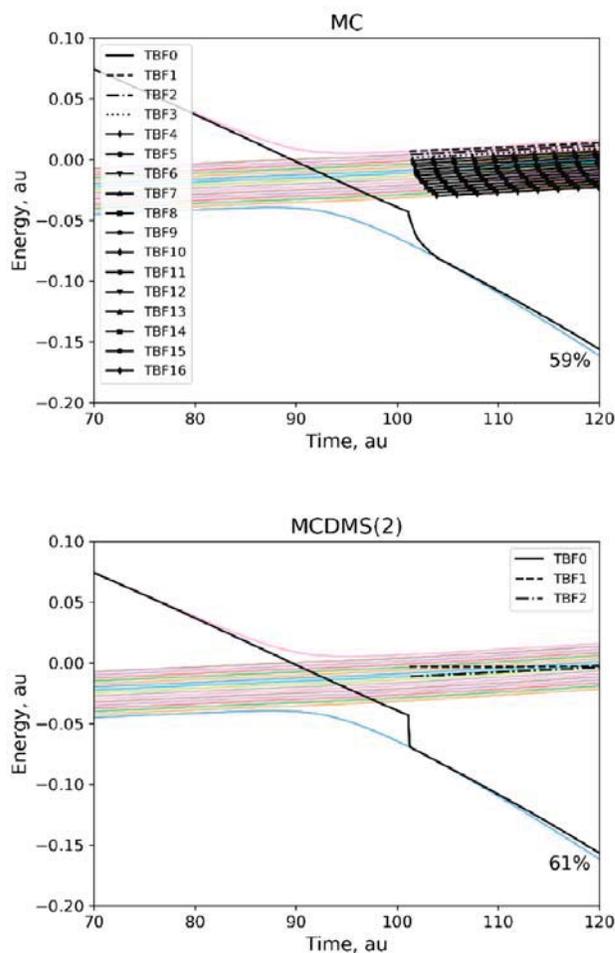
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### Abstract

Ab initio nonadiabatic molecular dynamics methods are valuable tools for modeling the dynamics of electronically excited molecules and materials, especially when prior knowledge of the reaction mechanism is not available. However, practical considerations limit most existing methods to systems where the dynamics span 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. These problems may involve anywhere from ten electronic states to a continuum of states. The broad goals of the present project are to develop ab initio nonadiabatic molecular dynamics methods that can accurately and efficiently model dynamics on large numbers 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.

When modeling molecular dynamics on many electronic states, methods such as trajectory surface hopping and full multiple spawning (FMS) can become intractable because explicit calculation of a large number of electronic states becomes intractable. Ehrenfest (mean-field) 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. Ehrenfest suffers from well-known issues with overcoherence, however, resulting in unphysical predictions of reaction outcomes. Decoherence corrections for Ehrenfest dynamics exist but typically require explicit calculation of the full electronic eigenspectrum, and



**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 colored lines. The probabilities of transmission through the band of 16 states are nearly identical: 59.0% and 61.0% with the full eigenspectrum and a minimal number of approximate eigenstates, respectively.

thus are not practical solutions for problems involving many electronic states.

To enable accurate nonadiabatic molecular dynamics on many electronic states, we have developed multiple cloning in dense manifolds of states (MCDMS; *J. Phys. Chem. Lett.*, **10**, 4542 (2019)). Like FMS, from which it is derived, MCDMS is a fully quantum dynamical approach capable of modeling dynamics of highly dimensional systems without preconceptions about the reaction path. The key advance in MCDMS is that it does not require calculation of the full electronic eigenspectrum during the simulation, yet still contains a proper treatment of decoherence between populations on different electronic states. This is done by employing a set of approximate eigenstates. The approximation of these states is systematically improvable. To date, we have implemented MCDMS in the pySpawn software package, which is open-source and freely downloadable (<https://github.com/blevine37/pySpawn17/tree/MCDMS/pyspawn>). MCDMS has been tested on several model systems. For example, 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. Proper treatment of coherence requires consideration of not only the electronic and nuclear wave functions, but also the photonic wave function. In the most basic approximation, the mere photon number can be used. Thus, to enable accurate treatment of coherence in a light field, we have developed a GPU-accelerated time-dependent Floquet configuration interaction (TD-F-CI) method for modeling light-matter interactions. Though the Floquet approach is not a truly quantum mechanical treatment of the light field, it does enable the determination of the photon number, and therefore can serve as a very basic approximation to a quantum mechanical treatment of the light field. We have implemented TD-F-CI in the TeraChem software package, where 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. proper treatment of Rabi oscillations and systematic improvability. Our approach utilizes efficient 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. Our algorithm scales linearly with the number of photons. Rabi oscillations (Figure 2) and linear and nonlinear optical absorption spectra can be accurately computed in the TD-F-CI formalism.

Work is underway to incorporate TD-F-CI with MCDMS to enable first principles modeling of dynamics on many electronic states in the presence of a light field.

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

**Postdoc(s):** Dmitry A. Fedorov

**Student(s):** Andrew Durden, Dylan Hardwick, Fangchun Liang

## Electrode materials for electrochemical desalination of water

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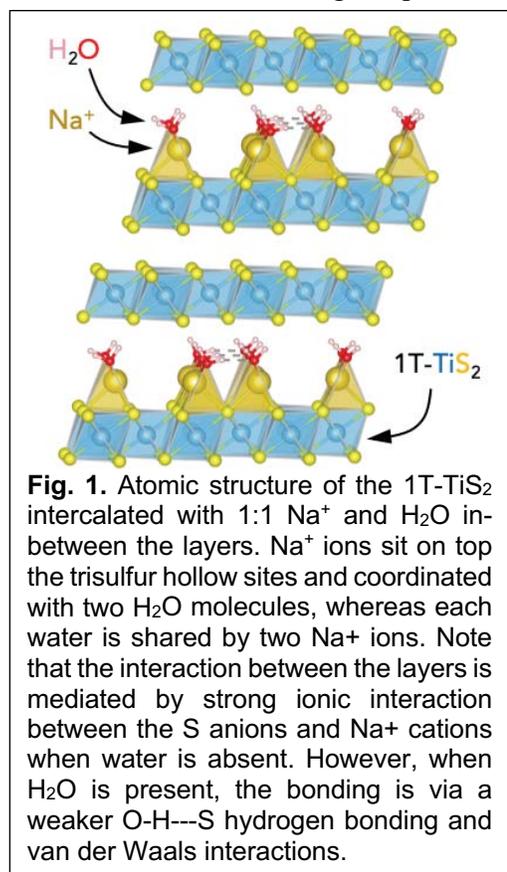
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**Carter** (Princeton/UCLA) aims to explore new or improve existing materials for their use as capacitive deionization (CDI) electrodes for water desalination. The target material under consideration is the layered 1T phase of  $\text{TiS}_2$  (1T- $\text{TiS}_2$ ) due to its high theoretical capacity as a supercapacitor, where ion intercalation/de-intercalation takes place during charge/discharge cycles. To gain a clear understanding of the mechanisms involved in ion intercalation into the 1T- $\text{TiS}_2$  interlayers, we systematically investigated the stacking patterns, ion intercalation sites, convex hull of  $\text{M}_x\text{TiS}_2$  ( $\text{M}$  = intercalated ion, currently Na), and lattice deformation during the intercalation process. These simulations were performed at the atomic scale using DFT-PBE-D3 theory. The calculated interlayer spacing patterns during sodium ion intercalation agree quite well with XRD measurements. In addition, the calculated C-V curve for  $\text{Na}_x\text{TiS}_2$  exhibits three major plateaus, which coincide with measured values. Further, we predict that the measured lower capacity of  $\text{TiS}_2$  in aqueous environments ( $\sim 70$  mAh/g vs.  $\sim 240$  mAh/g dry) originates from the weaker interlayer interactions after  $\sim 33\%$  intercalation of  $\text{Na}^+\text{-H}_2\text{O}$  pairs, which is detrimental to the mechanical stability of the layered material. **Fig. 1** shows the 1T- $\text{TiS}_2$  structure with 33% ( $\text{Na}+\text{H}_2\text{O}$ ) intercalation (to be submitted).

We are commencing application of deep learning techniques to speed up materials screening for new layered materials as potential CDI electrodes. **Carter** and **Car** (Princeton) will collaborate to predict complex properties such as (1) maximum theoretical capacity; (2) battery-like charge profile; (3) mechanical stability; and (4) activation energy of ion diffusion within the interlayers, using atomic and electronic information calculated from DFT simulations.

**Carter** and **Selloni** (Princeton) together are conducting accurate simulations of water photo-oxidation on hematite ( $\text{Fe}_2\text{O}_3$ ). Hematite is a well-studied, inexpensive photoanode for water splitting with high predicted intrinsic activity that unfortunately suffers from short charge carrier lifetimes. *Ab initio* molecular dynamics trajectories performed by **Selloni** will characterize the aqueous interfaces of pure and hole-doped hematite at the level of hybrid DFT. These trajectories will elucidate the electronic and structural effects localized excitons may have on catalytic surface chemistries that follow photoexcitation. From the representative



**Fig. 1.** Atomic structure of the 1T- $\text{TiS}_2$  intercalated with 1:1  $\text{Na}^+$  and  $\text{H}_2\text{O}$  in-between the layers.  $\text{Na}^+$  ions sit on top the trisulfur hollow sites and coordinated with two  $\text{H}_2\text{O}$  molecules, whereas each water is shared by two  $\text{Na}^+$  ions. Note that the interaction between the layers is mediated by strong ionic interaction between the S anions and  $\text{Na}^+$  cations when water is absent. However, when  $\text{H}_2\text{O}$  is present, the bonding is via a weaker  $\text{O-H}\cdots\text{S}$  hydrogen bonding and van der Waals interactions.

trajectories and associated structures found by **Selloni, Carter** will perform accurate embedded multiconfigurational correlated wavefunction (CW) calculations to account explicitly for the influence of an electron hole and excited electronic states in the reaction energetics of the water oxidation reaction. This will be achieved using the newly developed capped density functional embedding theory (capped-DFET). Capped-DFET allows for the partitioning of covalent and ionic systems into fragments, and evaluation of the fragments' interaction via DFT. Smaller fragments containing the active site therefore may be described using CW, while also incorporating environmental effects through a quantum-mechanically-derived embedding potential.

**Grant DE-SC001934: Chemistry in Solution and at Interfaces**

**Postdocs:** Lesheng Li

# Modeling L<sub>2,3</sub>-Edge X-ray Absorption Spectroscopy with Linear Response Relativistic Time-Dependent Density Functional Theory

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## Abstract

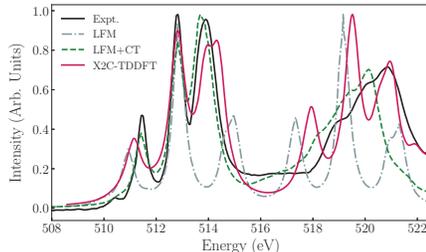
X-ray absorption spectroscopy (XAS) is an important tool that can give insight into local molecular geometry and electronic structure through the excitation of core electrons in molecular compounds. Advances in synchrotron technology with greatly improved temporal and spectroscopic resolution have made XAS a powerful tool for investigating the electronic and nuclear structure of molecules and condensed matter.

Relativistic effects are important to properly describe X-ray absorption because core electrons move at a significant percentage of the speed of light, causing core orbitals to contract and lower their energy. For K-edge XAS (excitations from the 1s core level), not accounting for relativity in *ab initio* calculations uniformly red-shifts the spectra compared to experiment. However, the relative peaks in the spectrum remain similar, so the overall characterization of K-edge spectra is commonly treated by using a non-relativistic Hamiltonian and uniformly shifting the computed spectrum.

This is not the case for L-edge spectra, where the core orbitals that are being excited are in principal quantum number  $n = 2$ . Like K-edge XAS, L-edge XAS is also element specific, but L-edge spectra have finer line-widths due to longer core-hole lifetimes. The finer line width allows for a higher sensitivity of element specific characterization, making L-edge XAS a unique probe of molecular properties. Transition probabilities for L-edge spectra are electric dipole-allowed, so issues with origin-dependence need not be considered in computations. In L-edge XAS, the 2s and 2p orbitals are not only contracted by relativistic effects, but the 2p orbitals are split in energy by spin-orbit coupling into 2p<sub>1/2</sub> and 2p<sub>3/2</sub> sets, denoted as the L<sub>2</sub> and L<sub>3</sub> edge in XAS respectively.

We have recently developed a linear response time-dependent density functional theory (TDDFT) in the relativistic Dirac equation for studies of X-ray spectroscopy. The new formalism of torque-conserving relativistic exchange-correlation functional is developed in the non-collinear two-component framework. The exact-two-component (X2C) transformation technique is used to construct an effective two-component relativistic Hamiltonian. The X2C-TDDFT approach uses the hybrid GPLHR-Davidson diagonalization method for the computation of  $L_{2,3}$ -edge spectra. Several different density functionals and basis sets are used in the benchmarking and comparison. While X2C-TDDFT cannot model satellite “shake-up” peaks due to their doubly excited character, it accurately captures the single excitation features and the energetic splitting of the  $L_2$  and  $L_3$  peaks. Figure 1 shows the experimental and computed L-edge spectra using the ligand field multiplet (LFM) method, LFM with additional doubly excited configurations (LFM-CT), and X2C-TDDFT for  $\text{VOCl}_3$ . Without any parametrization for spectral splitting or perturbative spin-orbit treatment, results from X2C-TDDFT, being a low-cost single reference one-electron excitation approach, are in satisfactory agreement with the experiment. However, shake-up or satellite peaks are missing in the linear response X2C-TDDFT results. These spectral features require a computational method be able to resolve doubly-excited character in the underlying electronic structure framework.

We find that the choice of basis set does not have a strong effect on the qualitative character of computed spectra, though a reasonable quantitative improvement is seen from using a triple- $\zeta$  rather than double- $\zeta$  basis. By contrast, the effect of the choice of exchange-correlation functional has a much stronger effect. Among standard GGAs and hybrid functionals such as B3LYP or PBE0, there was no significant difference, with each performing well in these data. Using range-corrected functionals had only marginal impact on overall quality, with HSE06 slightly less accurate than PBE0, and CAM-B3LYP slightly better than B3LYP. From our test set of metal-centered compounds, the combination of CAM-B3LYP and a relativistically optimized triple- $\zeta$  basis set gives us the best result for predicting L-edge spectra.



**Figure 1.** Experimental and computed L-edge absorption spectra comparing different computational methods for  $\text{VOCl}_3$ . The LFM and LFM+CT spectra use configuration interaction with a relativistic DFT reference, and each theoretical spectra was uniform shifted, and normalized to match the experimental peak at 513 eV. The X2C-TDDFT spectrum is from the PI’s work.

**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) variational relativistic TDDFT method to compute  $L_{2,3}$ -edge X-ray absorption spectrum; (2) variational approach to treat the effects of magnetic fields in response theory to compute magneto-optical spectra; (3) variational relativistic approach to compute intersystem crossing dynamics driven by spin-orbit couplings; (4) variational relativistic Kramers unrestricted complete-active-space self-consistent field approach.

New methods, algorithms, and research findings were published in peer-reviewed journals. The PI has presented 22 seminars at universities and invited talks in national and international conferences, including the American Chemical Society (ACS) National Conference, the International Society for Theoretical Chemical Physics (ISTCP), Telluride Scientific Research Conference (TSRC), *ect.*. 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 investigate new methodologies that can resolve "shake-up" peaks in X-ray spectroscopies.

**Postdoc(s):** Tianyuan Zhang

**Student(s):** Shichao Sun, Laurence Giordano

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

- (1) Kasper, J. M.; Gamelin, D. R.; Li, X. Theoretical Investigation of Quantum Confinement on the Rashba Effect in ZnO Semiconductor Nanocrystals. *J. Chem. Phys.* **2020**, *152*, 014308.
- (2) Koulias, L. N.; Williams-Young, D. B.; Nascimento, D. R.; DePrince, A. E.; Li, X. Relativistic Time-Dependent Equation-of-Motion Coupled-Cluster. *J. Chem. Theory Comput.* **2019**, *15*, 6617–6624.
- (3) Valentine, A. J. S.; Radler, J. J.; Castellano, F. N.; Chen, L. X.; Li, X. Resolving the Ultrafast Intersystem Crossing in a Bimetallic Platinum Complex. *J. Chem. Phys.* **2019**, *151*, 114303.
- (4) Valentine, A. J. S.; Li, X. Toward the Evaluation of Intersystem Crossing Rates with Variational Relativistic Methods. *J. Chem. Phys.* **2019**, *151*, 084107.
- (5) Williams-Young, D. B.; Petrone, A.; Sun, S.; Stetina, T. F.; Lestranger, P.; Hoyer, C. E.; Nascimento, D. R.; Koulias, L.; Wildman, A.; Kasper, J.; Goings, J. J.; Ding, F.; DePrince III, A. E.; Valeev, E. F.; Li, X. The Chronus Quantum (ChronusQ) Software Package. *WIREs Comput. Mol. Sci.* **2019**, e1436.
- (6) Stetina, T.; Sun, S.; Williams-Yong, D. B.; Li, X. Modeling Magneto-Photoabsorption Using Time-Dependent Complex Generalized Hartree-Fock. *ChemPhotoChem* **2019**, *3*, 739–746.
- (7) Stetina, T. F.; Kasper, J. M.; Li, X. Modeling L<sub>2,3</sub>-Edge X-ray Absorption Spectroscopy with Linear Response Exact Two-Component Relativistic Time-Dependent Density Functional Theory. *J. Chem. Phys.* **2019**, *150*, 234103.
- (8) Senanayake, R. D.; Lingerfelt, D. B.; Kuda-Singappulige, G. U.; Li, X.; Aikens, C. M. Real-Time TDDFT Investigation of Optical Absorption in Gold Nanowires. *J. Phys. Chem. C* **2019**, *123*, 14734–14745.
- (9) Jenkins, A. J.; Liu, H.; Kasper, J. M.; Frisch, M. J.; Li, X. Variational Relativistic Complete Active Space Self-Consistent Field Method. *J. Chem. Theory Comput.* **2019**, *15*, 2974–2982.
- (10) Hoyer, C. E.; Williams-Young, D. B.; Huang, C.; Li, X. Embedding Non-Collinear Two-Component Electronic Structure in a Collinear Quantum Environment. *J. Chem. Phys.* **2019**, *150*, 174114.

## Electron-Ion Dynamics with Time-Dependent Density Functional Theory

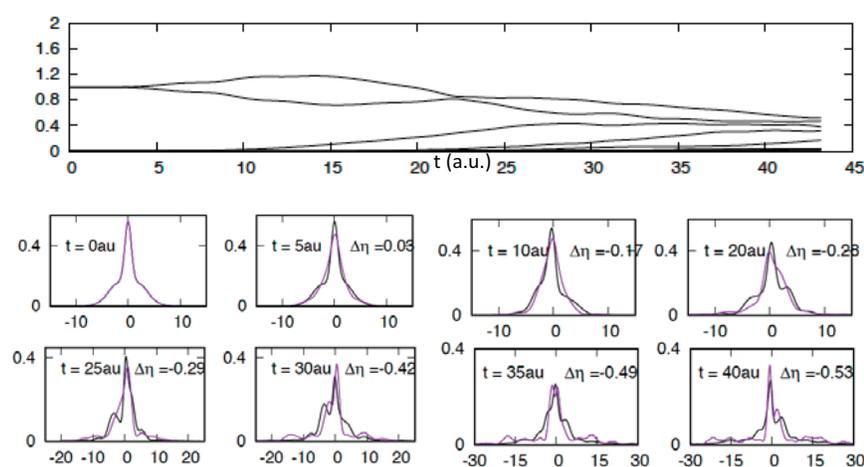
Lionel Lacombe and Neepa T. Maitra<sup>1</sup>

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### Abstract

This project focusses on two aspects of computational modeling with a view toward application for photovoltaic design: (i) increased reliability of exchange-correlation (xc) functionals in TDDFT especially for time-resolved dynamics, and (ii) the development of a practical but soundly-based method for coupling electronic and nuclear motion via the exact-factorization (EF) approach.

In (i), we have been developing approaches to go beyond the adiabatic approximation in TDDFT, since this has been shown to be responsible for inaccurate predictions of dynamics. A density-matrix coupled approach was introduced which appeared promising in that it reproduced some non-adiabatic structures however the propagation was too unstable to be practical. Aside from looking into ways to fix this, we are also exploring a different approach based on an extension of the coupling-constant integration idea to the time-domain. Yet, in some cases, the adiabatic approximation has turned out to work quite well, and an important question is then, can we characterize problems for which the adiabatic approximations are expected to work well and those for which it works badly? An exact expression suggests that the answer may lie in how far the natural orbital occupation numbers of a system deviate from their initial values: if not much, then, provided the Kohn-Sham initial state is chosen with a similar configuration as the physical initial state, and provided that the dynamics is not driven by resonant frequencies of the system, then the adiabatic approximations then could work qualitatively well. An illustration of this is in the Figure,



*Top panel:* Natural orbital occupation numbers for a laser driven excited 1D He atom.

*Lower panel:* Despite starting far from a ground-state, the adiabatic approximation ALDA (purple; exact is black) predicts relatively accurate density-dynamics if local details are averaged over, until the largest deviation of occupation number (indicated in the panels as  $\Delta\eta$ ) gets larger than about 0.4. The Kohn-Sham initial state must be chosen with similar initial occupation numbers to the exact; otherwise ALDA dynamics is much poorer.

which shows the density of an initially excited 1D He atom model subject to a non-resonant driving field. The system starts far from a ground-state, and there is considerable dynamics, yet until the deviations of the initial physical natural occupation numbers becomes larger than about 0.4, ALDA captures the

dynamics quite well. It misses the structures such as the shoulders in the density, but locally averages over them quite well, until times at which the occupation number deviation becomes too large.

In (ii), the EF provides a rigorous starting point for mixed quantum-classical approximations, and we are building on our earlier work of investigating coupled-trajectory schemes developed in this way. We are testing the performance of a surface-hopping scheme with decoherence corrections that directly arise from EF (synergistic with the participation of our group in the “Chemistry for Solutions and Interfaces” DOE Center Grant), analyzing the impact of the different decoherence approach on the resulting dynamics. We also will be looking into methods that utilize more directly the single-surface nature of the time-dependent constructs that arise out of the EF, to derive schemes that do not depend on an expansion in Born-Oppenheimer states.

Returning to the purely electronic problem, the EF approach suggested a new way to treat strongly-correlated systems within an embedding via the exact factorization (EVEF) that postdoc Lionel Lacombe has been developing. The factorization is extended to Fock space, and allows an accurate treatment of selected orbitals (most naturally chosen to be strongly correlated ones) interacting with the others with an embedding Hamiltonian arising from EF. Results on Hubbard model systems are promising.

## **DE-SC0020044, Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling**

**Postdoc(s):** Lionel Lacombe

### **Up to Ten Publications Acknowledging this Grant in the last 3-4 years**

1. Embedding via the Exact Factorization Approach, L. Lacombe and N. T. Maitra, to appear in Physical Review Letters (2020)

# Exact-Factorization Based Surface-Hopping for Non-Adiabatic Dynamics

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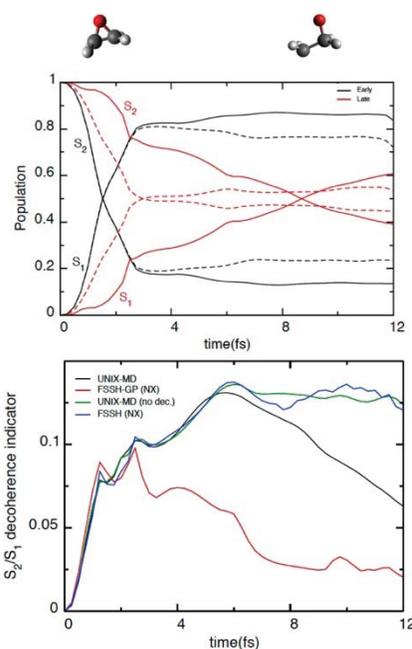
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## Abstract

We have been applying a recently proposed surface-hopping method derived from the exact factorization (EF) approach to photo-induced coupled electron-ion dynamics. This approach includes decoherence corrections derived from the formally-exact EF approach; such corrections correctly describe the correlation of the electronic system with the associated nuclear trajectory in mixed quantum-classical approaches. We find differences from the traditional surface-hopping methods in which decoherence corrections are added by hand to collapse the coefficients on one state or another after a region of non-adiabatic coupling. For example, the EF-based decoherence tends to occur over longer time-scales and this affects the ensuing dynamics of the trajectories. An example is shown in the figure, which studies the ring-opening mechanism in oxirane, that follows a photo-excitation to the  $S_2$  state. The EF-based surface-hopping has been implemented with the CASSCF utility of the Molpro code, by Seung-Kyu Min and Jong-Kwon Ha and their group at UNIST. The figure shows that neglecting decoherence (dashed curves) yields significantly different electronic population dynamics on the  $S_2$  and  $S_1$  surfaces compared to the EF-based method (solid curves), particularly for trajectories arriving at the conical intersection later (red curves). The EF-based decoherence corrections yields somewhat different results than the traditional Granucci-Persico (GP) one, affecting the time scales; for example, as shown by the decoherence indicator shown in the lower plot, with UNIX-MD labelling the new EF-based method. A comparison with more accurate quantum dynamics methods such as ab initio multiple spawning (AIMS) and multi-configuration time-dependent Hartree (MCTDH) will help to characterize the performance of this new method in the future. Studies of dynamics of the uracil cation are underway to compare with the already available MCTDH data, and we will then apply this to study charge-transfer within DNA, and relaxation dynamics and lifetimes of a hydrated electron, and eventually interactions of an electron with DNA bases in solution.



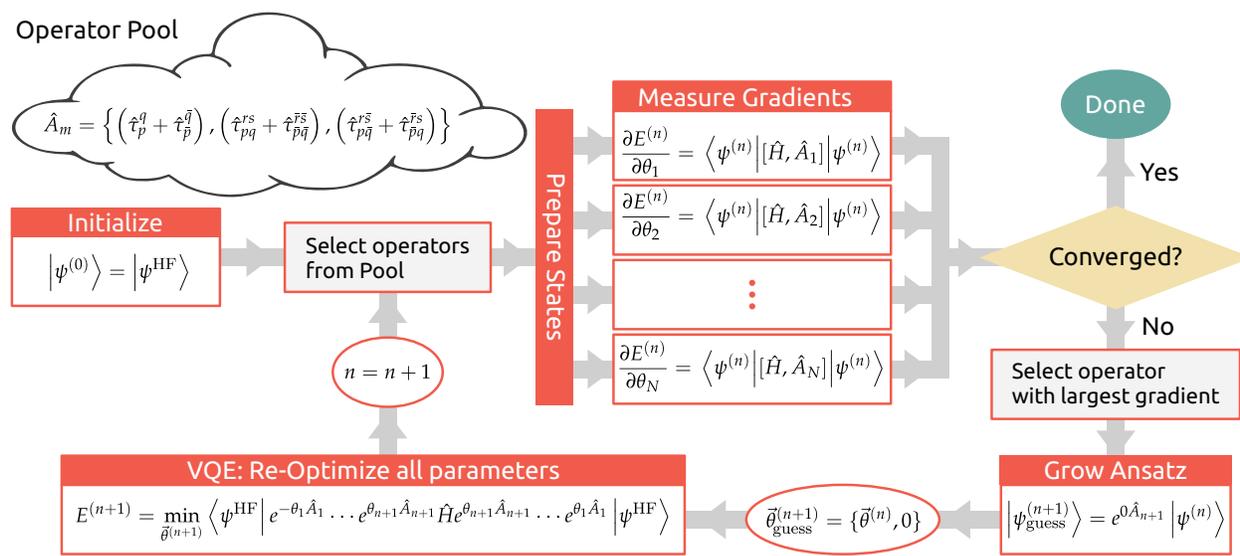
**DE-SC0019394, Chemistry at Solutions and Interfaces, CCS Center Grant**

**Postdoc(s):** Patricia Vindel Zandbergen

## Simulating strongly correlated molecules with a superconducting quantum processor

Nicholas J. Mayhall, Sophia Economou, Edwin Barnes, David Pappas

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 an alternative potential 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 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 computed on customized quantum hardware. Our focus is on reducing quantum resources (namely coherence times) while maintaining sufficient accuracy to resolve the chemical questions associated with the target strongly correlated systems. An early development on this project has been the development of an adaptive variational algorithm, ADAPT-VQE (*Nat. Comms.* 10, 3007, 2019), which is both parameter efficient and avoids the accuracy problems associated with a fixed ansatz, and which has recently been extended to also improve gate efficiency in the (qubit-ADAPT) algorithm (<https://arxiv.org/abs/1911.10205>).



# Elucidating Energy Storage Mechanisms in Carbon-based Supercapacitors

Yi-Jung Tu<sup>1</sup>, Suehyun Park<sup>1</sup>, Samuel Delmerico<sup>1</sup>, and Jesse G. McDaniel<sup>1</sup>

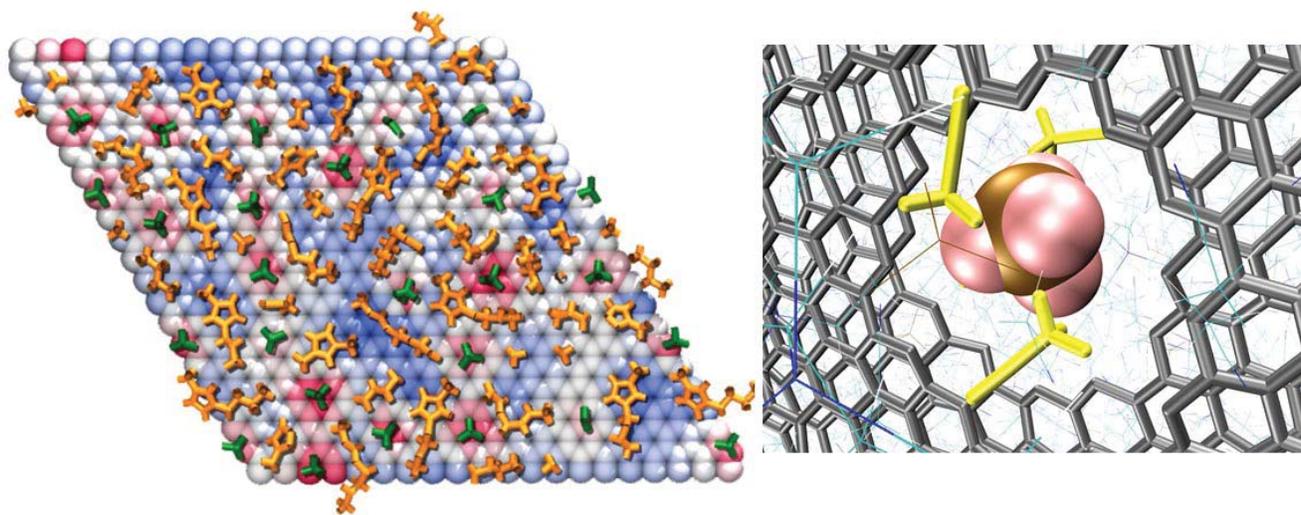
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Supercapacitors (SCs) complement batteries as an essential energy storage technology, being unique in their exceptionally high power output and fast charging times. Recent progress for increasing the energy density of SCs has been enabled by utilizing highly nanoporous carbon electrode materials and/or introducing Faradaic or redox-active components to create hybrid/pseudo-capacitor devices. Incorporating both of these design paradigms in a synergistic manner can often be difficult, however, requiring a detailed understanding of the complex electrode/electrolyte chemistry and physics at the nanoscale. Our research program focuses on developing and applying novel theoretical/computational techniques to elucidate the coupling of redox chemistry and electrolyte double layer physics in nanoscale supercapacitor devices.

We have made progress in understanding mechanisms dictating the energy storage of electrical double layer (EDL), carbon-based supercapacitors. This has been enabled by the development of new computational algorithms and software implementation to enable significant performance improvements of high-accuracy computer simulations for predicting properties such as capacitance and kinetic barriers of these systems. Specifically, we have developed a novel, constant-voltage molecular dynamics (MD) algorithm that is implemented in the GPU-accelerated OpenMM software allowing for significantly enhanced statistical sampling with fully-atomistic and polarizable electrolyte force fields.<sup>1</sup> We utilized these simulations to predict both capacitance and free energy barriers for ion diffusion through sub-nanometer pores in carbon electrodes, to identify tradeoffs between optimizing energy density and power output of such devices.<sup>2</sup> Figure 1 shows representative images for these types of computer simulation predictions. Continuing work in our group will generalize these methods to investigate more complex electrode architectures, and couple with novel biased-sampling approaches to predict phase transitions and redox processes within the EDL.



**Figure 1. Energy storage mechanisms in carbon supercapacitors, depicting voltage-modulated electrostatic ion-adsorption on cathode surface (Left),<sup>1</sup> and ion diffusion through sub-nanometer pores in carbon electrodes (Right).<sup>2</sup>**

Our computer simulations have benchmarked the validity of existing theories/models of EDL capacitance. The EDL is generally composed of several different layers of solvent molecules/ions, and the “inner-layer” or region very close to the electrode interface largely dictates the resulting energy storage of a double-layer capacitor. From extensive characterization of numerous organic solvents and organic electrolytes, we found the important result that the inner-layer capacitance of graphite electrodes was surprisingly similar for many of these different electrolyte compositions. We rationalized such behavior in terms of strong hydrophobic interactions between aliphatic functional groups of electrolyte molecules and the carbon electrode surface, and found that such hydrophobic interactions were similar across systems.<sup>1</sup> This indicates that even at high voltages and in the presence of strong electrostatic interactions, hydrophobic forces can significantly affect system properties and must be considered for optimizing supercapacitor design. Another important conclusion from our simulations is that Gouy-Chapman-Stern (GCS) theory, which is often utilized for predicting/interpreting double layer capacitance, qualitatively fails to describe the organic electrolytes utilized within supercapacitors. Specifically, our simulations predict both voltage and concentration invariant differential capacitance, contradicting GCS theory.<sup>1</sup> This motivates further exploration to develop a more accurate and general theory for the EDL physics within organic electrolyte supercapacitors.

State-of-the-art supercapacitor electrodes often consist of highly nanoporous carbon materials such as activated carbon or carbide-derived carbon. Adsorbed electrolyte ions within these electrode materials are subject to a high degree of nanoconfinement that can significantly alter their physical properties and the resulting device performance. We have combined statistical mechanical theory with high-performance computer simulations to investigate the modulation of electrical double layer properties within highly nanoconfined carbon electrodes.<sup>3</sup> We have predicted an anomalous kinetic effect in which ion dynamics and diffusion rates exhibit a local maximum at several nanometer confinement distances for ionic liquid electrolytes. Utilizing statistical mechanical linear-response theory, we rationalized this behavior in terms of electrostatic screening and ion correlation lengthscales within the EDL.<sup>3</sup> We demonstrated that the EDL susceptibility and ion correlation increase non-monotonically as confinement constraints are relaxed, causing variation in ion dynamics. This trend results from interference between opposite double layers as the confinement distance becomes smaller than the intrinsic electrostatic screening lengthscale of the electrolyte. These simulations were unique and novel in that microsecond timescales were achieved for fully polarizable, atomistic electrolyte force fields coupled with constant voltage MD, rendering a high-fidelity comparison of theory and simulation.

Future direction of our research program will center on the following thrusts: First, we will generalize our constant voltage MD algorithm to enable capacitance predictions for more complex carbon electrode architectures. Focus will be on highly efficient implementation within GPU codes to allow long simulation timescales utilizing accurate atomistic and polarizable electrolyte force fields. We will utilize this novel software to investigate voltage-modulated phase transitions of electrical double layers, with important implications for both device capacitance as well as redox chemistry. By combining our algorithms with novel biased-sampling approaches that rely on utilizing ion structure factors as collective variables, we will predict free energies of EDL phases as a function of applied voltage; these predictions will be compared/benchmarked to previously published AFM/STM measurements. We will also begin work on the second major component of our research, which is investigating how redox chemistry is altered by the strong electrostatic interactions within electrical double layers. We will investigate redox functionalization of electrode surfaces and incorporation of redox-active molecules as

electrolyte additives. Such “hybrid” or “pseudo” capacitors are an extremely promising direction for enhancing net energy storage in these devices. We will develop new Monte Carlo and free-energy methods to calculate standard-state redox potentials for different electrolyte composition within complex electrode architectures. The goal will be to elucidate how redox activity and double layer physics are correlated under applied voltages. Such insight will provide essential design criteria for developing the next-generation of hybrid supercapacitor devices.

**Grant Numbers and Grant Titles: DE-SC0020279** “Theoretical Characterization of Correlated Redox Activity and Nanostructure in Hybrid Supercapacitors”

**Postdoc(s):** Dr. Yi-Jung Tu

**Student(s):** Suehyun Park, Samuel Delmerico

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

1. Y.-J. Tu, Delmerico, S., and McDaniel, J.G., “Inner Layer Capacitance of Organic Electrolytes from Constant Voltage Molecular Dynamics”, *J. Phys. Chem. C*, 124, 2907-2922, **2020**
2. S. Delmerico and McDaniel, J.G., “Free Energy Barriers for TMEA<sup>+</sup>, TMA<sup>+</sup>, and BF<sub>4</sub><sup>-</sup> Ion Diffusion through Nanoporous Carbon Electrodes”, *Carbon*, 161, 550-561, **2020**
3. S. Park and McDaniel, J.G., “Interference of Electrical Double Layers: Confinement Effects on Structure, Dynamics, and Screening of Ionic Liquids”, *J. Chem. Phys.*, 152, 074709, **2020**

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

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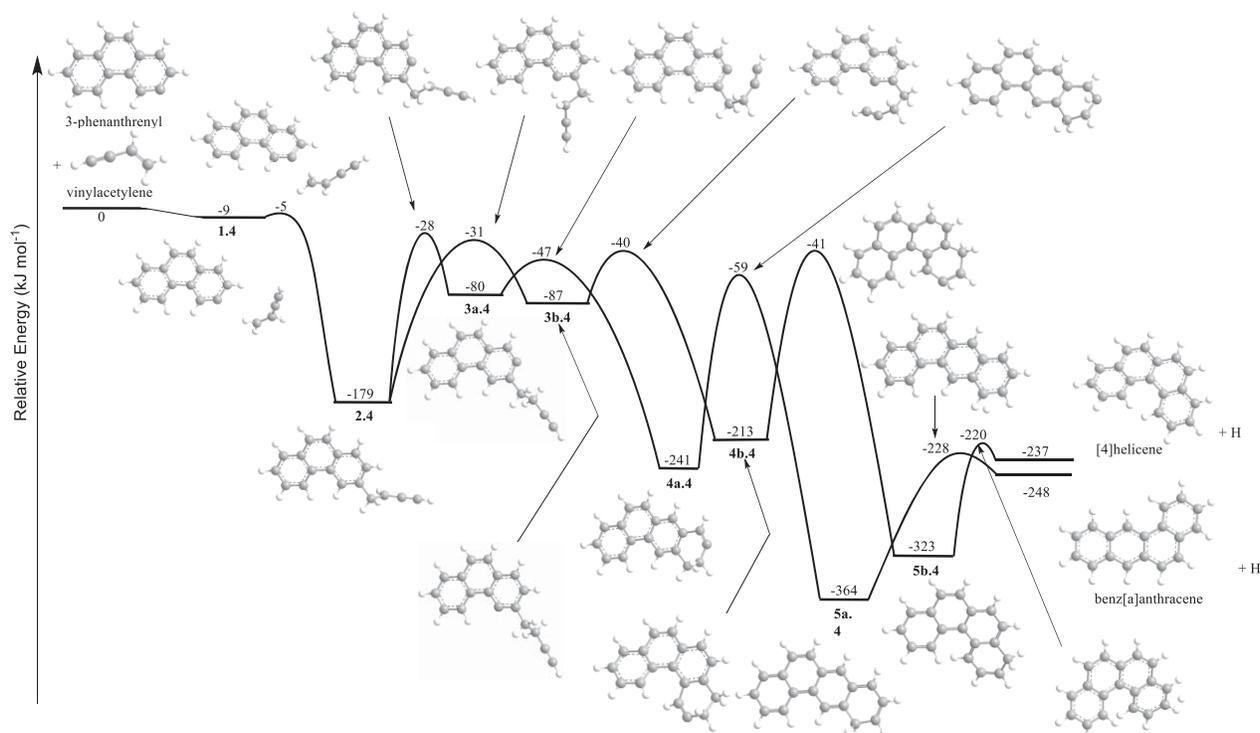
### Program Scope

In this project, we investigate complex chemical mechanisms of PAH formation, growth, and oxidation via theoretical studies of their critical elementary reactions. Our primary objectives include (i) to unravel reaction mechanisms through detailed, accurate, and reliable calculations of pertinent potential energy surfaces (PESs); (ii) to compute rate constants for individual reaction steps and total absolute reaction rate constants and product branching ratios depending on reaction conditions, such as collision energy or temperature and pressure; (iii) to characterize molecular, energetic, and spectroscopic parameters of various possible reaction intermediates and products including their enthalpies of formation, geometric structure, vibrational frequencies and rotational constants, as well as photoionization and photoexcitation spectra. To achieve these goals, we employ chemically accurate density functional and ab initio calculations (using CCSD(T)/CBS, G3, and explicitly correlated methods) of the PESs of these reactions 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 2019, we continued investigating potential energy surfaces, reaction mechanisms, and kinetics for the reactions of PAH growth via the HAVA (Hydrogen-Abstraction-Vinylacetylene-Addition) and  $C_3H_4$  addition mechanisms, considering in particular larger PAHs with 3-5 aromatic rings. For instance, based on our electronic structure calculations combined with experimental studies in a high-temperature micro reactor (HTMR) with product detection using photoionization mass spectrometry (PIMS) carried out by R. I. Kaiser's and Musahid Ahmed's groups at the University of Hawaii and LBNL, respectively, we proposed a unified reaction mechanism for the formation of acenes, phenacenes, and helicenes – PAHs that are distinct via the linear, zig-zag, and ortho-condensed arrangements of fused benzene rings. This mechanism is facilitated through a barrierless, vinylacetylene mediated gas phase chemistry utilizing tetracene, [4]phenacene, and [4]helicene as benchmarks contesting established paradigms that molecular mass growth processes to PAHs transpire at elevated temperatures. This mechanism opens up an isomer-selective route to aromatic structures involving submerged reaction barriers, resonantly stabilized free radical intermediates, and systematic ring annulation potentially yielding molecular wires along with racemic mixtures of helicenes in deep space. Recently, we have shown that this mechanism is also operational for the formation of pentacene from a tetracenyl radical. An example of the calculated PES for the formation of four-ring PAHs [4]helicene and benz[a]anthracene from the 3-phenanthrenyl radical is illustrated in Figure 1.

By investigating the reactions of 2- and 1-naphthyl radicals with the  $C_3H_4$  isomers, allene and methylacetylene, we established a mechanism of a five-member ring addition to PAHs. Our ab initio and RRKM-ME calculations carried out in parallel with the HTMR-PIMS experiments



**Figure 1.** Calculated PES of the 3-phenanthrenyl + vinylacetylene reaction leading to the formation of benz[*a*]anthracene and [4]helicene. Relative energies with respect to the reactants are given in  $\text{kJ mol}^{-1}$ .

reveal critical mass growth processes via annulation of a five-member ring from the reaction between aryl radicals and distinct  $\text{C}_3\text{H}_4$  isomers at elevated temperatures as present in combustion processes and in circumstellar envelopes of carbon stars. The underlying reaction mechanisms proceed through the initial addition of the 2-naphthyl radical with its radical center to the  $\pi$ -electron density of the allene and methylacetylene reactants via entrance barriers between 8 and  $14 \text{ kJ mol}^{-1}$ , followed by isomerization (hydrogen shifts, ring closure), and termination via atomic hydrogen losses accompanied by aromatization and the formation of benzindenes. The reaction mechanisms reflect the formation of indene – the prototype PAH carrying a single five- and a single six-member ring – synthesized through the reaction of the phenyl radical  $\text{C}_6\text{H}_5$  with allene and methylacetylene. This led us to predict that aryl radicals – upon reaction with allene/methylacetylene – may undergo molecular mass growth processes via ring annulation and de-facto addition of a five-member ring to form molecular building blocks essential to transit planar PAHs out of the plane. Alternatively, by exploring the reaction of the 1-naphthyl radical with the  $\text{C}_3\text{H}_4$  isomers under conditions prevalent in carbon-rich circumstellar environments and combustion systems, we discovered a facile formation of, in addition to benzindenes, 1H-phenalene ( $\text{C}_{13}\text{H}_{10}$ ) – the prototype of a  $12\pi$  non-benzoid PAH and central molecular building block of graphene-type nanostructures. Beyond PAHs, molecular mass growth processes from 1H-phenalene via ring-annulation through  $\text{C}_3$  molecular building blocks may ultimately lead to two-dimensional structures such as graphene nano flakes and after condensation of multiple layers to graphitized carbon.

PES for the phenyl + propargyl radical recombination reaction was studied by high-level ab initio calculations and its rate constant was evaluated by combining VRC-TST and RRKM-ME

calculations. We found that, at combustion relevant conditions, the phenyl + propargyl recombination provides a feasible mechanism for the addition of a second five-member ring to the first six-member aromatic ring producing the prototype two-ring species indene and indenyl.

Ab initio and RRKM-ME calculations have been carried out to map out the  $C_9H_7O_2$  PES in relation to the reaction of 1-indenyl radical with molecular oxygen and to determine temperature- and pressure-dependent rate constants. The results demonstrated that, while the reaction is insignificant at low temperatures, above 800 K the prevailing reaction channel leads to the formation of the 1-H-inden-1-one + OH products via a 1,3-H shift from C to O in the initial association complex accompanied by OH elimination. The indenyl +  $O_2$  reaction is concluded to be too slow to play a substantial role in oxidation of the five-member ring in indenyl and the results corroborated the assertion that molecular oxygen is not an efficient oxidizer of five-member-ring radicals. Alternatively, similar calculations showed that indenyl oxidation with atomic oxygen is fast and efficient. The  $C_9H_7 + O$  reaction begins with highly exothermic barrierless addition of the oxygen atom to the radical site in the five-member ring of indenyl and then, the reaction mostly proceeds by  $\beta$ -scission in the five-member ring, which may be preceded by H migrations, and completes by the CO loss forming the highly exothermic  $C_8H_7$  radical products, *ortho*-vinyl phenyl and styrenyl. Modified Arrhenius expressions for the rate constants of all reactions on the  $C_9H_7O_2$  and  $C_9H_7O$  PESs have been generated and proposed for combustion kinetic modeling. It was concluded that the oxidation reactions of a five-member ring with atomic oxygen remain fast in the presence of attached or surrounding six-member rings.

We began a critical analysis of the mechanism of carbon particulate (soot) inception, which currently remains a hot subject of numerous studies and debates. We carried out a thorough review of the prior proposals, analyzed factors enabling the development of a meaningful nucleation flux, and then introduced new ideas that lead to the fulfillment of these requirements. In the new proposal, a rotationally-activated dimer is formed in collision of aromatic molecule and radical, the two react during the lifetime of the dimer to form a stable, doubly-bonded bridge between them, with the reaction rooted in a five-member ring present on the molecule edge. Several such reactions were examined theoretically and a most promising one generated a measurable nucleation flux. Consistency of the proposed model with known aspects of soot particle nanostructure was discussed. The foundation of the new model appeared to be fundamentally the H-Abstraction-Carbon-Addition (HACA) mechanism with the reaction affinity enhanced by rotational excitation.

### 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, as well as in soot nucleation. To accomplish this goal, in the next project period we plan to focus on the following tasks: 1) investigating the remaining prototype reactions for the formation of two- and three-ring PAHs; 2) studying the formation of larger benzenoid PAHs up to coronene via HACA and HAVA mechanisms; 3) elucidating the formation of curved 3D PAH up to coranullene; 4) studying HACA routes involving five-member rings; 5) investigating the low-temperature PAH oxidation mechanism; and 6) unraveling chemical dimerization of PAH as a critical step in soot nucleation. We will continue our close 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 high-temperature micro 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 formation, soot nucleation and growth, and oxidation. Our ongoing collaborations with other members of the DOE/BES Fundamental Interactions Programs including A. Suits, T. Zwier, S. Klippenstein, A. Jasper, W. Green, and W. Pitz will also carry on.

#### **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

**Graduate Research Assistant:** Galiya R. Galimova

**Graduate Students:** Juan Alarcon, Lotefa Binta Tuli, Galiya R. Galimova

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# Ab initio Molecular Dynamics Beyond Density Functional Theory

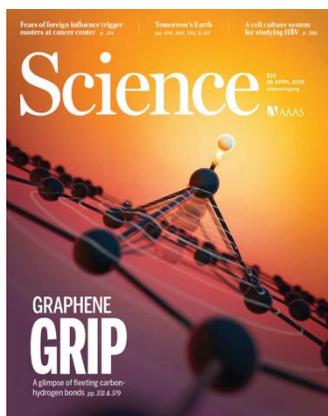
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## Abstract

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.

In the past year, 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 have distributed the program both via the cloud and JupyterHub. We have made a number of major advances in terms of efficient path-integral numerical integration and non-adiabatic dynamics [4-8], including 5 papers that have been selected as Editor's Choice or Feature Articles. We have additionally made advances in coupled-cluster embedding descriptions in the context of dynamical mean-field theory embedding [4]. 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 [5]. 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. Submitted work in this direction explores the H/D isotope effect in these systems [11].



**Figure 1. H-on-graphene scattering. EMFT simulations reveal a mechanism for extremely fast energy transfer, leading to the unexpected and experimentally confirmed stickiness of graphene to H atoms.**

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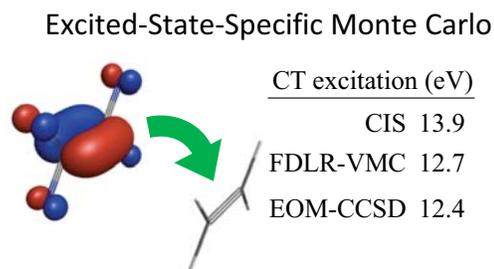
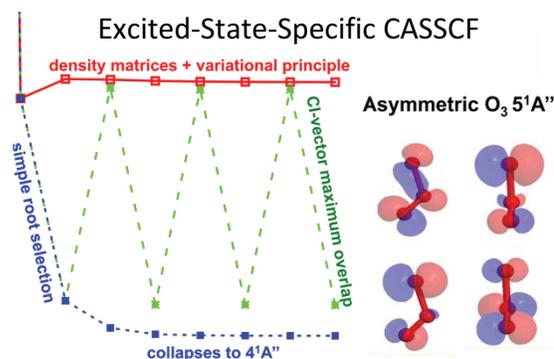
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# Variational Excited States, Quantum Monte Carlo, and Charge Transfer

Eric Neuscamman

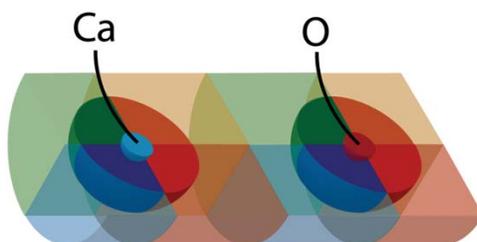
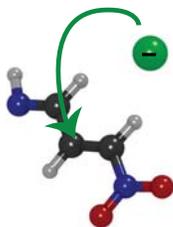
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This research program explores the intersection of variational principles for excited states, quantum Monte Carlo (QMC) methods, and charge transfer processes. While the foundations for this research lie in our DOE-funded work in the Gas Phase Chemical 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.



## 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 into 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 into 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 and Excited-State-Specific CASSCF**

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.

Excited state variational ideas have also proven useful in multi-reference quantum chemistry, where we have demonstrated their ability to enable fully excited-state-specific CASSCF. Our approach is to overcome root flipping by using an approximated excited state variational principle as the root-selector at each iteration in a two-step CASSCF optimization and to couple this with an excited-state-specific orbital optimization. We have found this approach to be more effective than both naïve root selection (which famously fails in the presence of root flipping) and a simple CASSCF adaptation of the maximum overlap method. As our approach shapes the orbitals for the purpose of individual states (rather than compromising their shapes between multiple states), early indications suggest it improves the accuracy of multi-reference perturbation theory as compared to the state-averaged starting points in common use today.

### **Grant Numbers and Grant Titles:**

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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:**

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**Next generation quantum-based molecular dynamics: simulations of reactive chemical systems**

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**Abstract**

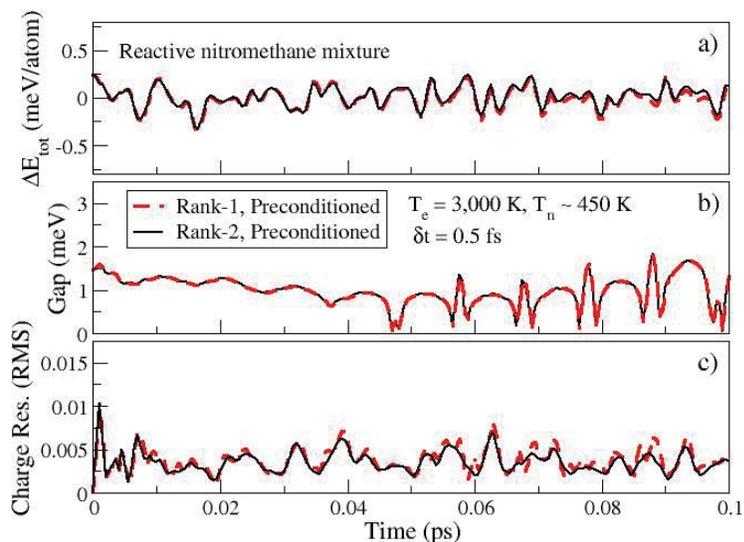
First principles, quantum-based Born-Oppenheimer molecular dynamics simulations are often painfully slow or exhibit an unphysical behavior with a systematic drift in the total energy. These problems are particularly limiting for long-term simulations of chemical systems with electronic instabilities. Extended Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD), which is being developed under current grant, is a new and general framework for quantum-based molecular dynamics simulations that tries to overcome previous shortcomings of quantum-based molecular dynamics simulations. To achieve this, it combines some of the best features of direct Born-Oppenheimer and Car-Parrinello molecular dynamics, at the same time as it tries to avoid some of their shortcomings. In particular, our new XL-BOMD simulation framework now fully avoids the non-linear eigenvalue problem and the iterative self-consistent-field optimization required prior to each force evaluation in direct Born-Oppenheimer molecular dynamics. It also avoids the tuning of material-dependent fictitious electron mass parameters and the limitation of a shorter integration time step required in Car-Parrinello molecular dynamics. XL-BOMD is particularly efficient in combination with fast linear scaling electronic structure theory, for which it is often difficult or impossible to reach a sufficiently accurate ground state optimization in a regular, direct Born-Oppenheimer molecular dynamics simulation.

A major breakthrough during the last year has been the completion of a theory for an adaptive and tunable integration of the equations of motion for the extended electronic degrees of freedom in XL-BOMD. The new technique allows fast and stable simulations even of highly unstable reactive chemical systems. This is of particular importance when we try to understand more complex systems at larger time and length scales and it makes it possible to apply XL-BOMD simulations to a much broader range of problems. The new theory is focused on a kernel that appears like a preconditioner in the electronic equations of motion. The kernel is derived from a pseudoinverse of a Jacobian of a charge residual function. This inverse Jacobian kernel determines the metric of the harmonic oscillator in the extended Lagrangian and is approximated by a low-rank expression using a set of directional derivatives that are chosen from a preconditioned Krylov subspace, which can be calculated using quantum response theory.

The new theory also provides a transparent framework to solve systems of non-linear equations when applied to Newton's method. Popular techniques such as Broyden's methods and Anderson or Pulay mixing, as well as Jacobian-free Newton-Krylov methods,

all appear naturally as particular examples from our theory. In this way our new theory also provides a complementary formulation to well-established techniques.

Our near term focus is to get the most recent simulation tools implemented in a variety of state-of-the-art quantum chemistry software packages, including graph-based electronic structure methods developed under current grant.



**Figure 1** The convergence as a function of rank- $m$  updates of various properties in XL-BOMD simulations for a reactive mixture of liquid nitromethane: a) the total energy, b) oscillations in the minute HOMO-LUMO gap, and c) the root-mean-square of the residual error in the electron charge per atom [from Refs. (2) <https://doi.org/10.1063/1.5143270>].

### LANLE8AN, “Next generation quantum-based molecular dynamics” (2016-2020)

- 1) “*DFTB+, a software package for efficient approximate density functional theory based atomistic simulations*”, Ben Hourahine, Balint Aradi, Volker Blum, Frank Bonafe, Alex Buccheri, Cristopher Camacho, Caterina Cevallos, MY Deshayé, T Dumitrică, A. Dominguez, S. Ehlert, M. Elstner, T. van der Heide, J. Hermann, S. Irle, J.J. Kranz, C. Köhler, T. Kowalczyk, T. Kubař, I.S. Lee, V. Lutsker, R.J. Maurer, S.K. Min, I. Mitchell, C.F.A. Negre, T.A. Niehaus, A.M.N. Niklasson, A.J. Page, A. Pecchia, G. Penazzi, M.P. Persson, J. Řezáč, C.G. Sánchez, M. Sternberg, M. Stöhr, F. Stuckenberg, Alexandre Tkatchenko, VW-z Yu, T. Frauenheim, *The Journal of Chemical Physics* 152 (12), 124101 (2020).
- 2) “*Extended Lagrangian Born–Oppenheimer molecular dynamics using a Krylov subspace approximation*”, A.M.N. Niklasson, *The Journal of Chemical Physics* 152 (10), 104103 (2020)

- 3) *“Using Graph Partitioning for Scalable Distributed Quantum Molecular Dynamics”*, H.N. Djidjev, G Hahn, S.M. Mniszewski, C.F.A. Negre, A.M.N. Niklasson, *Algorithms* 12 (9), 187 (2019)
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- 7) *“Next generation extended Lagrangian first principles molecular dynamics”*, A.M.N. Niklasson, *The Journal of Chemical Physics*, 157 (5), 054103 (2017)
- 8) *“Accurate Classical Polarization Solution with No Self-Consistent Field Iterations”*, A. Albaugh, A.M.N. Niklasson, and T. Head-Gordon, *The Journal of Physical Chemistry Letters*, 8, 1714 (2017)
- 9) *“Performance of extended Lagrangian schemes for molecular dynamics simulations with classical polarizable force fields and density functional theory”*, V. Vitale, J. Dziedzic, A. Albaugh, A.M.N. Niklasson, T. Head-Gordon, and C-K Skylaris, *The Journal of Chemical Physics*, 146, 124115 (2017)
- 10) *“Recursive Factorization of the Inverse Overlap Matrix in Linear-Scaling Quantum Molecular Dynamics Simulations”*, C.F.A. Negre, S.M. Mniszewski, M.J. Cawkwell, N. Bock, M.E. Wall, A.M.N. Niklasson, *The Journal of chemical theory and computation* 12 (7), 3063-3073 (2016)
- 11) *“Graph-based linear scaling electronic structure theory”*, A.M.N. Niklasson, S.M. Mniszewski, C.F.A. Negre, M.J. Cawkwell, P.J. Swart, J. Mohd-Yusof, T.C. Germann, M.E. Wall, N. Bock, E.H. Rubensson, H. Djidjev, *The Journal of Chemical Physics* 144 (23), 234101 (2016) [Editor’s choice 2016 article]

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

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## 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  $3d$  transition metal monoxide and dioxide clusters, small-to-medium size anionic clusters of the form  $M_xO_y^-$  with  $M = \text{Cu, V, and Cr}$  containing up to  $\sim 25$  atoms, and bulk-truncated  $\text{Cu}_2\text{O}$  and  $\text{Ag}_2\text{O}$  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.

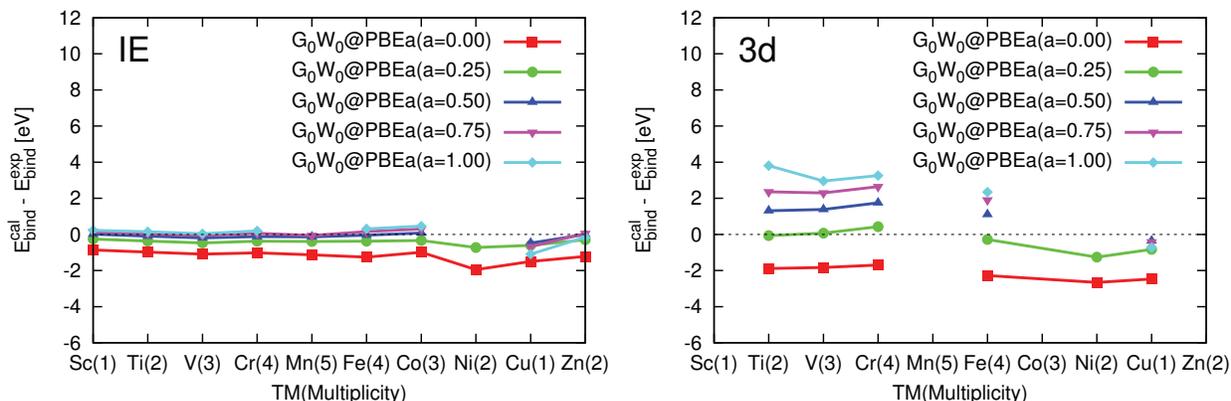
## RECENT PROGRESS

### *Electronic Structure of 3d-Transition Metal Monoxide Anions*

We have computed the quasiparticle spectra of  $3d$ -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). For hybrid functional starting points, we used the functional

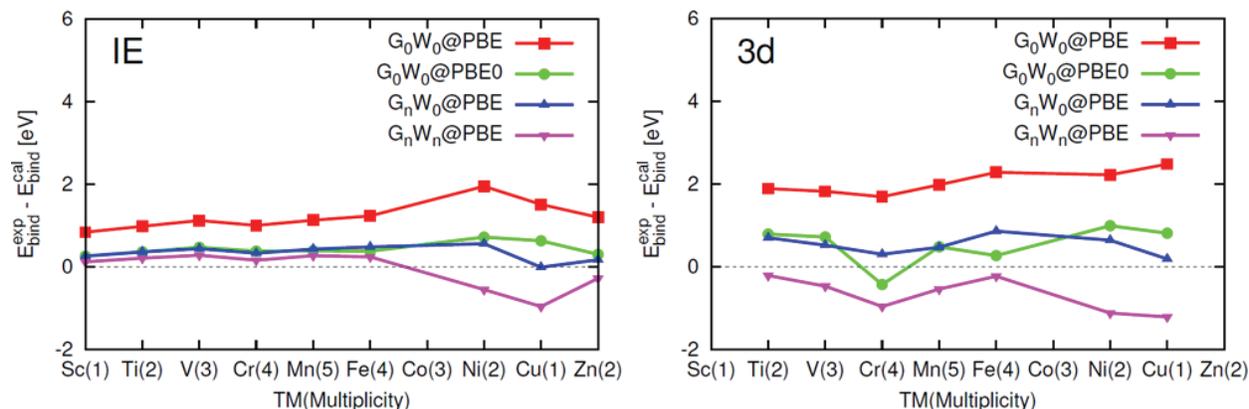
$$E_{xc}^{PBEa} = aE_x^{HF} + (1 - a)E_x^{PBE} + E_c^{PBE}$$

where  $a$  denotes the amount of exact exchange. The results for first ionization energy (IE) and lowest  $3d$  binding energies (corresponding to the orbital with 100%  $3d$  character) for all TMO anions are plotted in Fig. 1 for values of  $a$  ranging from 0 (PBE functional) to 1 (Hartree-Fock with PBE correlation). Note that the highest occupied molecular orbitals (HOMOs) of TMO anions have different strengths of TM  $3d$  character: HOMOs of  $\text{NiO}^-$  and  $\text{CuO}^-$  have moderate ( $\sim 50\%$ ), and those of other anions have weak ( $\sim 10\%$ )  $3d$  character. For IE, the results for  $G_0W_0@PBEa$  are in pretty good agreement with experimental data for all values of  $a$ , except for  $a = 0$  (which corresponds to one-shot  $GW$  calculations with a PBE starting point). For the lowest  $3d$  binding energies, on the other hand,  $a = 0.25$  (corresponding to one-shot  $GW$  calculations with a PBE0 starting point) is the only amount of exact exchange that uniformly provides very good agreement with experimental data across the  $3d$  series.



**Fig. 1:** First ionization energies (left) and lowest 3d binding energies (right) of TMO (TM = Sc, Ti, ..., Cu, Zn) anions from  $G_0W_0@PBEa$  calculations for values of  $a$  ranging from 0 to 1. 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.

Our results for IE and lowest 3d binding energies for TMO anions at the eigenvalue-only self-consistent  $GW$  level of theory (along with  $G_0W_0@PBE0$ , i.e.  $a = 0.25$ ) are plotted in Fig. 2. We observe several trends in Fig. 1. First,  $G_0W_0@PBE$  underestimates the IE by  $\sim 1$  eV and the 3d-electron BE by  $\sim 2$  eV, which is significantly more than the typical underestimation of the IE of  $sp$ -bonded molecules ( $\sim 0.5$  eV). Note that the IEs of  $NiO^-$  and  $CuO^-$  are outliers, because HOMOs of  $NiO^-$  and  $CuO^-$  are more strongly hybridized with 3d orbitals than those of the other anions.

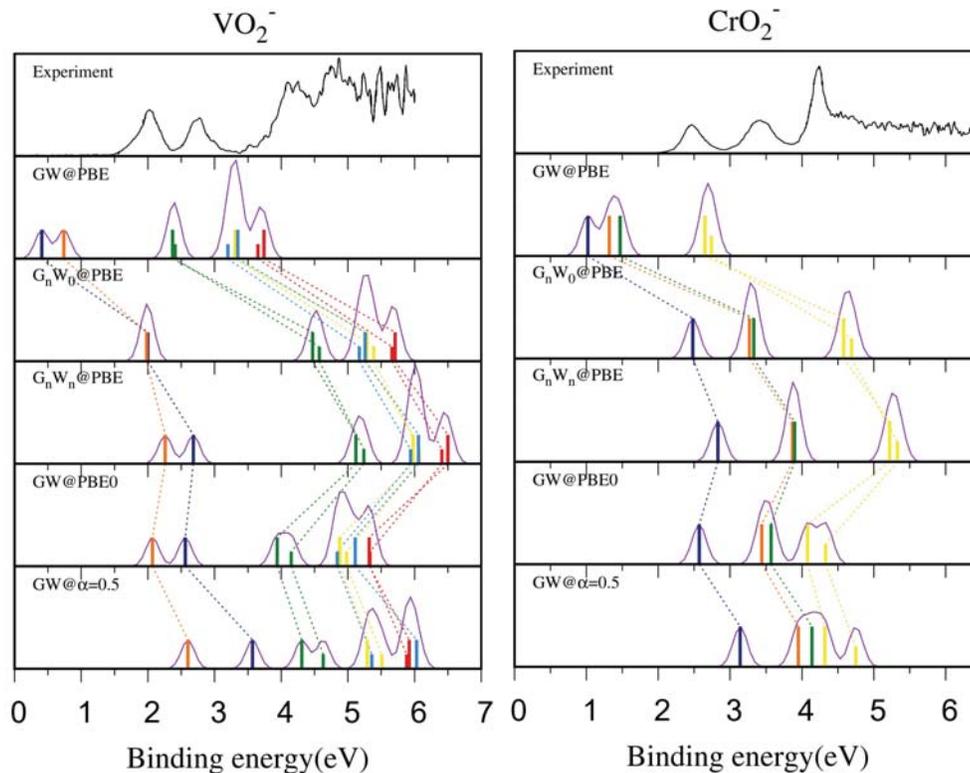


**Fig. 2:** First ionization energies (left) and lowest 3d binding energies (right) of TMO (TM = Sc, Ti, ..., Cu, Zn) anions. The vertical axis represents the difference between experimental and calculated binding energies.

Second, both  $G_0W_0@PBE0$  and  $G_nW_0@PBE$  lead to much improved predictions, which underestimate the IE and the 3d-electron BE by  $\sim 0.1-0.5$  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 3d-electron BE by  $\sim 0.1-1$  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 3d-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 3d-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.

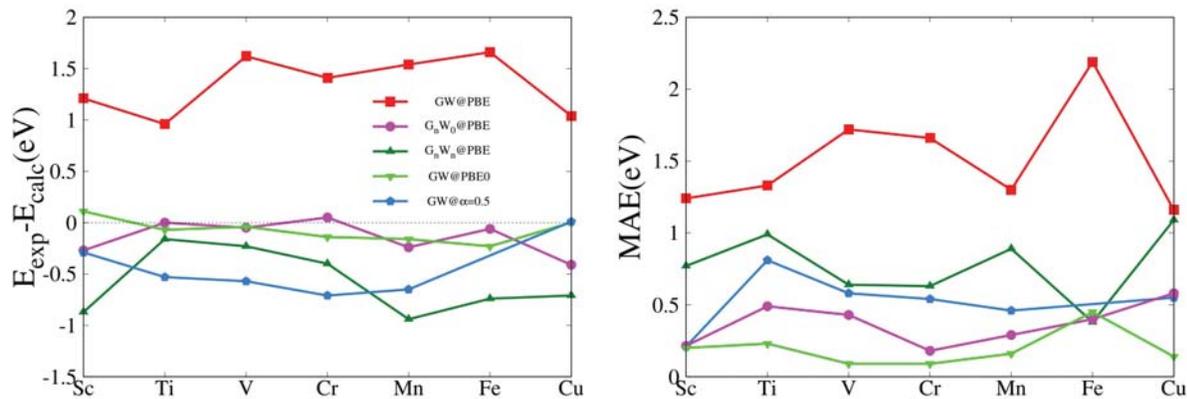
### Electronic Structure of 3d-Transition Metal Dioxide Anions

We have also computed the quasiparticle spectra of 3d TM anion dioxide molecules ( $\text{TMO}_2^-$ ) using various levels of  $GW$  theory to evaluate the performance of the  $GW$  approximation. Similar to the monoxide case, we have applied perturbative non-self-consistent  $GW$  ( $G_0W_0$ ) with PBE and hybrid functional starting points and the  $evGW$  calculations of the type  $G_nW_0$  and  $G_nW_n$ . Some representative examples for  $\text{VO}_2^-$  and  $\text{CrO}_2^-$  are shown in Fig. 3.



**Fig. 3:** Computed photoelectron spectra of  $\text{VO}_2^-$  and  $\text{CrO}_2^-$  at various levels of  $GW$  theory compared with experiment.

As can be observed from Fig. 3, the two levels of theory, which are quite successful for monoxide anions, i.e.  $G_0W_0@PBE0$  and  $G_nW_0@PBE$ , are also very successful in not only predicting the IE (first peak), but also the higher energy peaks that appear in the experimental photoelectron spectra. The deviations of calculated IE from experimental data and the mean absolute error averaged over all experimentally available peaks for  $\text{TMO}_2^-$  anions are plotted in Fig. 4, which show that  $G_0W_0@PBE0$  provides the best agreement with experiment (typically less than 0.1 eV errors for IE, and less than 0.2 eV for MAE), and  $G_nW_0@PBE$  is a close second.



**Fig. 4:** Deviation of calculated IE from experimental values (left) and mean absolute error averaged all experimentally available photoelectron peaks (right) at various levels of  $GW$  theory for transition metal dioxide anion molecules.

## 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 and our in-house computer cluster 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.C. We also added new capabilities to MOLGW, such as (i) a new quasiparticle equation solver, (ii) eigenvalue-self consistent COHSEX, (iii)  $G_0W_0$ ,  $G_nW_0$ , and  $G_nW_n$  calculations with self-consistent COHSEX starting points.

## FUTURE WORK

Currently, we are testing the performances of COHSEX (a lower, but cheaper level of theory than  $G_0W_0$  and  $evGW$ ),  $G_0W_0@COHSEX$ , and quasi-particle-self-consistent  $GW$  (a higher and less starting-point-dependent, but more expensive level of theory), and MP2 levels of theory for TMO anions. We are working on two manuscripts related to TMO, TMO<sub>2</sub> anion clusters discussed above, and another manuscript on computing multiplet splittings with  $GW$  theory in molecular systems (discussed in last year's report).

## 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).
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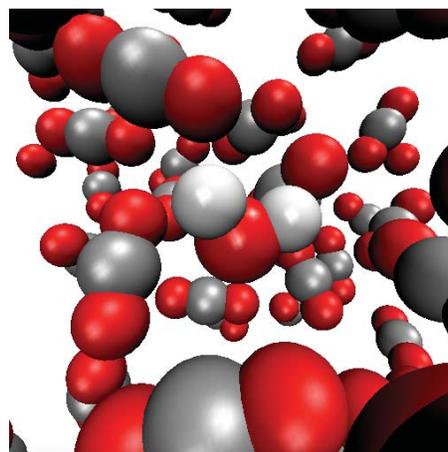
## Towards Realistic Simulations of Fluid Mixtures Through Many-Body Representations

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### 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<sub>2</sub>O in CO<sub>2</sub>*

Our initial efforts have focused on developing an accurate and efficient theoretical/computational framework 1) to investigate the relationship between individual many-body effects and the local structure of water, 2) to model fluid mixtures from the gas to the condensed phase through many-body molecular dynamics (MB-MD) simulations, and 3) to model chemical reactions in solutions through adQM/MB simulations.

In our first study, we demonstrated that the local structure of liquid water at room temperature is determined by a delicate balance between two-body and three-body energies, which is further modulated by higher-order many-body effects. Our analysis also emphasized that a correct representation of two-body and three-body effects requires sub-chemical accuracy that is nowadays only achieved by many-body models, such as our MB-pol model, that are rigorously derived from the many-body expansion of the total energy. Besides providing fundamental insights into the relationships between many-body effects and the local structure of water, our study introduced many-body representations of water derived from various exchange-correlation functionals selected across the hierarchy of density functional theory (DFT) approximations, including revPBE-D3 (rung 2), B97M-rV (rung 3), revPBE0-D3 (rung 4) and  $\omega$ B97M-V (rung 4). We are planning to use these many-body DFT models in our adQM/MB simulations of chemical reactions in water.

In our second study, we extended the scope of our many-body TTM-nrg and MB-nrg potential energy functions (PEFs), originally introduced for halide ion–water and alkali-metal ion–water interactions, to the modeling of carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) mixtures as prototypical examples of molecular fluids. Although both PEFs adopt the same functional forms to describe permanent electrostatics, polarization, and dispersion, they differ in the representation of short-range contributions, with the TTM-nrg PEFs relying on conventional Born-Mayer expressions and the MB-nrg PEFs employing multidimensionally

invariant polynomials. We showed that, by providing a physically correct description of many-body effects at both short and long ranges, the MB-nrg PEFs are able to quantitatively represent the global potential energy surfaces of the CO<sub>2</sub>-CO<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub>O dimers and the energetics of small clusters, as well as to correctly reproduce various properties of both gas and liquid phases. Building on this study, we are currently developing a library of many-body models for molecular fluids and solvents relevant to energy applications.

Finally, we have developed our first adQM/MB implementation in which water (i.e., the MB region) is described by our MB-pol model and the QM region is represented by various DFT models, and mutual polarization between the two regions is explicitly taken into account. Our preliminary results indicate that treating water with MB-pol suppresses, if not completely eliminates, the discontinuities that affect conventional QM/MM approaches. Our future work will focus on extending our adQM/MB approach to other solvents and modeling chemical transformations in complex fluid mixtures.

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

**Postdocs:** Vinicius W. Cruzeiro, M. Riera

**Students:** Alessandro Caruso, Colin Egan, Kartik Rallapalli

#### **Publications**

1. M. Riera, E. Lambros, T.T. Nguyen, A.W. Götz, F. Paesani, “Low-order many-body interactions determine the local structure of liquid water”, *Chem. Sci.* **10**, 8211 (2019).
2. M. Riera, E.P. Yeh, F. Paesani, “Data-driven many-body models for molecular fluids: CO<sub>2</sub>/H<sub>2</sub>O mixtures as a case study”, *J. Chem. Theory Comput.* **16**, 2246 (2020).

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

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### Abstract

Nanoscale magnetic molecules or single-molecule magnets (SMMs) have unique quantum properties which can be used for potential applications for data storage, molecular spintronics, and quantum information science. Compared to conventional silicon-based solid-state materials, magnetic molecules or SMMs have much more degrees of freedom in tailoring their properties for specific purposes by varying chemical environments.

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. In a majority of SMMs, electron correlation effects play a prime role in the magnetic properties, which suggests insufficiency of computationally inexpensive density functional theory (DFT) and demands multireference quantum chemistry calculations. However, in reality, multi-center SMMs cannot be reliably treated using multireference quantum chemistry methods due to the large system sizes. Thus, we will need alternative methods to study magnetic properties of SMMs.

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 and Fermi orbital descriptors (FODs) has been proposed and this method was successfully implemented into open-source FLOSIC code and applied to non-magnetic molecules with improved electronic 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.

We have been investigating magnetic properties of a mononuclear Fe-based SMM and  $[\text{Cu}(\text{C}_6\text{H}_4\text{S}_2)_2]^{2-}$  molecule using DFT with and without SIC and Hartree-Fock methods in collaboration with the FLOSIC teams from Central Michigan University and University of Texas at El Paso (FLOSIC v.0.2). For the Fe-based SMM, the magnetic anisotropy barrier calculated using DFT without SIC was an order of magnitude smaller than the experimental value. For an initial guess of FOD positions, we considered two basic schemes: (i) FODs optimized from individual atoms by Der-you Kao et al. and (ii) FODs guessed by the Monte Carlo method developed by Prof. K. A. Jackson group (Central Michigan University). Our initial attempt on the Fe-based SMM showed that the initial FOD positions need to be more elaborated than the above two methods for reliable inclusion of SIC. In order to gain more insight into the FOD positions, we chose the Cu molecule which is smaller than the Fe-based SMM. In this case, the above two schemes to

generate initial FOD positions seem to work. We briefly present our preliminary results on the Cu molecule below.

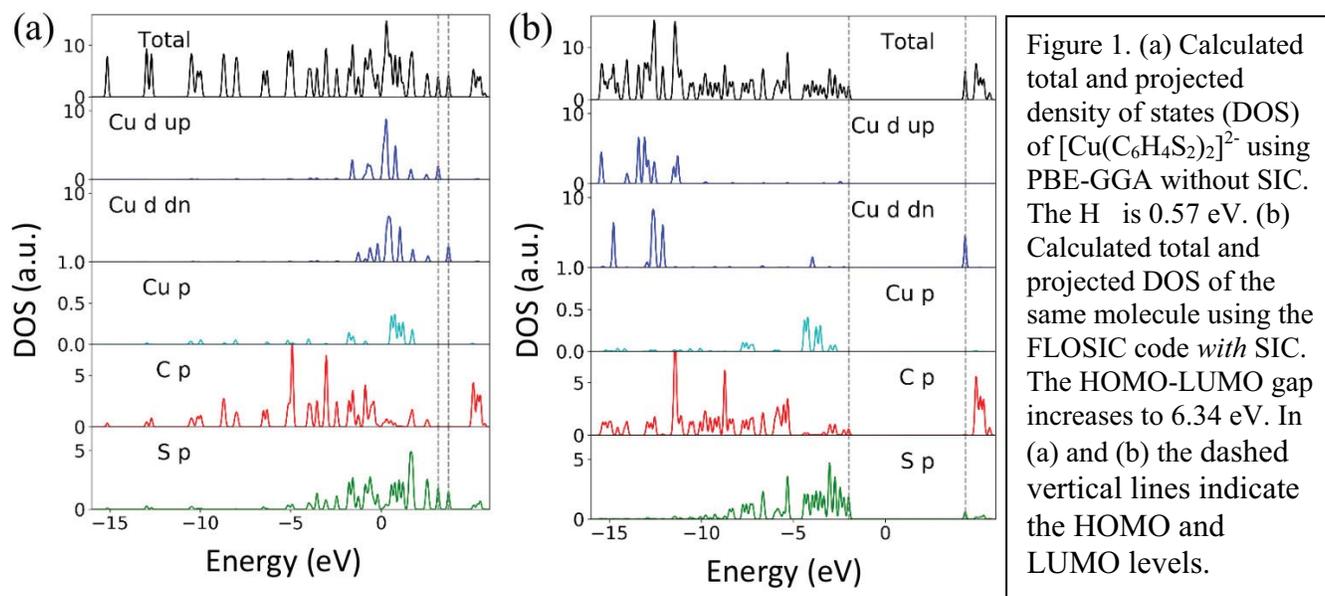


Figure 1. (a) Calculated total and projected density of states (DOS) of  $[\text{Cu}(\text{C}_6\text{H}_4\text{S}_2)_2]^{2-}$  using PBE-GGA without SIC. The H is 0.57 eV. (b) Calculated total and projected DOS of the same molecule using the FLOSIC code *with* SIC. The HOMO-LUMO gap increases to 6.34 eV. In (a) and (b) the dashed vertical lines indicate the HOMO and LUMO levels.

After the FOD optimization, the maximum force is at the order of 0.001 atomic units and the dipole moment is below 0.01 atomic units. Figure 1 shows our calculated density of states (DOS) of the Cu molecule using DFT+SIC within the FLOSIC code in comparison to that without SIC. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is about 0.57 eV without SIC, while it increases to 6.34 eV with SIC. Furthermore, the orbital characteristics of the HOMO also changes from Cu d to S p with SIC. The orbital character of the LUMO does not change with SIC because SIC was applied to only occupied orbitals.

During the next year, we plan to investigate more electronic properties of the Cu molecule in different charge states with SIC compared to those without SIC, by implementing the frozen-density FOD optimization method (as a speed-up) developed by Prof. Jackson group from Central Michigan University, and publish this work. In addition, we will investigate electronic and magnetic properties of the Fe-based SMM or other interesting SMMs with SIC as well as work on the implementation of hyperfine coupling with SIC in the FLOSIC code in collaboration with the two FLOSIC teams. The graduate student will present his work in the APS March or ACS meeting in 2021, and will write and submit manuscripts for his work.

**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

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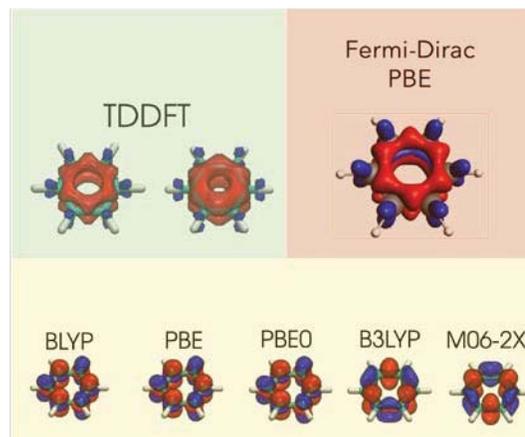
### Abstract

We develop methods for simulating 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. Even though approximations are needed, all methods developed in this project are all-electron, mean field and self-consistent. In the past year, we focused on developing 3 approaches:

1. eXcited Constrained DFT (XCDFT) [2,7] a variational method for calculating low-lying excited states of molecular systems that is as balanced as possible with ground state calculations and that can be seamlessly extended to a subsystem (embedding) formulation.
2. Time-dependent subsystem DFT. We developed an adiabatic-connection fluctuation-dissipation theorem time-dependent subsystem DFT capable of describing spectral broadening and van der Waals interactions of molecules at surfaces (metallic and semiconducting) [6].
3. Atomistic time-dependent Thomas-Fermi [8] with applications to quantum dots and metal clusters.

In 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 achieve an accuracy in the predicted excitation energy only slightly worse than linear-response time-dependent DFT (TDDFT), but including orbital relaxation and without incurring into problems of variational collapse typical of the more commonly adopted  $\Delta$ SCF method. 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. We recently [7] implemented an extension of XCDFT that employs ensemble states delivering excited states with much improved character compared to Aufbau XCDFT (see **Figure 1**).

In addition, leveraging an open-subsystem formulation of DFT, we are developing real-time subsystem TDDFT methods for simulating the electron-nuclear 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



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

Fermi Golden Rule. We have recently [6] built on this platform and developed a general theory (and associated software) for evaluating the spectral broadening and van der Waals interactions between molecules nearby a surface. We plan to apply such a theory to the development of force fields for interfaces of molecular systems (liquid and solids) with surfaces.

Current developments involve implementation of nonadiabatic dynamics based on a subsystem real-time TDDFT approach as well as 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. We have already made progress in this direction [8] by developing an atomistic time-dependent Thomas-Fermi method capable of semiquantitatively compute the optical spectra of metal clusters and semiconducting quantum dots.

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**Students:** Alina Umerbekova (graduate student)

**Postdoc:** Dr. Pablo Ramos, Dr. Kaili Jiang

#### **Publications Acknowledging the Grant**

1. J. Phys. Chem. Lett., **8**, 5077 (2017)  
Sudheer Kumar P. and Alessandro Genova and Michele Pavanello  
*Cooperation and Environment Characterize the Low-Lying Optical Spectrum of Liquid Water*
2. J. Chem. Phys., **148**, 144103 (2018)  
Pablo Ramos and Michele Pavanello  
*Low-lying Excited States by Constrained DFT*
3. Eur. Phys. J. B, **91**, 214, (2018) [Special Issue: Hardy Gross]  
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*
4. Nanoscale, **10**, 17603 (2018) [Selected as “hot” article]  
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Probing charge transfer dynamics in a single iron tetraphenylporphyrin dyad adsorbed on an insulating surface
5. Int. J. Quantum Chem., **119**, e25801, (2019) [Special Issue: Advances in Simulating Solvation]  
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*
6. Int. J. Quantum Chem., **120**, e26243, (2020) [Special Issue: Quantum Embedding]  
Alina Umerbekova and Michele Pavanello  
*Many-body response of benzene at monolayer MoS<sub>2</sub>: Van der Waals interactions and spectral broadening*
7. Physical Review A **101** (3), 032510, (2020)  
Nell Karpinski, Pablo Ramos and Michele Pavanello  
*Capturing multireference excited states by constrained-density-functional theory*
8. WIREs: Comp. Mol. Sci. accepted, (2020)  
Xuecheng Shao, Kaili Jiang, Wenhui Mi, Alessandro Genova and Michele Pavanello  
*DFTpy: An efficient and object-oriented platform for orbital-free DFT simulations*

# Density Functional Theory Methods for Spin-Related Molecular Properties

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## Abstract

Recent Progress:

(a) Supported by DE-SC0005027: We continue working on a new approach based on the direct propagation of the driven Liouville von Neumann (DLvN) equation for the simulation of many-electron quantum systems out of equilibrium. While the DLvN method has been implemented in combination with tight-binding and semi-empirical methods, the DFT version needs some careful analysis. Once completed,

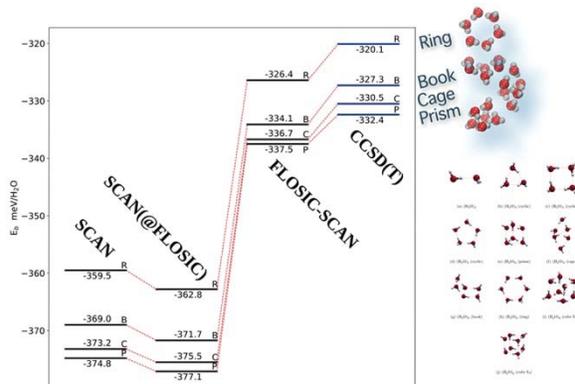


this approach can be used to simulate the transient current and find stationary solutions of realistic molecular complexes placed between explicit leads subject to an energy bias using a DFT framework. At this point the code is advanced but still needs adjustments (not published). In the future, we will be able to incorporate noncollinear magnetism and relativistic effects to model problems that involve electron spin transport with direct applications in spintronic devices. Some other

projects involve the search for high magnetic anisotropy mononuclear Co(II) complexes inspired by recent experimental work where an anisotropy  $D \sim -73 \text{ cm}^{-1}$  was observed.

(b) Supported by DE-SC0018331: The effect of self-interaction error (SIE) in DFT for calculated molecular and solid-state properties has been known for a long time. The most widely accepted context

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 has been limited. A few years ago, an efficient implementation for SIE removal based on Fermi orbitals was proposed (FLOSIC) [JCP 140, 121103 (2014)]. This method replaces the unitary



transformation from canonical to localized orbitals that is needed in standard PZ and 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. FLOSIC effectively eliminates the self-interaction error in a manner similar to traditional PZ. We have also shown recently that FLOSIC combined with the SCAN density functional approximation leads to an improved description of the energetics of small water clusters. We expect to work on FLOSIC improvements in 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.

† **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; currently a post-doctorate at PNNL).

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- † Self-interaction Error Overbinds Water Clusters but Cancels in Structural Energy Differences, K. Sharkas, K. Wagle, B. Santra, S. Akter, R. R. Zope, T. Baruah, K. A. Jackson, J. P. Perdew, and J. E. Peralta, *Proc. Natl. Acad. Sci. U.S.A.* (in press, **2020**).
- † Accuracy of Density Functional Theory Methods for the Calculation of Magnetic Exchange Couplings in Binuclear Iron(III) Complexes, R. P. Joshi, J. J. Phillips, K. J. Mitchell, G. Christou, K. A. Jackson, and J. E. Peralta, *Polyhedron* 176, 114194 (**2020**).
- ‡ 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* 11, 18494 (**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**).
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- ‡ Local Noncollinear Spin Analysis, B. A. Abate, R. P. Joshi, and J. E. Peralta, *J. Chem. Theory and Comput.* 13, 6101-6107 (**2017**).

# Phase equilibrium of water and ice from enhanced sampling molecular dynamics simulations

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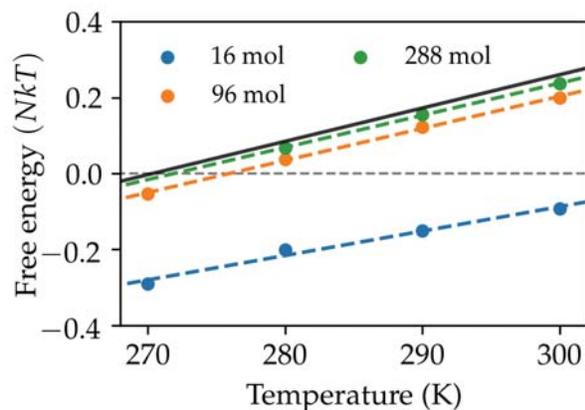
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## Abstract

Water is a ubiquitous and fascinating substance that has at least 18 solid polymorphs with rich and diverse characteristics. The most stable form of ice at ambient pressure is ice Ih, which is the most common polymorph in planet Earth's surface and atmosphere. Ice Ih has a crystalline oxygen lattice with a disordered distribution of the hydrogens (protons) in the bonds connecting neighboring oxygens. Each bond has one proton that can sit at one of two equivalent positions closer, respectively, to one or the other oxygen of the bond. Proton disorder is constrained by the ice rules, which led Pauling to estimate with a stroke of genius the residual entropy of ice to be  $k \log\left(\frac{3}{2}\right)$  per molecule. Pauling's estimate should be included when calculating the phase equilibria of water models by thermodynamic integration. In this project we follow a different path as we harness several recently developed tools for calculating free energy differences to study the equilibrium between liquid water and ice Ih. In our approach, we do not need to account for the residual entropy of ice since the ice structures spontaneously emerging from the liquid are proton disordered. Interestingly, our estimate of the melting temperature is within error bars the same of thermodynamic integration approaches.

Our method is based on the calculation of free energy differences from molecular simulations that visit reversibly ice and liquid phases. In unbiased molecular dynamics simulations, the transition between phases is hampered by the large free energy barrier of nucleation. To facilitate interconversion between the two phases we introduce a static bias potential that reduces the free energy barrier. The bias potential is a function of an order parameter that is tailored to crystallize the hexagonal diamond structure of oxygen in ice Ih. In this way we are able to observe many transitions in a short simulation time and extract free energies from the simulation.

We applied this technique to the extensively studied TIP4P/Ice water model.



We calculated the free energy differences that we show in the figure and we obtained a melting temperature of 270 K in agreement with state-of-the-art techniques that rely on Pauling's model for proton disorder. In our approach, the order parameter does not include information on the location of the protons. Yet, spontaneously formed solid configurations contain proton disorder as expected for ice Ih.

We are currently applying our method to the more challenging case in which the potential energy of interaction among the atoms is described by a deep potential (DP), i.e. a deep neural network potential trained with DFT energies and forces derived from the SCAN functional. This potential is completely flexible and reproduces accurately *ab-initio* molecular dynamics simulations based on SCAN. Our estimate for the melting temperature of SCAN ice Ih is 318 K, about 50 K higher than the experimental melting temperature. These simulations did not include nuclear quantum effects (NQE), which are expected to lower the melting temperature. Work is in progress to estimate these effects with path integral simulations. We also intend to assess the effect on the phase equilibrium of the DFT self-interaction error, which can be reduced by replacing SCAN with SCAN0, its hybrid counterpart. In the future, we plan to use our approach to study the homogeneous nucleation of DP water. This should provide new insight on long standing issues regarding ice nucleation. Further down the road we intend to address heterogenous nucleation, which is at the basis of important natural phenomena such as ice nucleation in the atmosphere.

## **Grant DE-SC001934: Chemistry in Solution and at Interfaces**

**Postdocs:** Pablo M. Piaggi

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

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## I. Program Scope

This research program focuses on the development, dissemination, and applications of *ab initio* electronic structure approaches and computer codes exploiting the exponential wave function ansätze of single- and multi-reference coupled-cluster (CC) theories. Our main interest is in methodologies that can provide an accurate description of chemical reaction pathways and potential energy surfaces involving closed- and open-shell molecular species, excited states characterized by one- as well as many-electron transitions, strong correlations and 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, 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 systems with dozens or hundreds of atoms, in addition to smaller species, 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, are well suited for automated implementations and are shared with the community through the GAMESS package [10] and plugins to PSI4, deposited in GitHub. Some of them can also be found, in the original or modified form, in the NWChem, Q-Chem, and MRCC codes.

## II. Recent Progress (2017 – 2019 and January 1 – April 17, 2020)

Our research in the reporting period consisted of three distinct and yet related components, including (1) development of new generations of deterministic *ab initio* electronic structure approaches exploiting the exponential CC ansatz, with a focus on methods for strongly correlated systems and highly complex dynamical correlations, (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 and property surfaces, followed by spectroscopic and dynamical simulations, singlet–triplet gaps in biradical and prototype magnetic species, photochemistry, and structural, electronic, and spectroscopic properties of small metallic clusters relevant to ultracold and collisional phenomena. (1) and (2) were accompanied by substantial mathematical and programming work and numerous benchmark calculations. Our method development work was facilitated 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 [2–4,6,8], 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  $CCSDT$  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 [2,4]. By examining the double dissociation of water, insertion of Be into  $H_2$ , and singlet–triplet gap in a prototype magnetic (HFH)<sup>+</sup> 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 fractions of a millihartree at small fractions of the computational effort involved in the parent CCSDTQ calculations, even when electronic quasi-degeneracies are substantial [2]. Papers [4,6] extended these studies by examining the performance of CCSD, CCSD(T), CCSD(2)<sub>T</sub>, 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 weakly bound beryllium [4] and magnesium [6] 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 reproducing the respective parent CCSDT and CCSDTQ calculations. In the case of  $Be_2$  [4], 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  $\sim 1\text{ cm}^{-1}$  ( $5\text{ cm}^{-1}$  at worst). In the case of  $Mg_2$ , which is bound by only about  $430\text{ cm}^{-1}$  [6], in addition to reproducing the experimentally determined part of the vibrational spectrum to within  $\sim 1\text{ cm}^{-1}$ , the analogous composite scheme combining the nearly all-electron CCSDT and valence  $CC(q;4)$  energetics predicted the existence of five extra vibrational levels, which were previously, as elaborated on below, the subject of speculation, with the last,  $v'' = 18$ , state located only  $0.2\text{ cm}^{-1}$  below the dissociation threshold [6]. Once again, 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.

Encouraged by the above successes, we used our most accurate representation of the ground-state  $X\ ^1\Sigma_g^+$  potential for  $Mg_2$ , obtained by combining the nearly all-electron CCSDT and valence FCI, and the similarly accurate excited-state  $A\ ^1\Sigma_u^+$  potential, along with the corresponding transition dipole moment function, to address a half-century-old enigma regarding the elusive high-lying vibrational states of the magnesium dimer [9]. We determined the entire rovibrational manifolds corresponding to the  $X\ ^1\Sigma_g^+$  and  $A\ ^1\Sigma_u^+$  states for all stable isotopologs of  $Mg_2$ , including bound as well as quasi-bound states, and simulated the laser-induced fluorescence (LIF) spectra corresponding to the  $A\ ^1\Sigma_u^+(v',J') \rightarrow X\ ^1\Sigma_g^+(v'',J'')$  transitions, including line positions and intensities. The resulting ground-state potential confirmed the existence of 19 bound vibrational levels, i.e., five more than detected experimentally, with  $\sim 1\text{ cm}^{-1}$  root-mean-square deviation between the calculated and experimentally derived rovibrational term values. The computations reproduced the latest experimentally observed LIF spectra and provided detailed guidance for the detection of the rovibronic transitions involving the previously unresolved levels [9]. This work may have significant implications for a number of fundamental phenomena at the intersection of chemistry and atomic, molecular, optical, and ultracold physics, such as the coherent control of binary collisions, doped helium nanodroplets, and optical lattice clocks, where  $Mg_2$  and heavier alkaline-earth diatomics have emerged as important probes. It also demonstrates that the predictive power of modern electronic structure methodologies is no longer limited to small few-electron species.

Other examples of successful exploitation of the  $CC(P;Q)$  methodology can be found in [E. Pastorzak *et al.*, *J. Chem. Theory Comput.* **13**, 5404 (2017)], where we took advantage of our  $CC(t;3)$  and CCSDT codes, incorporated in the reporting period (along with CCSDt) in GAMESS [10] and, via the plugin deposited in GitHub ([https://github.com/piecuch-group/psi4\\_cct3](https://github.com/piecuch-group/psi4_cct3)), in PSI4, to examine the novel geminal-based approach, abbreviated as EERPA-GVB. We focused on challenging 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  $NH_3\dots F_2$  complex, in which we dissociated the F–F bond in  $F_2$ , and the strongly correlated  $H_{12}\dots H_{12}$  dimer, in which we stretched all

H–H bonds in the linear H<sub>12</sub> chains (as in models of metal–insulator transitions). We also implemented the excited-state CC(t;3) methodology correcting EOMCCSDt for the triples outside the active set.

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 [3]. According to one of the reviewers, 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. 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 the CC(*P*;*Q*) corrections, to provide the rest of the information. As shown in [3] and a longer paper in preparation, independent of the type of MC sampling, the convergence toward target CCSDT and CCSDTQ energetics 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 user and system dependent active orbitals. More recently, we extended the idea of identifying the leading higher–than–doubly excited determinants in the ground-state CC calculations via stochastic CIQMC propagations [3] to excited electronic states by merging CIQMC with the deterministic EOMCC framework [7]. By calculating several excited states of CH<sup>+</sup> at the equilibrium and stretched geometries, in which the required lists of triples were extracted from the FCIQMC propagations for the lowest-energy states in the relevant irreducible representations, 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, after relatively short CIQMC runs [7]. A few days ago, we submitted a follow-up paper heading in the same direction [S.H. Yuwono *et al.*, submitted to *Mol. Phys.* on April 8, 2020], which is even more profound. By identifying the leading higher–than–two-body contributions of the parent EOMCC approach using the stochastic CIQMC sampling and taking advantage of the CC(*P*;*Q*) corrections to capture the remaining correlations, we demonstrated that one can converge target EOMCC energetics, represented by EOMCCSDT, to within a millihartree or fractions of a millihartree out of the early stages of CIQMC propagations. We illustrated the performance of this new semi-stochastic CC(*P*;*Q*) approach to excited states by converging the EOMCCSDT energetics for a few benchmark systems, including CH<sup>+</sup> at the equilibrium and stretched geometries and the open-shell CH and CNC species. In yet another study [5], we demonstrated that one can take the merger of stochastic and deterministic ideas to the ultimate level and use it to extract the exact, FCI, energetics out of the early stages of FCIQMC propagations with the help of relatively inexpensive polynomial steps, similar to those of CCSD, eliminating exponential complexity of FCI altogether [5]. The advantages of the resulting cluster-analysis-driven (CAD) FCIQMC approach were illustrated using the double dissociation of water [5]. Work is underway to extend CAD-FCIQMC to strongly correlated systems (models of metal–insulator transitions) and many-electron species beyond the reach of FCI.

Another significant advance in the area of new CC and EOMCC methods in the reporting period was presented in [1], where we continued our work on extending the active-space EOMCC theories to the double electron-attachment (DEA) formalism applicable to open-shell species with two electrons outside the closed-shell cores, especially the electronic spectra of biradicals, without invoking complicated (and not necessarily robust) steps of multi-reference CC. Encouraged by our earlier 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 (*4p-2h*) excitations can be extended to a much less expensive model, in which both *3p-1h* and *4p-2h* terms are selected using active orbitals [1]. By examining the low-lying singlet and triplet states of the methylene, (HFH)<sup>−</sup>, trimethylenemethane, cyclobutadiene, and cyclopentadienyl cation biradicals and bond breaking in F<sub>2</sub>, we showed that the DEA-EOMCC methods with an active-space treatment of *3p-1h* or *3p-1h* and *4p-2h* 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  $3p-1h$  and  $4p-2h$  or only  $4p-2h$  excitations considerably improve the DEA-EOMCC theories truncated at  $3p-1h$  excitations, while making the results almost insensitive to the type of molecular orbitals (MOs) used in the calculations [1]. The latter observation should be contrasted with the DEA-EOMCC method truncated at  $3p-1h$  excitations and its double ionization potential (DIP) EOMCC analog truncated at  $3h-1p$  terms, which can be sensitive to the choice of MOs. We also published a paper, in collaboration with Professors Laura Gagliardi and Donald Truhlar, in which our well-converged DEA-EOMCC singlet–triplet gaps for several antiaromatic molecules, including cyclobutadiene and its derivatives and cyclopentadienyl cation, provided definitive information for benchmarking CASPT2 and RASPT2 [S.J. Stoneburner *et al.*, *J. Chem. Phys.* **147**, 164120 (2017)]. Our DEA/DIP-EOMCC codes with up to  $4p-2h/4h-2p$  terms will soon be available in GAMESS [10].

Among other examples of collaborations in the reporting period was our work with the experimental group of Professor Marcos Dantus, in which 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 [G. Rasskazov *et al.*, *Chem. Phys. Lett.* **683**, 121 (2017)]. This collaboration has recently been extended to other important applications, including our work with Professor Dantus and synthetic, physical organic, and analytical chemists from our department aimed at the exploration of the strongest super photobase known to date called **FR0-SB** [8]. The change in  $pK_a$  upon photoexcitation characterizing **FR0-SB** is so big that the photoexcited **FR0-SB\*** species, which is benign in the ground state, extracts protons from alcohols. By performing high-level *ab initio* calculations exploiting parallel EOMCCSD and  $\delta$ -CR-EOMCC(2,3) codes developed in this program, we have been able to understand the mechanism behind the experimentally observed photoreactivity of **FR0-SB**, which can be traced to the significant, about three-fold, enhancement of its dipole moment upon photoexcitation [8]. Based on our microscopic understanding of the experimentally observed photobasicity of **FR0-SB**, we are now in a position to propose novel super photobases, which will potentially be even stronger than **FR0-SB**.

### III. Future Plans

Our immediate future plans include (i) further work on extending the semi-stochastic  $CC(P;Q)$  approach, which combines  $CC(P;Q)$  with CIQMC, to excited states and exploration of similar 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 approximate coupled-pair theories with the active-space, QMC, and adaptive CI methodologies, and (iii) continuation of our work on accelerating convergence of FCIQMC by cluster analysis of the corresponding wave functions, with a focus on strongly correlated systems. 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] A.O. Ajala, J. Shen, P. Piecuch, *J. Phys. Chem. A* **121**, 3469 (2017). DOI: [10.1021/acs.jpca.6b11393](https://doi.org/10.1021/acs.jpca.6b11393)
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- [4] I. Magoulas, N.P. Bauman, J. Shen, P. Piecuch, *J. Phys. Chem. A* **122**, 1350 (2018). DOI: [10.1021/acs.jpca.7b10892](https://doi.org/10.1021/acs.jpca.7b10892)
- [5] J.E. Deustua, I. Magoulas, J. Shen, P. Piecuch, *J. Chem. Phys.* **149**, 151101 (2018). DOI: [10.1063/1.5055769](https://doi.org/10.1063/1.5055769)
- [6] S.H. Yuwono, I. Magoulas, J. Shen, P. Piecuch, *Mol. Phys.* **117**, 1486 (2019). DOI: [10.1080/00268976.2018.1564847](https://doi.org/10.1080/00268976.2018.1564847)
- [7] J.E. Deustua, S.H. Yuwono, J. Shen, P. Piecuch, *J. Chem. Phys.* **150**, 111101 (2019). DOI: [10.1063/1.5090346](https://doi.org/10.1063/1.5090346)
- [8] J. Lahiri, M. Moemeni, J. Kline, B. Borhan, I. Magoulas, S.H. Yuwono, P. Piecuch, J.E. Jackson, M. Dantus, G.J. Blanchard, *J. Phys. Chem. B* **123**, 8448 (2019). DOI: [10.1021/acs.jpcc.9b06580](https://doi.org/10.1021/acs.jpcc.9b06580)
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- [10] G.M.J. Barca *et al.*, *J. Chem. Phys.* **152**, 154102 (2020). DOI: [10.1063/5.0005188](https://doi.org/10.1063/5.0005188)

## Applications of computational materials modeling to electrocatalysis: From realistic phosphide surfaces to tunable covalent organic frameworks

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### Abstract

Heterogeneous catalysis remains a compelling challenge for theoretical energy science because the catalytic surface has a wealth of dynamic aspects that elude simple formulation. The surface of a material is where the continuous bonding network of the bulk is broken. The surface is also under constant interaction with an active chemical [1] and electronic [2] environment e.g., the atmosphere, the solvent, the gas intake in a thermal catalytic reaction, or an electrolyte. In order to cope with the broken bonding network and the exchange of chemical species and charges with the environment, surfaces undergo what is known as surface atomic reconstruction. This phenomenon comprises adatoms, vacancies, substitutions, and wholesale changes to the surface stoichiometry and structure, rendering the surface in many cases substantially different from the bulk.

In our group, we have created systematic methodologies to investigate the important effect of surface reconstructions on catalytic properties of surfaces. Our previous works have laid out foundations of using grand canonical Monte Carlo (GCMC) algorithms for automating the computational workflow of finding non-trivial surface reconstructions. We have previously demonstrated the application of such an algorithm for predicting the structure and composition of the oxide AgO layer formed on Ag metal surfaces. [3] More recently, we have investigated the important role of atomic surface reconstructions in understanding the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) on nickel phosphides, as well as oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) on molybdenum phosphide-based catalysts for Li/air batteries.

Similar in spirit to surface reconstructions which are changes to surface composition as a result of exchanging chemical groups with surrounding environment to minimize its Gibbs free energy, we have conducted studies to identify novel phases of bulk materials resulting from incorporation of guest molecules (from a solvent) to stabilize their internal bonding network. More specifically, in a joint experimental-theory work [4], we have demonstrated how a hybrid material resulting from incorporation of (solvent) pyridine molecules into porphyrin-based covalent organic frameworks (COFs) can help crystallize organized stackings of these materials with additional (pyridine-intercalated) interlayer spacing. This hybrid material is shown to exhibit considerably enhanced ORR activity relative to the bare COFs. Thus, we propose that the intercalation of small

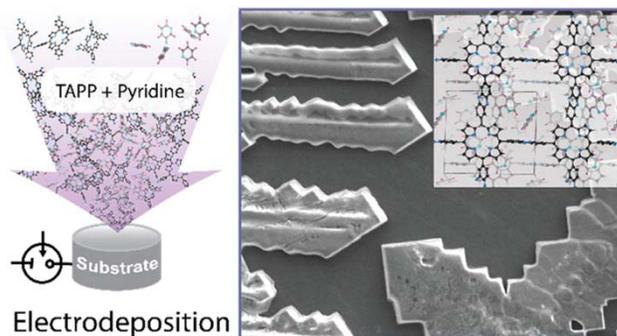


Figure 1: (left) In a recent theory/experiment study (*JACS* Nov 2019), research in the Rappe and Nejati groups demonstrate electrochemical deposition of crystals of (right inset) linked porphyrin sheets. (right) The resulting dendritic crystals assume a hybrid structure with nanostructured pyridine between sheets. This system exhibits catalytic activity and offers compelling opportunities for future catalyst design and synthesis. [4]

molecules (e.g., pyridine) into COF structures can provide a viable pathway to tune the structural and electronic properties of these materials. Here, we briefly discuss each of these fronts and how we envision the next steps in their evolution. The general underlying theme is to try to bring the attention of the catalysis community to the great potential in the materials design space resulting from the possibility of realizing novel material phases on surfaces, interfaces or bulk materials by carefully adjusting the synthesis or operating methods.

We showcase our efforts on studying catalytic properties on nickel phosphide surfaces by our recent work on CO<sub>2</sub>RR on Ni<sub>2</sub>P. The selective formation of multi-carbon products using CO<sub>2</sub>RR can provide great advancement for production of chemical feedstocks. Recent experiments have shown that nickel phosphides selectively catalyze CO<sub>2</sub>RR, producing C<sub>3</sub> and C<sub>4</sub> products while suppressing the hydrogen evolution reaction at 0 V *vs.* the reversible hydrogen electrode. We find that the surface hydrogen affinity, the consequent surface reconstructions, and tandem thermal and electrochemical steps are crucial for achieving the high selectivity. Further, we unveil that the CO<sub>2</sub> activation step via surface hydride transfer limits the catalytic activity, resulting in the low turnover frequency observed experimentally. The mechanistic knowledge gained here can lead to the design of chemically-selective nickel phosphide-based CO<sub>2</sub>RR catalysts that more active, and thus industrially viable.

Another example of surface atomic reconstructions on phosphides will be discussed by studying the application of tri-molybdenum phosphide (Mo<sub>3</sub>P) nanoparticles in lithium-air batteries. Lithium-air batteries are promising competitors to replace traditional lithium-ion batteries due to the extremely high theoretical energy density. Despite extensive experimental research for decades, it is still a challenge to find a stable cathode material for both discharge (ORR) and charge (OER) reactions with a low overpotential. Here, we discuss how our computations have helped us understand the roots of great efficiency of Mo<sub>3</sub>P nanoparticles as ORR and OER catalyst for Li-air batteries, as measured by our experimental collaborators in the Asadi group. Our DFT results show that the Mo-terminated Mo<sub>3</sub>P (110) surface will be spontaneously oxidized in the oxygen-rich environment, thus forming a kinetically stable MoO layer to bring about the initial Li<sup>+</sup>/e<sup>-</sup> transfer from aprotic electrolyte to cathode. This study can help shed fundamental insight on the role of ultrathin oxide monolayers on phosphide nanoparticles, and how this can potentially lead to a new nanomaterials design dimension.

Finally, we will also present the result of our recent collaboration aimed at creating a novel electrochemical synthesis route for porphyrin-based COFs. [4] We discovered the important role of solvent molecules used during the synthesis process in dictating the composition of synthesized crystals, which turned out to be pyridine-COF co-crystals. The hybrid structures are shown to be ORR active. In addition to the degree of freedom provided by introducing different (pyridine-like) groups into the COF network, such systems can be doped with single-atom active sites at the porphyrin rings. We will discuss how changing the metallic dopant and the COF stacking structure (coupled to the guest molecules), can create a considerable design space to significantly enhance the ORR activity of these materials.

### Grant Numbers and Grant Titles:

DE-SC0019281 : De novo Materials Design of Catalytic Surface Motifs for Water-Gas-Shift

**Postdoc(s):** Arvin Kakekhani, Zhen Jiang

**Student(s):** Tian Qiu, Robert Wexler, Sayan Banerjee

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

1. Barzilay M, Qiu T, Rappe AM, Ivry Y. Epitaxial  $\text{TiO}_x$  Surface in Ferroelectric  $\text{BaTiO}_3$ : Native Structure and Dynamic Patterning at the Atomic Scale. *Advanced Functional Materials*. 2019 Jun 17;1902549. <https://doi.org/10.1002/adfm.201902549>
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3. Wexler RB, Qiu T, Rappe AM. Automatic Prediction of Surface Phase Diagrams Using *Ab Initio* Grand Canonical Monte Carlo. *The Journal of Physical Chemistry C*. 2019 Jan 3;123(4):2321-8. <https://doi.org/10.1021/acs.jpcc.8b11093>
4. Tavakoli E, Kakekhani A, Kaviani S, Tan P, Mohammadi Ghalehi M, Asle Zaeem M, Rappe AM, Nejati S. In Situ Bottom-up Synthesis of Porphyrin-based Covalent Organic Frameworks. *Journal of the American Chemical Society*. 2019 Nov 11. <https://doi.org/10.1021/jacs.9b10787>
5. Rappe AM. Ionic gating drives correlated insulator–metal transition. *Proceedings of the National Academy of Sciences*. 2018 Sep 25;115(39):9655-7. <https://doi.org/10.1073/pnas.1812913115>
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# Learning Quantum Monte Carlo Forces

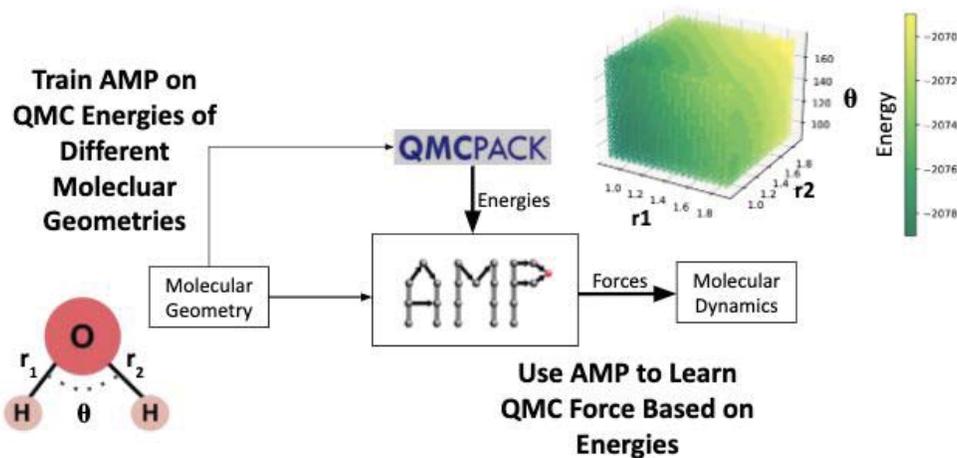
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Department of Chemistry, Brown University, Providence, RI 02906

Part of the “Bridging the Time Scale in Exascale Computing of Chemical Systems” DOE CCS Center,  
Lead PI: Prof. Andrew Peterson, Brown University

## Abstract

For decades, the primary Achilles’ heel of Quantum Monte Carlo (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 [1, 2]. Indeed, soon to be published Diffusion Monte Carlo studies have shown that QMC force calculations can scale as high as  $N^7$  with the usual statistical QMC prefactor. Here, we use artificial neural networks within the Atomic Machine Learning Package (AMP) [3] to learn the potential energy landscapes and forces governing intra- and intermolecular dynamics. As illustrated in the Summary Figure below, we obtain QMC energies using the Diffusion Monte Carlo (DMC) method within QMCPACK. We then employ those



**Summary Figure:** In this work, we use QMC energies for different molecular geometries and molecular ensembles from QMCPACK to train neural networks in AMP that output forces for use in molecular dynamics simulations.

energies to train an energy-based neural network in AMP. Lastly, AMP provides forces that are employed to run molecular dynamics simulations in the NVT ensemble. In contrast with most approaches, because QMC cannot readily provide our networks with forces, we extract forces from a network exclusively trained on energies. Our work is therefore also an exacting test of the quality of our neural networks. As an initial demonstration of our technique, we have used our network to relax the geometry of a single, distorted water molecule and the configurations of water clusters, whose subtle

intermolecular interactions benefit from the high-accuracy energies QMC techniques can provide. We show that, with just a few hundred DMC energies, we can obtain sufficiently accurate forces for the water molecule that we can successfully reproduce average bond lengths and angles, as well as position correlation functions, from *ab initio* molecular dynamics simulations. Moving forward, we will benchmark our forces against those directly produced via QMC simulations and adapt our methods to the relaxation of small transition metal-containing molecules known to require high accuracy electronic structure techniques. We moreover look forward to integrating our work with larger center efforts to develop active learning techniques that will be able to selectively train on QMC energies to correct Density Functional Theory-based models of water dynamics.

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**Grant Number:** SC0019441

**Grant Title:** “Bridging the Time Scale in Exascale Computing of Chemical Systems” DOE CCS Center

**Student:** Cancan Huang

**Publication Forthcoming**

## Theoretical and Experimental Studies of Elementary Hydrocarbon Species and their Reactions

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### Abstract

Our current DOE grant involves both theory and experiment. Our colleague Gary Douberly carries out beautiful spectroscopic experiments in liquid helium droplets. Part of our DOE research program involves the theoretical interpretation of these challenging experiments. In 2019 we had four joint papers together.

*Ethyl + O<sub>2</sub> in Helium Nanodroplets: Infrared Spectroscopy of the Ethylperoxy Radical.* Helium-solvated ethylperoxy radicals (CH<sub>3</sub>CH<sub>2</sub>OO·) are formed via the *in situ* reaction between the <sup>2</sup>A' ethyl radical and <sup>3</sup>Σ<sub>g</sub><sup>-</sup> dioxygen. The reactants are captured sequentially through the droplet pick-up technique. Helium droplets are doped with ethyl radicals via pyrolysis of di-*tert*-amyl peroxide or *n*-propyl nitrite in an effusive, low-pressure source. An infrared spectrum of ethylperoxy, in the CH stretching region, is recorded with species-selective droplet beam depletion spectroscopy. Spectral assignments are made via comparisons to second-order vibrational perturbation theory with resonances (VPT2+K) based on coupled-cluster full quartic force fields. Cubic and quartic force constants, evaluated using a small basis set, are transformed into the normal coordinate system of the higher level quadratic force constants. This transformation procedure eliminates the mismatch between normal modes, which is a source of error whenever normal coordinate force constants from different levels of theory are combined. The spectrum shows signatures of both the *C*<sub>1</sub> *gauche* and *C*<sub>s</sub> *trans* rotamers in an approximate 2:1 ratio, despite the prediction that the *gauche* rotamer lies 44 cm<sup>-1</sup> lower on the zero-Kelvin enthalpic potential surface for torsional interconversion. Helium droplets are 0.4 K at equilibrium; therefore, *in situ* ethylperoxy production is highly non-thermal.

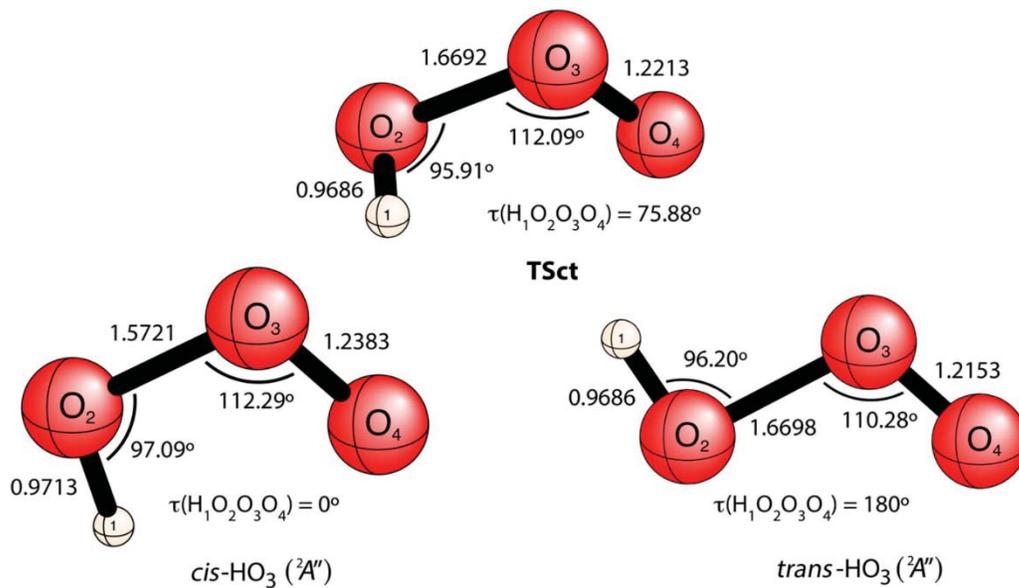
*Tert-Butyl Peroxy Radical: Ground and First Excited State Energetics and Fundamental Frequencies.* Alkylperoxy radicals (RO<sub>2</sub>) are key intermediates in combustion and atmospheric oxidation processes. As such, reliable detection and monitoring of these radicals can provide a wealth of information about the underlying chemistry. The *tert*-butyl peroxy radical is the archetypal tertiary peroxy radical, yet its vibrational spectroscopy is largely unexplored. To aid in future experimental investigations, we have performed a high-level theoretical study of the fundamental vibrational frequencies of the ground- and first excited states. A conformer search on both electronic surfaces reveals single minimum-energy structures. We predict an A <sup>2</sup>A' ← X <sup>2</sup>A'' adiabatic excitation energy of 7738 cm<sup>-1</sup> via focal point analysis, approximating the CCSDT(Q)/CBS level of theory. This excitation energy agrees to within 17 cm<sup>-1</sup> of the most precise experimental measurement. We compute CCSD(T) fundamental vibrational frequencies via second-order vibrational perturbation theory (VPT2), using a hybrid force field in which the quadratic (cubic/quartic) force constants are evaluated

with the ANO1 (ANO0) basis set. Anharmonic resonance polyads are treated with the VPT2+K effective Hamiltonian approach. Among the predicted fundamental frequencies, the ground state O-O stretch, excited state O-O stretch, and excited state C-OO bend fundamentals are predicted at 1138, 959, and 490  $\text{cm}^{-1}$ , respectively. Basis set sensitivity is found to be particularly great for the O-O stretches, similar to what has already been noted in smaller, unbranched peroxy radicals. Exempting these particular O-O stretches, agreement with the available experimental fundamentals is generally good ( $\pm 10 \text{ cm}^{-1}$ ).

*Criegee Intermediate Modeling.* Another paper that we would like to highlight is the published work titled “The Addition of Methanol to Criegee Intermediates.” Carbonyl oxides, commonly known as Criegee intermediates (CI), first gained attention as intermediates in the ozonolysis of alkenes. The important role that CIs play in tropospheric chemistry has motivated the study of its reactions with a number of different species including alcohols. In our research, we investigated using high-level theoretical methods the potential energy surface of the reactions between formaldehyde and acetone oxide with methanol, which proceeds through CIs. Experimentally it has been shown that there is a dual temperature dependence for the rate constant of the reaction of acetone oxide with methanol. We found that the height of the transition state barrier solely commands this behavior and not multiple reactions paths, as had been previously suggested.

*Collaborations with DOE Laboratories.* The HFS PhD student Sarah Elliott holds a prestigious DOE Computational Science Graduate Fellowship. This has allowed Sarah to spend the summers of 2017, 2018, and 2019 at Argonne National Laboratory. Sarah reported to Stephen Klippenstein, but also interacted with Ahren Jasper, Yuri Georgievskii, and Murat Keceli. As a result, Sarah was second of eleven authors on the paper “Automated Computational Thermochemistry for Butane Oxidation: A Prelude to Predictive Automated Combustion Kinetics,” published in the *Proceedings of the Combustion Institute* 37, 363–371 (2019). In November 2019, as first author Sarah submitted another paper (#10 in the list below), to be published in 2020 in the same journal. Because of Sarah’s role at Argonne, two of my excellent PhD students, Andreas Copan and Kevin Moore, accepted postdoc positions at Argonne in June 2018. Andreas accepted a faculty position in August 2019, while Kevin continues as a postdoc with Stephen Klippenstein.

A more recent but very productive collaboration is underway with Sandia Laboratory Livermore scientists Leonid Sheps, David Osborn, and Craig Taatjes. The glue that holds this venture together is Brandon Rotavera, a former Sandia Livermore postdoc who is now an assistant professor of Engineering at the University of Georgia. Our HFS PhD student Matt Davis and our CCQC Senior Scientist Justin Turney are very involved in this collaboration, as is HFS. Two papers, submitted recently to the *Proceedings of the Combustion Institute*, investigate reaction mechanisms associated with the cyclic ether intermediates ethyloxirane and dimethyloxirane.



Very high level theoretical studies of the *cis* and *trans* structures of HO<sub>3</sub> and the transition state connecting them. The *trans* HO<sub>3</sub> structure lies 0.52 kcal/mol below *cis*. The barrier for the *cis-trans* isomerization is 0.27 kcal/mol. This miniscule barrier demonstrates that HO<sub>3</sub> can undergo isomerization at energies significantly below the dissociation threshold, which is 2.80 kcal/mol. See Reference 3 on the next page.

Theoretical and Experimental Studies of Elementary Hydrocarbon Species and Their Reactions

Senior Scientist: Justin T. Turney

Students: Gustavo Aroeira, Marcus Bartlett, Matthew Davis, Sarah N. Elliott, Marissa L. Estep, Whitney J. Morgan, Jared Weidman, Mark Wolf

Ten Recent DOE Sponsored Publications, 2019 - 2020

1. A. E. Wiens, A. V. Copan, and H. F. Schaefer, "Multi-Fidelity Gaussian Process Modeling for Potential Energy Surfaces," *Chem. Phys. Lett. X* **3**, 100022 (2019).
2. G. J. R. Aroeira, A. S. Abbott, S. N. Elliott, J. M. Turney, and H. F. Schaefer, "The Addition of Methanol to Criegee Intermediates," *Phys. Chem. Chem. Phys.* **21**, 17760 (2019).
3. M. A. Bartlett, A. H. Kazez, H. F. Schaefer, and W. D. Allen, "Riddles of the Structure and Vibrational Dynamics of HO<sub>3</sub> Resolved Near the *Ab Initio* Limit," *J. Chem. Phys.* **151**, 094304 (2019).
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## Surface Plasmon Enhanced Chemistry

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**Program Scope:** This project is concerned with the development of computational methods and new theory that enable 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:****1. A nonadiabatic molecular dynamics study of plasmon-induced hot-carrier photochemistry.**

Recent experiments at Rice University 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  $D_2$ . We have recently used real-time TDDFT combined with Ehrenfest NAMD to model this process,<sup>2</sup> based a jellium description of a 2 nm gold nanoparticle that shows plasmonic excited states (see structure in Fig. 1a and spectrum in Fig. 1e) and a local density (LDA) approximation for  $H_2$ . Using the OCTOPUS code, we demonstrated how the excitation of plasmon modes of the cluster lead to electron transfer to an antibonding

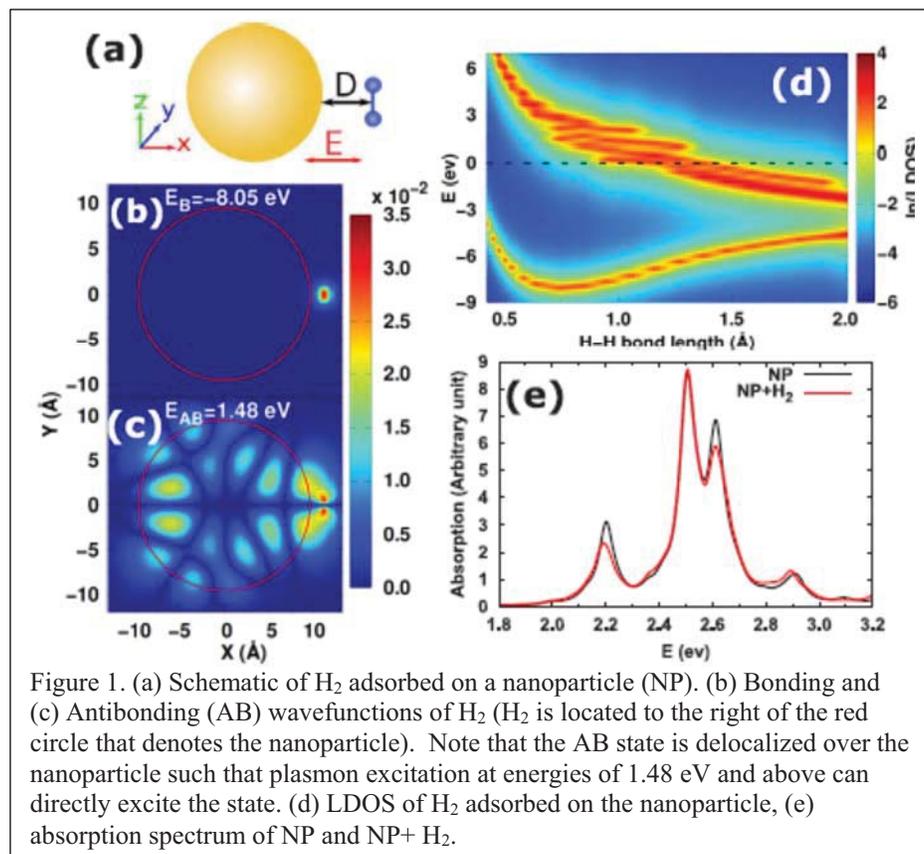


Figure 1. (a) Schematic of  $H_2$  adsorbed on a nanoparticle (NP). (b) Bonding and (c) Antibonding (AB) wavefunctions of  $H_2$  ( $H_2$  is located to the right of the red circle that denotes the nanoparticle). Note that the AB state is delocalized over the nanoparticle such that plasmon excitation at energies of 1.48 eV and above can directly excite the state. (d) LDOS of  $H_2$  adsorbed on the nanoparticle, (e) absorption spectrum of NP and NP+  $H_2$ .

state of  $H_2$  (see Fig. 1c and 1d) resulting in dissociation of the molecule as displayed in Fig. 2. Dissociation was found to be of high probability as long as the frequency of light was in the range 2-3 eV where

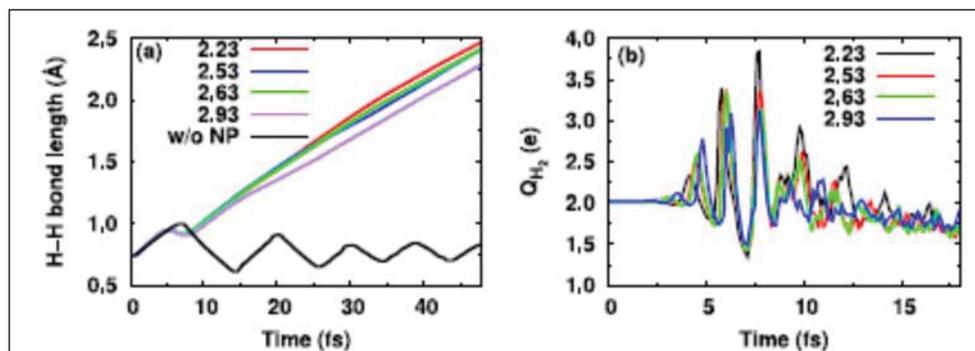


Figure 2. (a) Real-time dynamics of H<sub>2</sub> bond length with and without the NP. For H<sub>2</sub> without NP, no dissociation occurs at a photon energy of 2.53 eV, but with the NP, H<sub>2</sub> dissociation is rapid for photon energies that match the absorption peaks in Fig. 4. (b) Total charge on the H<sub>2</sub> molecule rises from 2 to about 3 as a function of time after the ultrafast pulse, corresponding to occupation of the antibonding orbital of H<sub>2</sub> that results in dissociation.

plasmonic states can be excited. An analysis of orbital populations (Fig. 2b) indicated that the antibonding state of H<sub>2</sub> transiently receives substantial occupation after photoexcitation. We also found that when H<sub>2</sub> is located at the hot-spot of a dimer of gold particles, electron transfer from one particle to H<sub>2</sub> is immediately followed by a second electron transfer to the other particle, and

dissociation is suppressed. This suggests that the most effective structures for local field enhancement are not necessarily the best for plasmonic chemistry.

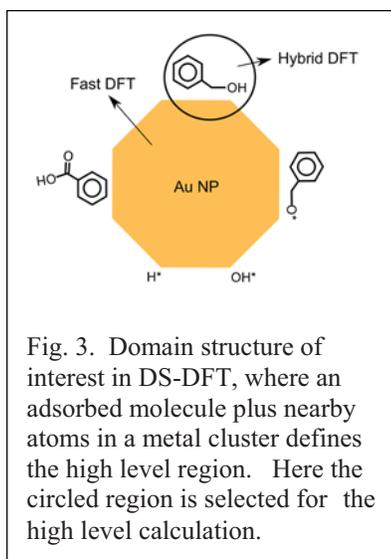


Fig. 3. Domain structure of interest in DS-DFT, where an adsorbed molecule plus nearby atoms in a metal cluster defines the high level region. Here the circled region is selected for the high level calculation.

**2. Embedding approaches to density functional theory (DFT).** A long term goal of theory in studies of plasmonic properties is to develop electronic structure methods that are capable of describing plasmons in metal nanoclusters (used both for understanding experimental studies of clusters and as models of the plasmonic behavior in much larger nanoparticles). Several years ago we discovered that TDDFT works well in this regard for bare clusters of silver and gold, however this approach encounters serious difficulty in the description of organic molecules interacting with the metal clusters due to delocalization/self interaction errors. These errors lead to charge transfer (CT) states that can be low in energy by 1 eV or more, often resulting in CT state energies that are below the plasmon energy rather than at or above as is usually the case. This leads to a number of problems, such as inaccurate estimates of CT contributions to SERS enhancements, and incorrect prediction of hot electron yields that result in chemical reactions in the adsorbed molecules. As an alternative we are developing a new embedding

electronic structure theory in which a high level method (capable of including CT) is used to describe dynamical properties in a small portion of a larger system, while a lower level theory is used to describe everything else. This is called domain separated DFT (DS-DFT).<sup>7,9</sup> DS-DFT defines regions within a molecule (circled in Fig. 3) where the higher level theory is to be turned on relative to a low level theory that is used everywhere, and then DFT is developed with a Hamiltonian that smoothly evolves (as dictated by a switching function) from one region to the other. A key aspect of this approach is that the modified Hamiltonian can be evaluated using conventional density fitting methods, and therefore that this algorithm can be implemented with small modifications into any conventional DFT code. We have demonstrated its capabilities with applications to model systems involving small hydrocarbons, where the high level theory, such as a hybrid functional is turned on for a selected portion of the molecule and then a generalized gradient method is used elsewhere.

**3. Developing semiempirical electronic structure methods for describing plasmonic silver clusters.** As an alternative to DS-DFT, we have developed semiempirical theory (INDO with single CI) to describe

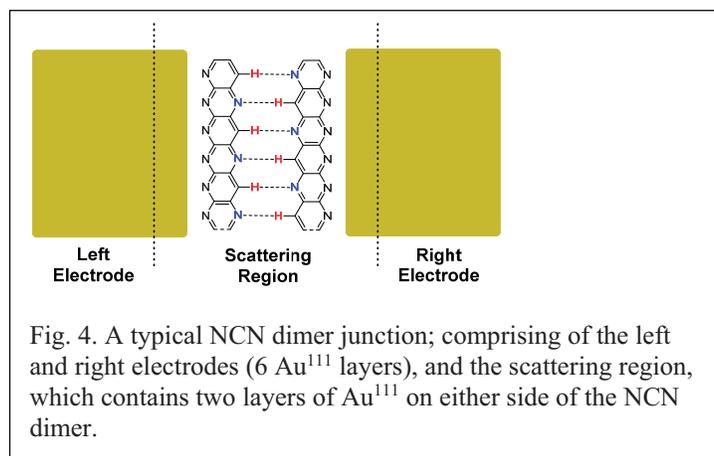
plasmon excited states, including a recent study in which we demonstrated that one can describe electrochemical formal potentials and plasmonic properties with the same INDO/S method, which is of interest in describing electrochemical SERS and TERS.<sup>3</sup> Of course, INDO/S methods have their own errors, so our recent attention to DS-DFT will hopefully supersede INDO/S.

**4. Hybrid Maxwell-Liouville and Maxwell-master equation approaches to describing excited state dynamics in the presence of plasmonic particles.** An important issue in plasmonics involves the time evolution of excited molecules in the presence of plasmonic particles. Even when there isn't charge transfer, the nanoparticle can still strongly influence a number of optical processes involving the molecule including absorption and emission that is enhanced (or quenched) by the particles. The particles can also influence nonradiative processes, and the transfer of energy from the molecule to the particle or to other molecules. We have developed a master equation approach to describe these processes in which the master equation describes the evolution of populations of 4 or 6 quantum states of the molecules that are coupled to Maxwell's equations for describing the effect of an external light source that interacts with the plasmonic particles. By including stimulated emission in the rate equations, we have used this approach to describe an unusual laser system that consists of an array of aluminum nanoparticles that supports lattice-mode plasmon resonances that are coupled to laser dyes. This application has proven useful for interpreting experiments done in the lab of my colleague Teri Odom.<sup>1,4,10</sup>

**5. Electronic structure approaches for characterizing the excited states of plasmonic clusters interacting with ligands.** We have used TDDFT methods to develop new approaches to the characterization of electronic states in ligand-protected metal clusters. In a recent study,<sup>8</sup> we developed an algorithm for examining electronic structure results that allows us to identify plasmonic states even when the states are strongly perturbed by ligands. This knowledge is important to understanding the transition from non-plasmonic spectra for small clusters to plasmonic spectra for large ones.

**6. Electron transport in molecular junctions.** Molecules that bridge the gap between two gold electrodes

provide both an opportunity to study plasmonics, and to study electron transport. Our studies of electron transport<sup>6</sup> were concerned with model junctions (Fig.4) which have hydrogen-bonds between the edges of a series of prototype noncovalent nanobelts (NCNs). Their conductance properties were studied with non-equilibrium Green's functions density functional theory (NEGF-DFT). We found the trends in their electrical properties are correlated with the nature of the H-bond arrays; notably those of an uncooperative nature have large electrical n-type conductances, while those of



cooperative have low p-type conductances.

**Future Plans:** Our renewal proposal seeks to extend our studies of plasmon-enhanced chemistry through the development of domain separated time dependent density functional theory (DS-TDDFT), which generalizes DS-DFT to the calculation of optical properties. This embedding theory should be capable of defining the electronic states of metal nanoparticles plus adsorbed molecules including both plasmonic states and states associated with charge transfer. We have also proposed to develop methods for describing the time dependence of the electron and nuclear dynamics that occurs when the nanoparticles are irradiated with a pulse of light, including theories that describe both direct charge transfer to the adsorbed molecules,

and that describe plasmon excitation followed by dephasing to electron-hole pairs and the indirect excitation of charge transfer states. Another component of this project is the use of a recently developed second linear response TDDFT method to calculate transient absorption spectra and electronic Raman spectra for the metal plus molecule systems, and using these new approaches to provide insights about excited state dynamics that relates to plasmon induced chemistry.

### **Grant Numbers and Grant Titles**

Theory work in the work described above was supported by: DOE DE-SC0004752: **Surface Plasmon Enhanced Chemistry**

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

Postdocs: Charles Cherqui (12), Martin Mosquera (1p)

Students: Marc Bourgeois (12)

### **Up to Ten Publications Acknowledging the Grant**

1. Stretchable nanolasing from hybrid quadrupole plasmons, Danqing Wang, Marc R. Bourgeois, Won-Kyu Lee, Ran Li, Dhara Trivedi, Michael P. Knudson, Weijia Wang, George C. Schatz, Teri W. Odom, *Nano Lett.* 18, 4549-4555 (2018) DOI:10.1021/acs.nanolett.8b01774

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## Crystal growth and nucleation at metal-organic framework / solution interfaces

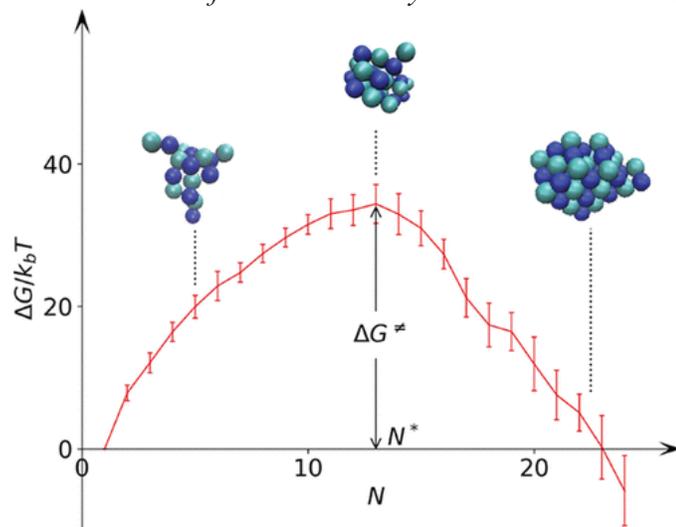
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### Abstract

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 simulate the nucleation of weak electrolytes, and the extension of these methods to large/complex solutes such as MOFs; and (ii) studies of the structure of ZIF interfaces under conditions relevant to crystal growth; and (iii) addressing important open questions in the mechanism of MOF solvent-assisted linker exchange (SALE), and important synthetic pathway for MOFs.

*Nucleation of weak electrolytes.* Predictive modeling of the nucleation of weak electrolytes presents



**Figure 1. Free energy of salt cluster as a function of cluster, under modest supersaturation conditions.**

fundamental challenges of widespread relevance in many domains (e.g.  $\text{CaCO}_3$ /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.

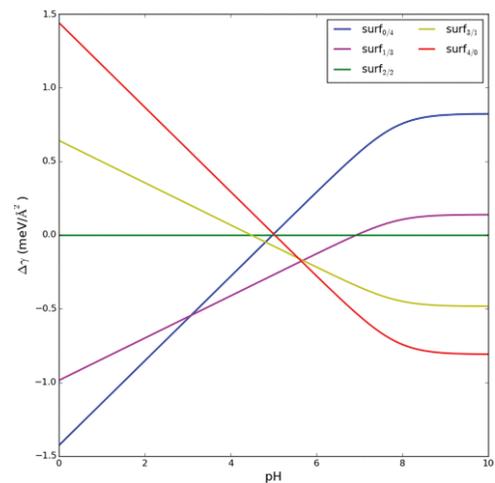
We recently published a manuscript documenting this method and demonstrating its application in a low-solubility rock salt structure (e.g. LiF) in aqueous solution (see Figure 1). The elegance of this choice of model system is that it makes it possible to “benchmark” our method via comparison with large-scale (multi- $\mu\text{s}$ ) brute-force molecular dynamics of the same system. Crucially, we find good agreement between the molecular dynamics (which is infeasible for most weak electrolytes) and our new method. Note that in addition to predicted free energies, we can also access structures of the evolving salt cluster during the course of nucleation, which provides additional mechanistic insight.

More recently we have been working to extend this method to apply to larger and far more structurally complex solutes, such as  $\text{CaCO}_3$  and MOFs. The presence of large, polyatomic cations/anions makes a simple GCMC-based approach more difficult to apply in such cases. As such, we have developed an elegant extension to the above protocol that utilizes a highly parallel “swarm” approach and GPU-accelerated thermodynamic integration to sequentially calculate the free energies on ensembles of increasing cluster size. We are currently benchmarking this method on a  $\text{CaCO}_3$  system for ultimate applications to ZIFs.

*Structure of ZIF-solution interfaces.* Over the last year, we also used a combination of DFT calculations and our previously developed ZIF force fields to predict the structure and surface termination of ZIF interfaces under both gas-phase “post-synthetic” and solution-phase conditions. In the case of gas-phase, we find that ZIF surfaces are almost inevitably terminated primarily by imidazole-related species, rather than residual adsorbed solvent. This termination remains stable even under high relative humidity and extremely low imidazole (Hmim) partial pressure, and thus we expect that it would be altered only via prolonged heating under vacuum (to remove any desorbed Hmim).

In the case of solution, the situation is more complex. Under high solute-phase imidazole concentrations, a fully imidazole terminated surface remains quite stable. However, at low pH, where the free (unprotonated) Hmim concentrations becomes low, partial and even total solvent incorporation may occur (see Figure 2), where we use the notation “surf<sub>n/m</sub>” to denote surface terminations with n imidazole species and m water ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ) species. These predictions are consistent with prior experimental observations of ZIF evolution under acid exposure, which was shown to result in water/hydroxyl incorporation as detected via both IR and XPS. Small free Hmim concentrations can also arise from the use of stoichiometric Zn:Hmim ratios, e.g., as is common in solvothermal synthesis, cases where in situ AFM has also shown evidence for surface solvent incorporation, consistent with our phase diagram predictions. We anticipate that these diagrams may provide a useful predictive tool in understanding how ZIF surface structure may be altered/controlled as a function of both synthetic and postsynthetic conditions, with associated impacts on ZIF interfacial properties, including those governing surface mass transport barriers.

*Mechanism of solvent-assisted linker exchange in ZIFs.* Very recently, we have also begun to examine another important process of relevant to MOF/ZIF synthesis: solvent-assisted linker exchange (SALE). In SALE, MOFs are exposed to concentrated solutions of alternative organic linkers, resulting in the slow exchange with the original linking groups. This SALE process is a vital tool in accessing MOFs in specific topologies for which often no direct synthetic route is possible. Our work is focusing on resolving significant open question in the mechanism in SALE, including the role of spontaneous or solvent-induced defects, associative vs. dissociate pathways, and/or the role of solvent in catalyzing the SALE process. We are utilizing plane-wave DFT calculations (and ultimately QM/MM approaches) in ZIFs to model the SALE process and its inherent barriers both in the presence and absence of additional solvent, making comparison against existing experimental data. We are also directly evaluating various proposed mechanisms for SALE. We anticipate that the resulting insights into the SALE mechanism will aid in the overcoming current challenges in the “targeted” synthesis of MOFs, including those identified by various ongoing high-throughput computational screenings.



**Figure 2.** ZIF-8 surface phase diagram at 298K in aqueous solution vs pH; favored surface exhibits lowest surface energy.

## 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., Structure and Thermodynamic Stability of Zeolitic Imidazolate Framework Surfaces. *J. Phys. Chem. C* **2020**, 124, 1458.
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## Accurate wave functions expressed as polynomial product states

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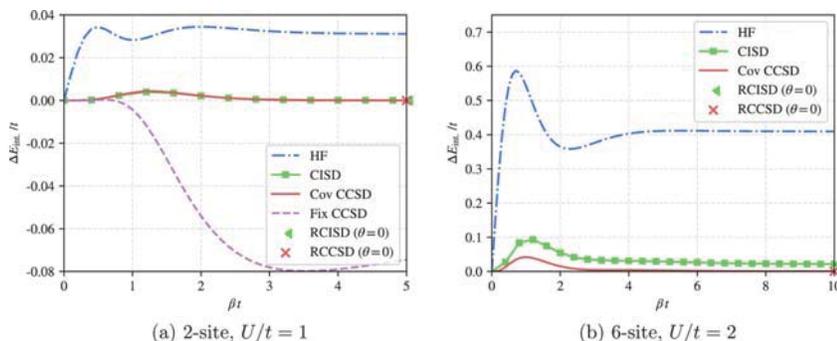
### Program Scope

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 [8] 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 [9-10], 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 [9-10].



**Figure Caption:** Error in internal energy for thermal HF, covariant CISD, fixed-reference and covariant thermal CCSD for (a) two-site and (b) six-site Hubbard models with  $U/t = 1$  and 2, respectively, 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%), Rishab Dutta (Graduate Student, 100%), Tom Henderson (Senior Research Associate, 30%)

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<https://doi.org/10.1021/acs.jctc.9b00744>

## Development of Metal-Free Photocatalysts (Grant Number DE-SC0019327)

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### 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.

### Recent Progress

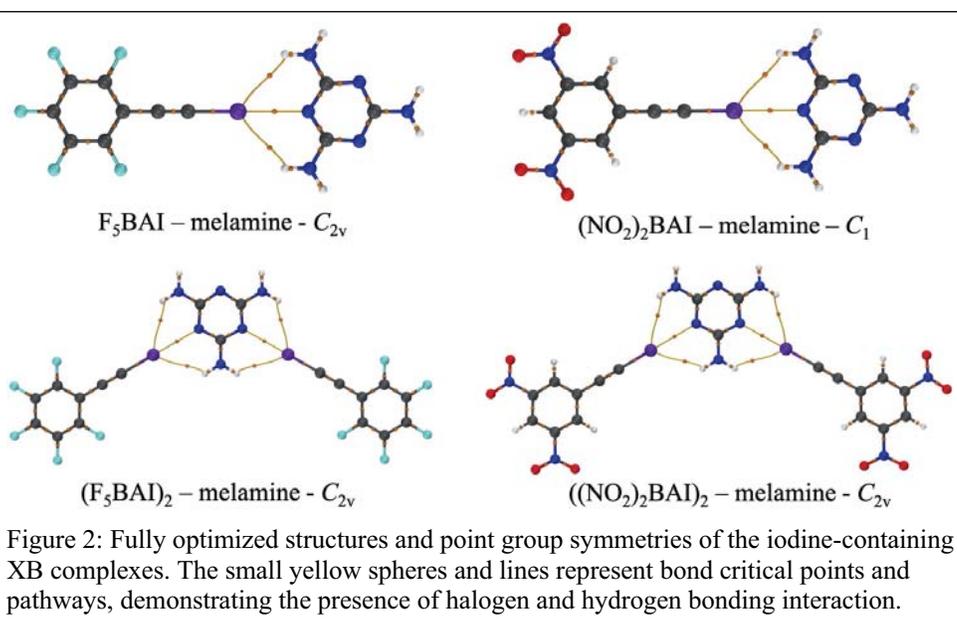
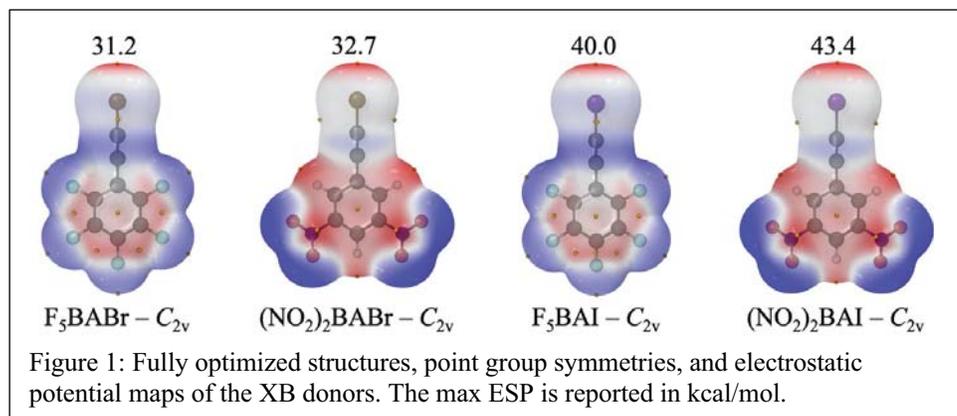
As a first step toward understanding the structure and surface chemistry of doped carbon 2D materials, we examined a set of molecular analogues to glean insight into how noncovalent interactions affect their assembly properties. An interaction similar to a hydrogen bond can occur between a terminal halogen atom within a molecule and a nucleophilic region on a Lewis base, known as a halogen bond (XB). A provocative concept is to leverage halogen bonding, in concert with other noncovalent interactions, to generate material assemblies with desired properties. Here we focus on structural, energetic, and vibrational properties in a series of dinitro and pentafluoro substituted bromo and iodoethynyl benzene XB donors (denoted  $F_5BAX$  and  $(NO_2)_2BAX$ , where  $X = Br, I$ ). Particular emphasis is placed on the molecular properties of not only the XB donors but also of the 1:1 and 2:1 donor:acceptor complexes formed between each XB donor and either of two graphitic carbon nitride building blocks, melamine or heptazine. Full geometry optimizations and harmonic vibrational frequency computations were performed using density functional theory with M06-2X and a suitable basis set augmented with diffuse functions on all atoms and relativistic pseudopotentials on bromine and iodine centers (*i.e.*, aug-cc-pVDZ for H, C, N, O, F and aug-cc-pVDZ-PP for Br, I; denoted aVDZ-PP). To better understand the relationship between the complex interaction strength and stretching frequencies (C–X and C≡C), the magnitude of electron density transfer upon complexation is probed using natural bond orbital, and bond critical point and pathway analyses on the M06-2X/aVDZ-PP optimized geometries. This prescription provides the means to systematically evaluate the connection between the various molecular properties of each XB donor, acceptor, and their corresponding complex.

The fully optimized structures, point group symmetries, and the corresponding electrostatic potential maps of the isolated XB donors are depicted in Figure 1. The planar  $C_{2v}$  structures exhibit several localized regions of electron density associated with the halogen atoms, namely the  $\sigma$ -hole and the belt. The effectiveness of a XB donor is governed by the magnitude of the  $\sigma$ -hole, which in this case ranges from +31 kcal mol<sup>-1</sup> to +43 kcal mol<sup>-1</sup> ( $(NO_2)_2BAI > F_5BAI > (NO_2)_2BABr > F_5BABr$ ). We surmise the overall interaction strength of a series of XB complexes will track with the magnitude of the  $\sigma$ -hole of the isolated XB donors. That is, XB donors with large  $\sigma$ -holes should exhibit stronger interactions than their less electropositive counterparts. Regarding the XB donors, acceptors, and

complexes studied in this work, that does appear to be the case. The interaction energies of the bromine- and iodine-containing 1:1 complexes are roughly  $-7$  kcal mol $^{-1}$  and  $-9$  kcal mol $^{-1}$ , whereas the 2:1 complexes are roughly  $-13$  kcal mol $^{-1}$  and  $-18$  kcal mol $^{-1}$ , respectively. The

relatively large differences between the interaction strengths of these nearly additive complexes are attributed to (i) the transfer of electron density from the acceptor to the donor upon XB formation and (ii) the emergence of supplemental hydrogen bonding interactions between the amine groups of the acceptor and the electronegative belt of the donor (Figure 2). Although these concepts are only presently discussed in terms of the structure and energetics, they can certainly be extended to trends in the vibrational properties of the donors. Overall, the results of this work suggest that the tunability of XBs is perfectly suited to

adjust the interaction strength on a fine level, allowing for additional control over co-crystal formation and supramolecular assembly. This investigation is ongoing and computations involving additional donors, including ones involving astatine atoms, and other suitable graphitic carbon nitride derivatives are currently underway.



### Future Plans

Our previous work has demonstrated 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 continue 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 quantum dots. 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. These studies are underway currently. Later phases of the project will combine graphitic carbon nitride with other materials to form metal-free composites for photocatalysis.

**Postdoc:** Thomas Ellington

**Students:** Paul Brown, Emvia Calixte, Olatunde Olademehin

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## **Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment**

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### **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 (NPMs), (ii) discovery and selection of the most promising functional NPMs from databases of synthesized and hypothetical framework structures, and (iii) microscopic-level understanding of the fundamental interactions underlying the function of NPMs. A pivotal part of NMGC's success is a tight collaboration between leading experimental groups in the synthesis and characterization of NPMs and of computational groups that allows for iterative feedback.

Building upon prior NMGC research focused mostly on gas capture, separation and catalysis in crystalline NPMs, 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 NPMs, 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 NPMs 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 NPMs, 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 NPMs, and in computational methods to systematically identify and to characterize NPMs. The team is also working on the development of data repositories for NPMs 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 and the National Energy Research Scientific Computing Center.

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.

Research accomplishments achieved over the past 2.5 years include:

**Thrust A: Development of Methods to Accelerate Discovery of Functional NPMs:** (i) development of a systematic, machine-readable identification scheme for MOFs, called MOFid that includes the MOF topology and SMILES strings for the building blocks [63]; (ii) a major update to the Computation-Ready, Experimental (CoRE) MOF Database that includes about 15,000 and 10,000 porous structures with all or only free solvent molecules removed, respectively, and additional pore analytics, such as open metal site detection [69]; (iii) development of *SorbNet*, a deep neural network, that is trained on big data from high-throughput simulations and can predict multi-component adsorption isotherms over a wide range of temperatures and pressures to find optimal conditions for challenging separations (e.g., desorptive drying condition that enable the separation of valuable alkane diols (produced from renewable feedstocks) from water with 99.9% purity and > 99% recovery) [47]; (iv) development of M11plus, a range-separated hybrid meta functional with both local and rung-3.5 correlation terms and high across-the-board accuracy for chemical applications [59].

**Thrust B: Discovery of NPMs for Challenging Chemical Separations:** (i) high-throughput simulations to obtain the adsorption isotherms of 24 distinct molecules in 9 different hyper-cross-linked polymers that vary in both the monomer composition and cross-link density [52]; (ii) first principles Monte Carlo simulations in the Gibbs ensemble allowing us to predict unary and binary adsorption isotherms ( $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2/\text{N}_2$ , and  $\text{CO}_2/\text{H}_2\text{O}$ ) in Mg-MOF-74 and to assess the performance of ideal adsorbed solution theory for a MOF with open metal sites [24]; (iii) the discovery of zirconium-based MOFs for the removal of protein-bound uremic toxin from human serum albumin [36].

**Thrusts C & D: Discovery of NPMs for Challenging Chemical Transformations and NPMs with Tailored Electronic Structures:** (i) spectroscopic and computational studies of two iron–semiquinoid MOFs that possess exceptionally high electrochemical capacities that show the importance of energy alignment between metal and ligand orbitals and of high electronic conductivity for the utilization of MOFs as energy storage materials for a wide range of battery chemistries [76]; discovery of MOFs for the chemiresistive detection of small hydrocarbons where the relative sensitivity is found to correlate strongly with the gas-phase specific heat capacity of the adsorbate and not with its binding strength to the MOF [43]; (iii) discovery that NU-901, a porous zirconium-node-containing MOF, can be rendered electronically conductive by physically encapsulating  $\text{C}_{60}$  within a fraction of the diamond-shaped cavities, where the conductivity originates from electron donor–acceptor interactions and some of the pore remain available for adsorption of other guest molecules [15].

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.



NMGC also develops and maintains the <https://ccs-psi.org/home> pages for the Computational Chemical Science Open Source Development Group.

The screenshot shows the homepage of the Computational Chemical Sciences Open-Source Software Development Group. The main header includes the group's logo and a brief description of the initiative. Below the header is a navigation menu with links for Home, Awards, Software, Workshops, Highlights, and Submit. The page is divided into several sections:

- Recently Added Software:** Lists software packages like FLOSIC18, QMMM, and GAMESS with their release dates.
- Recently Added Highlights:** Lists research highlights such as 'Deep Neural Network Learning of Complex Binary Sorption Equilibria' and 'Energy-Based Descriptors to Rapidly Predict Hydrogen Storage'.
- Upcoming Workshops:** Lists workshops like 'Molecular Simulation with Machine Learning'.
- Project Table:** A table listing ongoing projects, their centers, and lead PIs.

Project Title	Center Name	Lead PI
Development of Exascale Software for Heterogeneous and Interfacial Catalysis	Development of Exascale Software for Heterogeneous and Interfacial Catalysis	Gordon
Scalable Predictive Methods for Excitations and Correlated Phenomena	SPEC	Xantheas
Exascale-Enabled Computational Tools for Complex Chemical Systems	Exascale Catalytic Chemistry (ECC) Project	Zádor
Predictive Hierarchical Modeling Of Chemical Separations And Transformations In Functional Nanoporous Materials	Nanoporous Materials Genome Center (NMGC)	Stepmann
Efficient Density Functional Theory Calculations without Self-Interaction	The Fermi-Löwdin Orbital Self-Interaction Correction (FLOSIC) Center	Jackson
Computational Chemical Science Center: Chemistry in Solution and at Interfaces	Chemistry in Solution and at Interfaces	Car
SPARC-X: Quantum simulations at extreme scale - reactive dynamics from first principles		Suryanarayana
Machine Learning for Excited-State Dynamics		Lewis
Ab initio Molecular Dynamics Beyond Density Functional Theory		Miller

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Kunhuan Liu (NU), Nathan London (Cornell), Mukunda Mandal (UMN), Ryan A. Murphy (UCB), Julia Oktawiec (UCB), Riddhish Pandharkar (UMN), Jesse G. Park (UCB), Roshan A. Patel (UMN), Hung Q. Pham (UMN), Thang Pham (NU), Debmalya Ray (UMN), Yangzhesheng Sun (UMN), Dayou Zhang (UMN).

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- [69] Y. Chung, E. Haldoupis, B. Bucior, **M. Haranczyk**, S. Lee, H. Zhang, K. Vogiatzis, M. Milisavljevic, S. Ling, J. Camp, B. Slater, **J. I. Siepmann**, **D. S. Sholl**, and **R. Q. Snurr**, “Advances, Updates, and Analytics for the Computation-Ready, Experimental Metal-Organic Framework Database: CoRE MOF 2019,” *J. Chem. Eng. Data* **64**, 5985–5998 (2019). DOI: [10.1021/acs.jced.9b00835](https://doi.org/10.1021/acs.jced.9b00835)
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- [43] 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)<sub>2</sub>] by Gas Adsorption,” *J. Am. Chem. Soc.* **141**, 5005–5013 (2019). DOI: [10.1021/jacs.9b00654](https://doi.org/10.1021/jacs.9b00654)
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# PROBING THE PARTIAL ACTIVATION OF WATER BY IONS & RADICALS

Program: *Vibrational Signatures of Electronic Properties in Renewable-Energy Catalysis*

PI: Prof. Ryan P. Steele

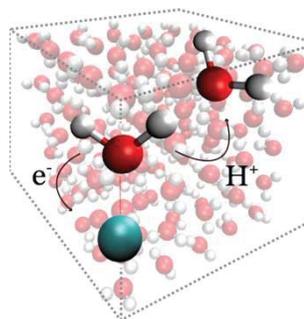
The University of Utah

Department of Chemistry &

Henry Eyring Center for Theoretical Chemistry

Salt Lake City, UT

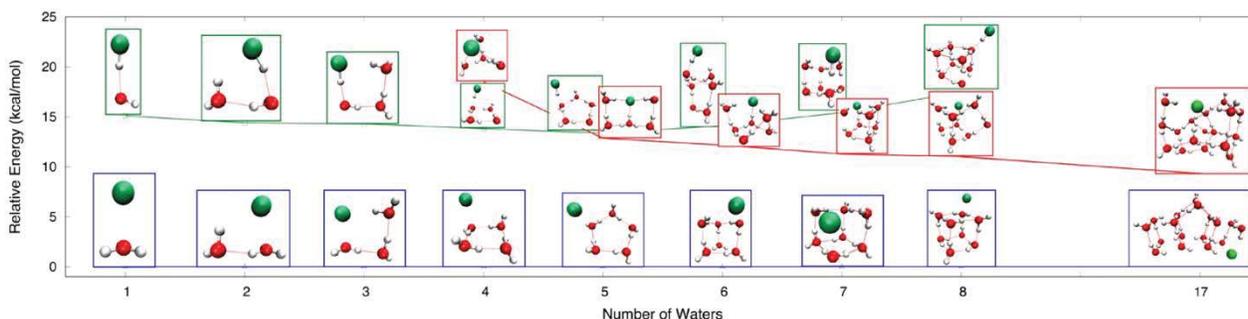
The interaction of water with reactive ions and radicals—including transition-metal catalysts—sits at the heart of water-oxidation chemistry for renewable-energy purposes. The scope of this program involves probing the manner in which the unique electronic interactions in catalysis manifest as observable vibrational signatures. Progress this year has involved the investigation of the spectral signatures of model complexes involving hydrated ions and radicals. This work has resolved long-standing mysteries in the literature, as well as predicted behavior of species in order to guide new experiments.



## Partial Activation via Open-Shell Interactions: $Cl\cdot(H_2O)_{1-17}$

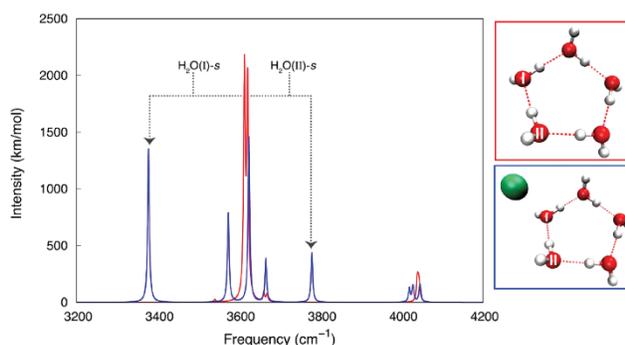
Serving as a model of both *d*-orbital-free water-splitting chemistry and atmospheric aerosol chemistry, these investigations sought to answer a seemingly simple question: What happens when a chlorine atom is dropped in a bucket of water? The thermodynamic limit of this process is known from simple energetic arguments. Namely, the high electron affinity of chlorine should lead to oxidation of the surrounding water. But in cluster environments and in the short timescales surrounding its behavior in the bulk, what does this process look like? What factors drive the possible structural regimes? And are any spectroscopic signatures available to track this process?

Through a pair of computational studies, the behavior of cluster sizes  $n=1-17$  was investigated, with the upper limit intentionally chosen to end prior to guaranteed internal solvation of the radical. The results were surprising. First, the interaction between a neutral chlorine atom and a water molecule—although relatively weak (3.6 kcal/mol)—exhibits clear signatures of partial covalency. Even at small cluster sizes, however, hydrogen-transferred analogues  $(HCl)(OH\cdot)(H_2O)_{n-1}$  were found to exist, as well. Upon continued hydration, these *HCl* units



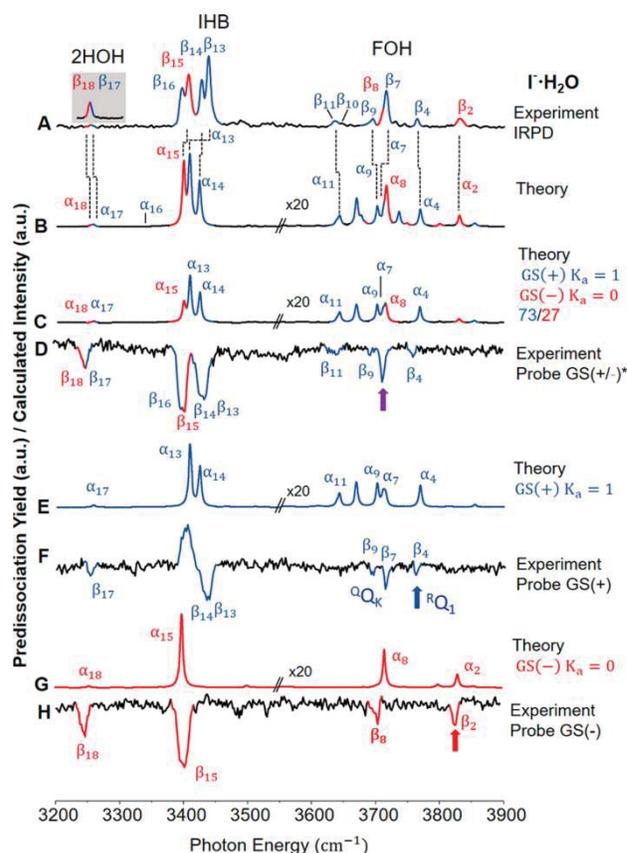
are more stably dissociated, yielding  $(H_3O^+)(Cl^-)(OH)(H_2O)_{n-2}$  clusters. The surprising finding of these two studies is that, although the latter charge-separated forms become lower in energy than the  $HCl$ -containing isomers by  $n=5$ , they do *not* become more stable than the original hydrated-chlorine forms, even at  $n=17$ ! The  $HCl$  molecule is known to dissociate in the presence of only four water molecules, for example, so this slow convergence toward the thermodynamic limit is particularly unique. The factors controlling these energetics were carefully disentangled, and the behavior in these complexes poses a daunting challenge to many-body methods.

Throughout these studies, vibrational spectral signatures of the electronic response were a key focus. The unique *chemical* interaction between the open-shell species and the surrounding water network yielded definitive signatures that could be used to guide future experiments (for anyone willing to risk their stainless steel vessels for such experiments!). The aforementioned crossover between  $Cl^-$  and  $H_3O^+$ -containing cluster forms was predicted to occur until 30-50 water molecules, and experiments to definitively probe the spectral signatures of this crossover are encouraged.



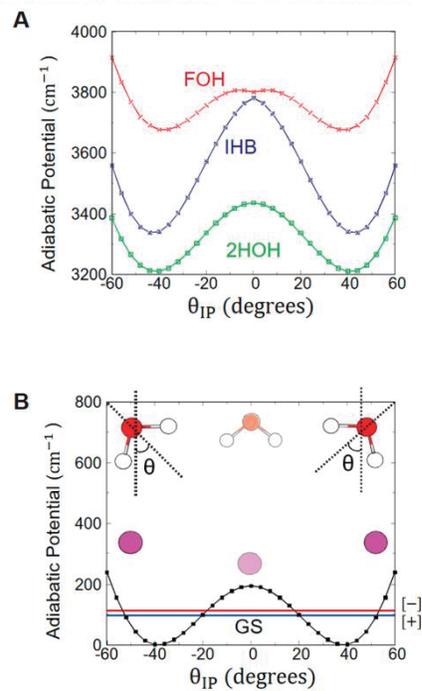
### Mode-Dependent Tunnel Splitting: $I^-(H_2O)_{1-17}$

The gas-phase vibrational spectrum of the isolated iodide-water cluster ion ( $I^- \cdot H_2O$ ), first reported in 1996, presents one of the most difficult, long-standing spectroscopic puzzles involving ion microhydration. Although the spectra of the smaller halides are well described in the context of an asymmetrical ground-state structure in which only one OH group is hydrogen-bonded to the ion, the  $I^- \cdot H_2O$  spectrum displays multiplet structures with partially resolved rotational patterns that are additionally influenced by quantum nuclear spin statistics. In this study, this complex behavior was unraveled with a combination of experimental methods, including ion preparation in a temperature-controlled ion trap and spectral simplification through applications of tag-free, two-color IR-IR double-resonance spectroscopy. Analysis of the double-resonance spectra revealed a vibrational ground-state tunneling splitting of about  $20 \text{ cm}^{-1}$ , which is on the same order



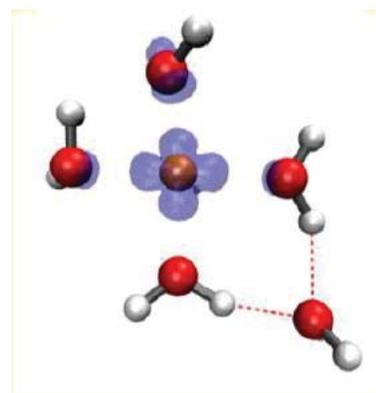
as the spacing between the peaks that comprise the multiplet structure. These findings are further supported by the results obtained from a fully coupled, six-dimensional calculation of the vibrational spectrum. The underlying level structure can then be understood as a consequence of experimentally measurable, vibrational mode-dependent tunneling splittings (which, in the case of the ground vibrational state, is comparable to the rotational energy spacing between levels with  $K_a = 0$  and 1), as well as Fermi resonance interactions. The latter include the hydrogen-bonded OH stretches and combination bands that involve the HOH bend overtones and soft-mode excitations of frustrated translation and rotation displacements of the water molecule relative to the ion. These anharmonic couplings yield closely spaced bands that are activated in the IR by borrowing intensity from the OH stretch fundamentals.

Interestingly, for three of the four main transitions of interest in this problem, a vibrationally adiabatic model performed nearly quantitatively. By performing five-dimensional, fully coupled anharmonic simulations at each angle along the low-frequency coordinate (and including non-Condon responses), vibrational adiabats were constructed for all of the “fast” degrees of freedom and explained nearly all of the behavior in the spectrum. The lone exception was behavior akin to a conical intersection between the free-OH and hydrogen-bonded stretches, where strong nonadiabatic couplings were required in order to quantitatively capture the tunnel splittings.



### Probing Water Activation by Transition-Metal Ions: $\text{Cu}^{2+}(\text{H}_2\text{O})_n$ and $\text{CuOH}^+(\text{H}_2\text{O})_n$

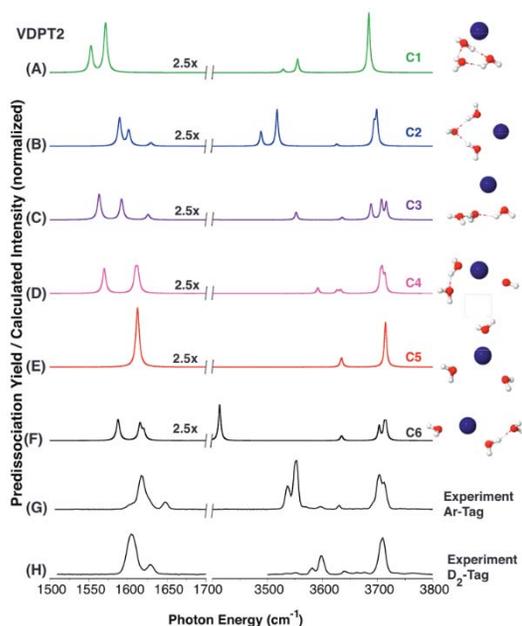
In a trio of soon-to-be submitted studies this year, the isomeric landscape, energetics, and spectroscopy of hydrated Cu(II) have been mapped. The focus of these studies included the energetic (and kinetic) crossover between the propensity of copper (II) to form  $\text{CuOH}^+$  and the hydration of  $\text{Cu}^{2+}$ . In both cases, the transition metal ion perturbed the surrounding water network in ways that are unique to metal ions and, in many aspects, unique to copper. In addition to definitive spectral signatures, the kinetic pathways to dissociation were also mapped, which should guide future mass spectrometry experiments of these reference ions.



For  $\text{CuOH}^+$  and the small hydrated analogues, a Renner-Teller effect was computed to occur, which explains the presence of Fano lineshapes in recently reported (Garand, 2014) experimental spectra. Furthermore, a low-barrier Grotthuss proton-shuttling mechanism was predicted to occur *within the first coordination sphere* of these complexes. This behavior should exhibit particularly unique spectral signatures, and collaborators are waiting to explore this behavior whenever labs reopen.

## Assessment of—and Improvements to—Local-Monomer Methodology: $Cs^+(H_2O)_3$

As both a test of recently developed potential energy surfaces and anharmonic vibrational simulation methodology, the hydration behavior of  $Cs^+$  was investigated in collaboration with Francesco Paesani and UCSD. For the  $n=3$  cluster size of this system, multiple conformers are energetically accessible, and recent cryogenic action experiments (Lisy, 2018) have demonstrated that the spectra/populations can be strongly impacted by the choice of the nominally benign tagging species. The results of this study were two-fold. First, replica-exchange path integral molecular dynamics simulations determined the temperature-dependent isomer populations (sans tag). Second, new methodology was developed in order to address the symmetry-induced errors in the “local monomer” approach to anharmonic spectra. In



this new approach, cross-monomer coupling was included perturbatively to address the (lack of) symmetry-breaking in the traditional local-monomer methodology. This approach was shown to perform nearly as well as a more general second-order degenerate perturbation theory (VDPT2), although the generality of the latter is likely still preferred. One remaining open question involves the role of low-frequency modes in these spectra. Solidifying these contributions is necessary before definitively assessing the accuracy of the potentials.

### Near-Future Plans

The behavior of hydrated copper complexes will continue to be a focus in the coming year. More accurate, anharmonic spectroscopy simulations will be used to explain experimental behavior, now that the structural and energetic behavior has been mapped. The coordination-sphere proton shuttling will be a key focus.

Methods development—including new approaches to local-mode couplings and determining the quantum-chemistry basis of these couplings—will also be a central focus in the coming grant year. These methodology assessments/developments will occur in concert with the continued development of a general-purpose anharmonic vibrational spectroscopy software package.

### Publications

*Stepwise Activation of Water by Open-Shell Interactions,  $Cl(H_2O)_{n=4-8,17}$*

E. G. Christensen, R. P. Steele, *J. Phys. Chem. A*, **124**, 3417 (2020)

*Spectroscopic Signatures of Mode-Dependent Tunnel Splitting in the Iodide–Water Binary Complex*

J. J. Talbot, N. Yang, M. Huang, C. H. Duong, A. B. McCoy,\* R. P. Steele,\* M. A. Johnson, *J. Phys. Chem. A*, **124**, 2991 (2020)

*Infrared Signatures of Isomer Selectivity and Symmetry Breaking in the  $Cs^+(H_2O)_3$  Complex Using Many-Body Potential Energy Functions*

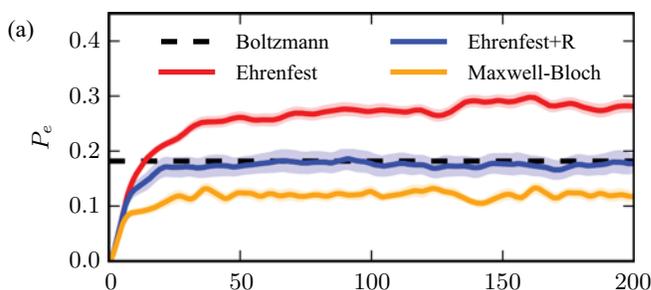
M. Riera, J. J. Talbot, R. P. Steele, and F. Paesani. To be submitted May 2020

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*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 interact 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 electrodynamic with coupled photonic and electronic degrees of freedom.

*Recent Progress:* Over the recent year, we have turned our attention to two interesting problems in light-matter interactions. First, we have investigated the origins of cavity related catalysis, following very exciting effects that have been reported by Ebbesen. Here, we have shown that these effects cannot be explained by a cavity-dressed potential of mean force. Thus, at least within classical mechanics, transition state theory (i.e. standard chemical rate theory) cannot be used to explain the observed catalytic effect. This then leaves open the question of either (i) quantum effects, (ii) nonequilibrium effects, or (iii) some other (as yet unknown) effect. An investigation here continues.

Second, we continue to explore semi-classical algorithms for light-matter interactions. Here, we have now shown that, as far as mean-field Ehrenfest models, including spontaneous emission is absolutely essential for recovering detailed balance. Thus, this finding validates the so-called Ehrenfest+R scheme that we have developed over the last two years.



A Figure demonstrating that Ehrenfest+R dynamics recover the correct Boltzmann statistics.

*Future Plans:* We are now planning a two fold approach. First, we are deeply interested in unraveling the physics underlying the cavity related catalytic effects mentioned above. Second,

we are beginning to address how strong fields may also lead to catalysis. Namely, we are developing techniques to study nonadiabatic dynamics with strong fields, using Floquet theory.

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., Zhou, Zeyu

**References:**

T. E. Li, A. Nitzan, and J. E. Subotnik "On the origin of ground-state vacuum-field catalysis: Equilibrium consideration"

J. Chem. Phys. 152, 234107 (2020)

T. E. Li, H-T Chen, and J. E. Subotnik. "Understanding the nature of mean-field semiclassical light-matter dynamics: An investigation of energy transfer, electron-electron correlations, external driving, and long-time detailed balance"

Phys. Rev. A 100, 062509 (2019)

H. T. Chen, T. E. Li, A. Nitzan and J. E. Subotnik, "Understanding detailed balance for an electron-radiation system through mixed quantum-classical electrodynamics"

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H-T. Chen and T. E. Li and A. Nitzan and J. E. Subotnik. "Predictive Semiclassical Model for Coherent and Incoherent Emission 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)

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J. Chem. Phys. 150, 044102 (2019)

## Development of a local hybrid density functional to treat the self-interaction error and the non-local many-electron interaction

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### Project Scope

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) meta-generalized gradient approximations (meta-GGA), greatly advanced the development of DFT methods giving improved accuracy over conventional density functionals without sacrificing computational efficiency. Despite this success all conventional density functionals (including SCAN) suffer errors from 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 present challenges when 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 local hybrid functional framework can provide a solution by incorporating *non-local* information to treat SIE and SMEI through a space dependent local admixture of exact exchange. The goal of this project 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 local hybrid density functional will build upon an improved SCAN as the *semi-local* core to correct properties and systems affected by SIE and SMEI while at least matching the popular conventional density functionals for other properties.

The SCAN functional has seen extensive use since its publication. We apply SCAN on difficult systems where SIE and SMEI play important roles, and reveal new understanding about such systems. Along with the successes, two key problems have been revealed for SCAN. Most critically, the twisted shape of the SCAN XC enhancement function results in an oscillating exchange-correlation (XC) potential that requires dense grids for accurate numerical integration. This harms the functional's computational efficiency and requires the user to check that all properties are converged with respect to grid parameters. Secondly, SCAN over-magnetizes bulk transition metals. Unlike SIE and SMEI, these problems are not theoretically expected for meta-GGAs. Their solution whilst maintaining the attractive features of SCAN stands as the last major hurdle of semi-local density functional approximations. As any local-hybrid functional is likely to inherit the problems of its semi-local components it is necessary to address these problems as a priority.

### Project progress

#### **1. Symmetry-breaking polymorphous descriptions of correlated materials using SCAN without U**

Correlated materials with open-shell *d*- and *f*-ions having degenerate band edge states show a rich variety of interesting properties ranging from metal-insulator transition to unconventional superconductivity. The textbook view for the electronic structure of these materials is that mean-field approaches are inappropriate, as the interelectronic interaction  $U$  is required to open a band gap between

the occupied and unoccupied degenerate states while retaining symmetry. We show that the latter scenario, often defining what Mott insulators are, is in fact not needed for the 3d binary oxides MnO, FeO, CoO, and NiO. The mean-field band theory can indeed lift such degeneracies in the binaries when nontrivial unit cell representations (polymorphous networks) are allowed to break symmetries, in conjunction with SCAN without an on-site interelectronic interaction  $U$ . This approach thus provides an alternative mechanism to the Mott-Hubbard approach. Figures 1 a) and b) show the bandgap opening in MnO and FeO by SCAN using the symmetry-breaking

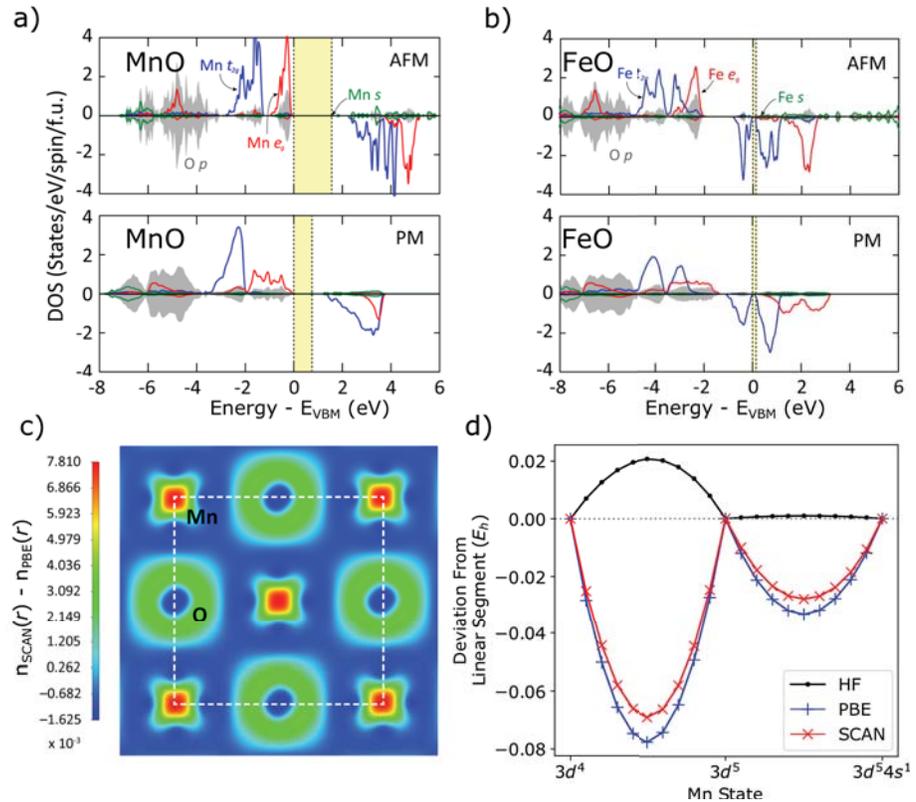


Figure 1. Density of States calculated using SCAN in connection with the symmetry-breaking polymorphous representation for a) MnO, and b) FeO in anti-ferromagnetic (AFM) and paramagnetic (PM) spin configurations. Band gaps are highlighted yellow. c) SCAN orbital localisation in MnO, shown as difference in electron density between PBE and SCAN orbitals. d) Severity of self-interaction error shown through deviation in energy from linear segments between integer electron numbers.

polymorphous representation. Figures 1 c) and d) show the mechanism for this opening through the localization of  $d$  states by SCAN, as compared to PBE. This localization is facilitated by SCAN's reduced SIE, as shown in d) through a smaller deviation from linear energy segments in the fractionally occupied Mn atom.

This work identifies, out of many possible other combinations, 4 specific conditions, that when used together, go a long way to solving the band gap opening problem encountered with naive DFT applications to Mott insulators. The first 3 conditions apply to the exchange correlation functional, whereas the fourth condition applies to the real-space representation of the structure. (i) XC functionals must distinguish occupied from unoccupied states. (ii) XC functionals that minimize self-interaction error should be used, enforced by the piecewise linearity of total energy. (iii) XC functionals should be used with spin symmetry breaking. (iv) The unit cell representation must allow symmetry breaking, possibly leading to polymorphous networks. It is important to emphasize that whereas individual conditions in isolation may not be sufficient, but when taken together they are both sufficient and necessary (although quantitatively not perfect). This work shows the importance of developing density functionals with reduced SIE and points out a way to deal with strong correlation or SMEI. This work is under review at PRX.

## 2. SCAN on cuprates:

We have continued our application of SCAN-based DFT to difficult systems in energy science by modelling the complex competing magnetic stripe phases of the optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) superconductor. This study demonstrated how implicitly orbital dependent meta-GGA functionals can address challenging classes of complex quantum materials without resorting to ad hoc empirical parameters, and at the same time allow lattice, charge, and spin degrees of freedom to relax. This capability is absent from effective Hamiltonian approaches. This significant finding shows that complex competing phase behavior can be amenable to first principles DFT study and was published in *PNAS*.

### 3. Restoring exact constraints for a regularized SCAN

Recent work by Bartók and Yates proposes a regularized SCAN, termed rSCAN, that aims to address the numerical performance problems of SCAN. Whilst the regularizations successfully reduce the functional's numerical sensitivity they break the exact constraints that SCAN was constructed around. It has been shown that for some systems this constraint breaking is harmless, however for other problems the good transferability of SCAN has been lost. Atomization energies are a notable example. This suggests the possible utility of restoring exact constraint adherence to rSCAN whilst preserving its useful regularizations. This possibility was explored as part of project and has resulted in three new functionals restoring varying levels of constraint adherence to rSCAN. Of these three the "r<sup>2</sup>SCAN" functional which restores every constraint except the fourth order gradient expansion for exchange is found to be most successful maintaining smooth XC potentials while showing transferable accuracy similar to SCAN in preliminary tests. During this work we showed that 4<sup>th</sup> order gradient expansion recovery is fundamentally incompatible with smoothness for interpolation based meta-GGA functionals.

Figures 2 a) and b) show the XC enhancement factors,  $F_{xc}$ , and gradient contribution to the XC potential,  $d\epsilon_{xc}/d|\nabla n|$ , for the Xenon atom from the SCAN, rSCAN, and r<sup>2</sup>SCAN functionals. The twisting of the SCAN enhancement factor can be seen as plateaus in  $F_{xc}$  of Fig. 2 (a) when the local environment is uniform electron gas like. No such twists are present in the regularized SCAN functionals. The plateaus in SCAN cause oscillations in the XC potential of Fig. 2 (b) while a smooth potential is seen for the regularized functionals. The improved numerical stability is realized in the fast grid convergence of the AE6 small atomization energy test set for rSCAN and r<sup>2</sup>SCAN, and the necessity of exact constraints is clear from the increased error of rSCAN.

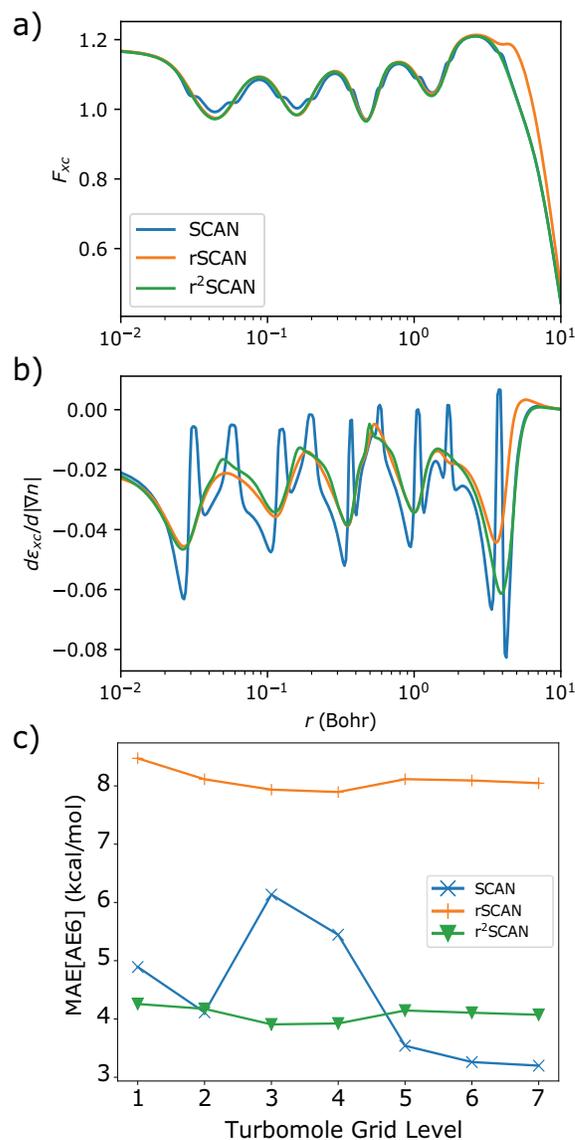


Figure 2. The a) exchange-correlation enhancement factor and b) density gradient component of the exchange-correlation potential for the Xenon atom from the SCAN, rSCAN, and r<sup>2</sup>SCAN functionals. c) Atomization energy test set accuracy as a function of integration grid density.

The  $r^2$ SCAN development work revealed a general method for reconciling a smooth XC model with exact constraint adherence, relieving problematic design constraints from the SCAN functional. In light of this a candidate SCAN2 functional has been constructed that builds on the success of  $r^2$ SCAN to resolve the remaining problem of transition metal over-magnetization.

The effect of the order-of-limits problem in the recently reported Tao-Mo functional was also analyzed and we showed how the functional can be revised to avoid the problem. This work is under review for publication in the *Journal of Chemical Physics*.

#### 4. Implementation of local hybrid density functionals

Development of local hybrid functionals requires non-standard computation machinery for the local exact exchange energy density. This project resulted in a prototype local hybrid implementation. However, in order to apply local hybrid functionals to larger systems we have moved to using of the high-performance local hybrid module in the TURBOMOLE program. This platform allows the immediate development of new local hybrid functionals and will form the basis of our future testing.

#### Future Goals

- The development of the accurate and numerically efficient meta-GGA functional will be concluded with the  $r^2$ SCAN and SCAN2 functionals published as workhorse meta-GGAs.
- The SCAN2 functional will be taken as the semi-local component of the proposed local hybrid functional to be developed within the TURBOMOLE program.
- The SCAN2 functional will be reparametrized for use in local hybrid functionals to match the gauge of exact exchange. This will solve the local hybrid gauge problem without resorting to explicit gauge calibration functions.

#### **Grant Numbers and Grant Titles:**

U.S. DOE, Office of Science, Basic Energy Sciences Grant No. DE-SC0019350 (core research); *Development of a local hybrid density functional to treat the self-interaction error and the non-local many-electron interaction*

**Postdoc(s):** James W. Furness

**Student(s):** Kanun Pokharel

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

[1] Y. Zhang, C. Lane, J. W. Furness, B. Barbiellini, J. P. Perdew, R. S. Markiewicz, A. Bansil, and J. Sun, *Competing stripe and magnetic phases in the cuprates from first principles*, Proc. Natl. Acad. Sci. **117**, 68 (2019).

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**SPARC-X: Quantum simulations at extreme scale — reactive dynamics from first principles**

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**Abstract**

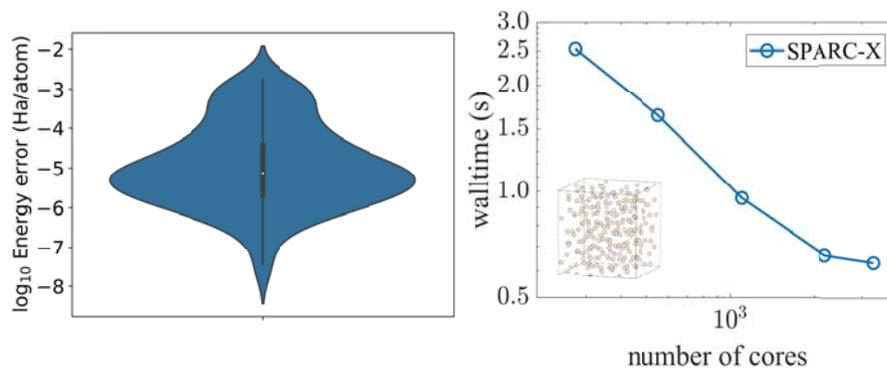
The objective of this project is to develop SPARC-X: an open source computational framework for performing Kohn-Sham Density Functional Theory (DFT) calculations that scale linearly with system size, leveraging petascale/exascale parallel computers to study chemical phenomena at length and time scales 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<sub>2</sub> 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 SPARC parallel electronic structure code, our recent additions include: (i) increased scope of application through additional features including the RPBE and PBEsol semilocal exchange-correlation functionals, cell relaxation, simultaneous cell and atom relaxation, and ability to perform spin polarized calculations; (ii) improved accuracy for slabs and wires through appropriate boundary conditions, and choice of shifted grids for Brillouin zone integration; (iii) higher efficiency through new matrix-matrix multiplication routines with superior data transmission, improved spline interpolation schemes arising within pseudocharge, force, and stress tensor calculations, efficient linear solver, and new preconditioned mixing schemes; (iv) improved parallel scalability through an additional level of parallelization over spin; (v) increased robustness through exhaustive testing; (vi) increased portability by only requiring industry-standard BLAS, LAPACK, ScaLAPACK, and MPI libraries; (vii)

improved automated testing framework with a comprehensive 100-system test suite; and (viii) increased ease of use by incorporating advanced restart features for geometry optimization/molecular dynamics (MD), equivalent planewave cutoff as input, choice of any boundary condition along any direction, and improved output formats, with additional important quantities output into these files. With these and other advances, SPARC-X is not only highly accurate, but is also able to reduce the wall time for a MD step to well under 1 second (**Figure 1**), enabling long timescale quantum MD.



**Figure 1:** Left: Difference in ground state energy computed by SPARC-X and ABINIT for 100 bulk systems, with both LDA and GGA. Right: Strong scaling of SPARC-X for a 250-helium atom ground state calculation, with all parameters chosen to obtain chemical accuracy within DFT.

Other recent work includes the development of open source M-SPARC [6]: a rapid prototyping platform in Matlab for the development and testing of new algorithms and methods in real-space DFT; ElectroLens: a visualization tool for high-dimensional spatially-resolved features [7]; formulation for a structure adapted eigensolver that can take advantage of the convergence within the self-consistent field method; framework for generating highly soft yet transferable pseudopotentials; prototype implementation of machine learning techniques in M-SPARC to identify the various regions of electronic structure space that occur in materials systems; study of the role of transition-metal dopants on photocatalytic nitrogen fixation on  $\text{TiO}_2$  surface [8]; and the development of surface models to assess the influence of finite size effects on surface energy and adsorption of nitrogen-containing species on  $\text{TiO}_2$  nanoparticles.

Going forward, we plan to first implement the structure-adapted eigensolver in SPARC-X 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 walltime 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. In order to enable the effective use of exascale computing platforms, a parallel engine for SPARC-X that provides a highly efficient framework for distributed memory communication and offloading to GPUs will be completed. With these advances, initial applications will focus on screening a large number of possible active sites for both slab and nanoparticle models of  $\text{TiO}_2$ , 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

**Postdocs:** Mostafa F. Shojaei, Milind Malshe

**Students:** Qimen Xu, Abhiraj Sharma, Benjamin Comer, Xiangyun Lei, Sushree J. Sahoo, Hua Huang, Shikhar Shah

**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.
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## Aqueous solutions and interfaces

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### Abstract

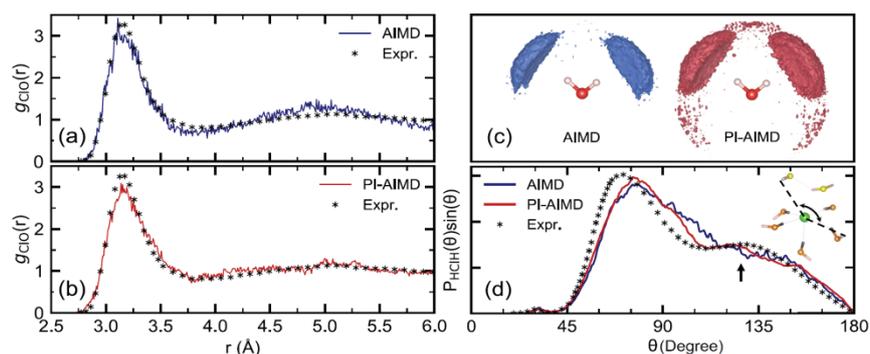
We have currently published four papers and submitted one paper focusing on the impact of exchange and correlation approximations at aqueous interfaces and in ionic solutions. In the first paper, the **Klein** group has simulated the Al<sub>2</sub>O<sub>3</sub>(001)-H<sub>2</sub>O interface using a range of GGA, meta-GGA, and hybrid functionals, showing that an accurate interfacial structure could be achieved only when explicitly modeling electron exchange-correlation with the SCAN meta-GGA functional<sup>1</sup>. In the second paper, **Klein** and **Wu** groups have investigated chloride solvation using a range of functionals and found that, while adding exact exchange improved the energetics, it significantly reduced the polarizability, leading to small improvements in the solvation structure<sup>2</sup>. The solvation structure was improved when using the meta-GGA functional SCAN over the hybrid functional PBE0, and we reasoned that this was due to the greater polarizability of chloride when using the SCAN functional. In the third paper, the **Wu** group has studied the effect of long-range van der Waals interactions in ionic solutions of Hofmeister series (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>)<sup>3</sup>. It was found that the liquid structures are softened in general, however, the degree that the hydration structure is revised by the van der Waals interactions is distinct for different ions, depending on the strength of short-range interactions between the hydrated ion and surrounding water molecules. In the fourth paper, **Car** and **Wu** groups have published together on the most recent implementation of order-N exact exchange methods for hybrid density functional theory for massively parallel computers<sup>4</sup>. In addition, we have also submitted one paper, in which **Wu** and **Klein** groups have studied the nuclear quantum effects on the solvation shell of chloride ionic solution. It has been shown that nuclear quantum effects reduce the disruptive effect of anion on the solvent water structure, resulting in a significantly improved agreement between neutron scattering experiment and ab initio theory for the hydration structure (Figure 1).

**Klein** and **Matsika** groups are collaborating on the study the solvation of the uracil anion, an important molecule which is a model for the impact of DNA damage. We are studying the solvation structure of both the neutral and charged uracil molecule using DFT-based molecular dynamics, while the trajectories are used by the Matsika group to study the nonadiabatic photochemistry of uracil (Figure 2).

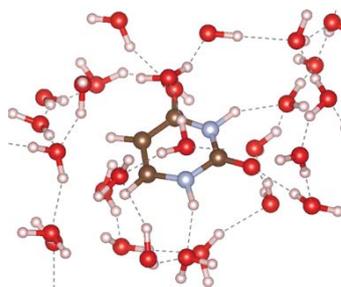
**Klein** is also working with Prof. Annabella **Selloni** (Princeton) to study the solvation of an excess electron and the Al<sub>2</sub>O<sub>3</sub>(001)-H<sub>2</sub>O interface, which serves as a model of radiolysis at the surface of oxides bearing radioactive waste. We have been investigating the electronic properties of alumina and the Al<sub>2</sub>O<sub>3</sub>(001)-H<sub>2</sub>O interface with DFT, showing that both SCAN and PBE0 significantly improve the band gap over the PBE functional, with PBE0 yielding the expected band gap of alumina (~8 eV) (Figure 3). We are now running preliminary simulations of the Al<sub>2</sub>O<sub>3</sub>(001)-H<sub>2</sub>O interface to test different functionals, pseudopotentials, and codes to determine the most effective simulation method, and will begin production simulations shortly.

**Klein** group is working with the group of Prof. Roberto **Car** (Princeton) and Dr. Thomas Gartner III (Princeton) to study aspects of machine learning for molecular simulation. Specifically, we are working with neural network potentials (NNPs), studying how the details of the neural network impact the potential, and are working to test and improve the DeepMD<sup>6</sup> method for neural network potentials. Recently, we have been able to show that the normalization of the inputs of the neural network significantly impacts the resulting potential (Figure 4). We have also built training and validation sets for LiCl in order to study the effectiveness of NNPs to model long-range electrostatic forces. Finally, we are also working to test the DeepMD method for aqueous systems and will add further data from our previous simulations to extend the current DeepMD water model to interfaces and ionic solutions.

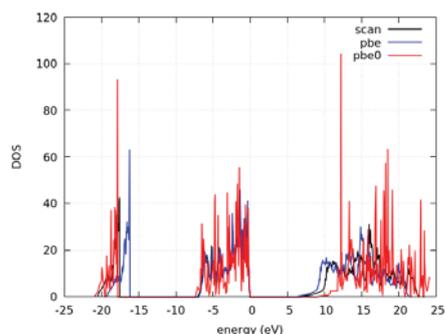
**Wu** group is collaborating with Prof. Steve Louie (UC Berkeley), Prof. Diana Qiu (Yale) and Prof. Roberto **Car** (Princeton) to study the X-ray absorption spectra in liquid water and ice. In particular, they have applied the Berkeley GW-BSE method to solve the Bethe-Salpeter equations in order to calculate the X-ray absorption spectra. The Berkeley GW-BSE method rigorously treats the dynamic effects of the interaction between core hole and excited electron as well as the effect due to the electronic screening. The preliminary results (Figure 5) performed in liquid water look very promising and qualitatively reproduce the experimental measurement.



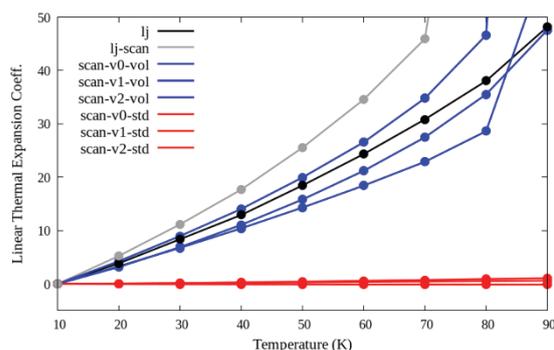
**Figure 1:** Cl-O RDFs of a water  $\text{Cl}^-$  solution from (a) AIMD (blue), (b) PI-AIMD (red) simulations, compared with neutron diffraction experiment<sup>7</sup> (black). (c) Probability isosurface for a  $\text{Cl}^-$  ion to be first neighbor of a water molecule from AIMD (blue) and PI-AIMD (red). The contrast level of the isosurfaces is set to 0.70. (d) Probability distribution of H-Cl-H angles in the first hydration shell from AIMD (blue), PI-AIMD (red), and neutron diffraction<sup>7</sup> (black). The inset shows the polarized  $\text{Cl}^-$  hydration structure, with water molecules bonded to the ion (orange) and non-bonded molecules (yellow).



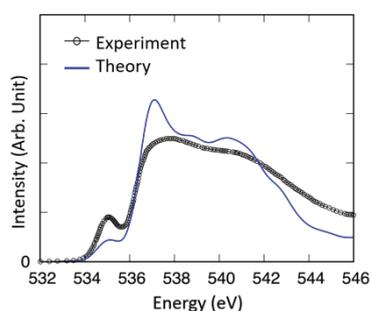
**Figure 2:** A snapshot of a solvated uracil molecule from DFT-MD simulations, showing only the first solvation shell.



**Figure 3:** The density of states of alumina computed with several different functionals. All DOS have been aligned with the valence band edge at the origin in order to better illustrate the difference in band gaps.



**Figure 4:** The linear thermal expansion coefficient of Ar modeled with a NNP. The red lines show results with the standard scaling of inputs, showing either no increase of the lattice constant with temperature or a contraction of the unit cell. The blue lines show the results when scaling by a constant related to the cutoff, a method we recently developed, which shows an expansion matching standard Lennard-Jones potentials.



**Figure 5:** Calculated and experimental XAS spectra of liquid water. The experimental XAS spectra is adopted from Ref. 8. The calculated XAS spectra is computed by using Berkeley-GW package based on a snapshot from AIMD at 363 K.

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**Grant DE-SC001934: Chemistry in Solution and at Interfaces**

**Postdocs:** Fujie Tang, Mark Dello-Stritto, Cate Anstöter, Thomas Gartner III  
(Princeton)

## CASPT2 Molecular Geometries of Transition Metal Complexes

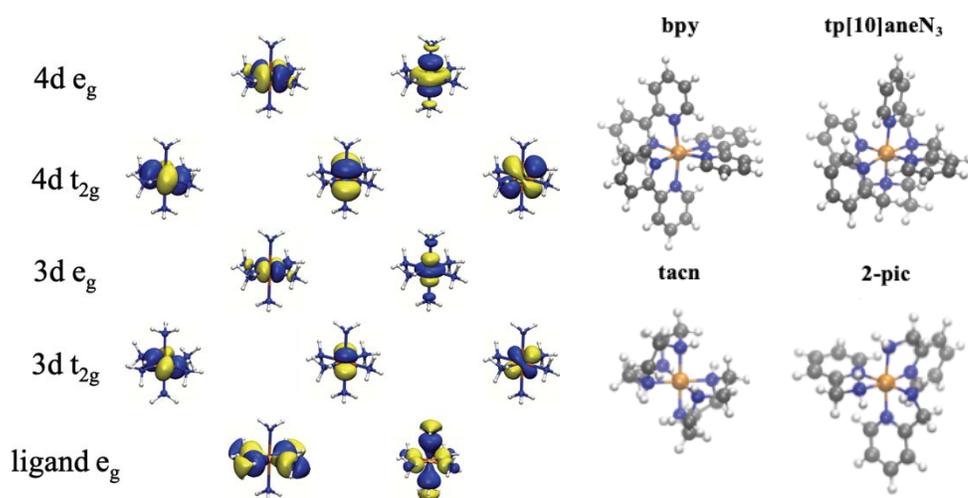
Brian A. Finney<sup>1</sup>, Rina Bhowmick<sup>1</sup>, Clara Kirkvold<sup>1</sup>, and Bess Vlaisavljevich<sup>1</sup>

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### Abstract

The optimization of molecular geometries for systems with multiconfigurational electronic structures can be performed using the recently implemented fully internally contracted analytical gradients for the second-order complete active space SCF method (CASPT2). Our recent progress has focused on exploring the performance of this method for three types of complexes: Spin-crossover (SCO) complexes, metal-metal bonds, and metallocorroles.

The first family of complexes explored are Fe(II) SCO complexes. Spin-crossover complexes exhibit a transition in spin-state due to external stimuli, frequently temperature. The change in spin state from the closed shell low spin (LS) state to the S=2 high spin (HS) state is accompanied



by a characteristic elongation in the bond distances within the first coordination sphere of the metal. The effects of basis set and active space choice upon the geometric parameters and the energy difference between the states,  $\Delta E_{\text{HS-LS}}$ , have been explored for a series of compounds ranging in size from 13 to 61 atoms. First, we studied six small Fe(II) complexes that range from weak- to strong-field ligands:  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Fe}(\text{NCH})_6]^{2+}$ ,  $[\text{Fe}(\text{PH}_3)_6]^{2+}$ ,  $[\text{Fe}(\text{CO})_6]^{2+}$ , and  $[\text{Fe}(\text{CNH})_6]^{2+}$ . The symmetry around the Fe center is octahedral; therefore, the orbitals are labeled as in the  $O_h$  point group even for complexes where there the molecule itself does not have symmetry (see Figure, left for the orbitals from  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ ). Single point energy calculations were performed on geometries optimized with the TPSSh functional. An active space that included the 12 orbitals shown in the figure and their corresponding 10 electrons. The spin state change occurs in the  $3d$  orbitals and the doubly occupied ligand  $e_g$  orbitals have been shown to be important for obtaining the correct energetics for some complexes in the literature. Likewise, the  $4d$  correlating orbitals must be included for first row transition metals that are more than half filled. Our results show that for weak field ligands such as  $\text{H}_2\text{O}$ , the  $e_g$  orbitals are not required to be in the active space since their inclusion does not improve  $\Delta E_{\text{HS-LS}}$ .<sup>1</sup> However, for strong field ligands such as CO, they are essential. It is well-known that CASPT2 over stabilizes the HS state, so a correction to the energy from coupled cluster, ranging from 2.3 to 5.5 kcal/mol, is applied to improve the  $3s3p$  correlation which improves  $\Delta E_{\text{HS-LS}}$ .<sup>2</sup> Next, we performed CASPT2 geometry optimizations for these complexes and

determined how the geometry and  $\Delta E_{\text{HS-LS}}$  changed. Larger deviations in geometries are observed for stronger field ligands, typically on the order of 0.1 Å. Additionally, the LS state is more effected by active space choice and basis set than the HS state, since the orbital hybridization in the ligand  $e_g$  orbitals is larger. Geometry does change  $\Delta E_{\text{HS-LS}}$  values computed at our best level of theory. In the most dramatic case, it changes by 32 kcal/mol while for the least dramatic case it changes by 5 kcal/mol. Next, we demonstrate that these optimizations are not only possible on relatively small complexes, but can be used to study medium to large transition metal complexes. Complexes of the tacn (1, 4, 7-triazacyclononane), 2-pic (2-picolylamine), tp[10]aneN<sub>3</sub> (N, N', N''- 2-pyridylmethyl) -1, 4, 7 - triazacyclodecane), and bpy (2, 2'-bipyridine) ligands have been studied (see Figure, right). The [Fe(tacn)<sub>2</sub>]<sup>2+</sup>, [Fe(2-pic)<sub>2</sub>]<sup>2+</sup>, [Fe(tp[10]aneN<sub>3</sub>)]<sup>2+</sup>, and [Fe(bpy)<sub>3</sub>]<sup>2+</sup> complexes have been optimized using the best practices determined by the studies on the small complexes. At minimum, a triple- $\zeta$  quality basis set must be used on the metal (double  $\zeta$  basis sets can be used on the remainder of the molecule) and the (6e,5o) active space gives reasonable geometries with weak-field ligands. We recommend that strong-field ligands be optimized with the larger (10e,12o) active space.

Future work will include a complex with a carbene ligand to show the performance for a larger complex of a strong-field ligand. Finally, for SCO complexes that transition due to changes in temperature, the free energy must be computed. The next step in this study will be to determine the sensitivity of the vibrational contributions to the level of theory. Finally, the above calculations have been performed in the gas phase and the role of solvent must also be explored; however, this requires software enhancement. The role of external stimuli will be the primary focus of the postdoctoral researcher in years 3 and 4 of the project.

The second type of complexes we are exploring are chromium-chromium metal-metal bonds. These bonds are prototypical examples of multiconfigurational electronic structures. We have explored four complexes and not only predict good geometries, but are able to calculate the Raman active symmetric stretch in the metal-metal bond that are qualitatively incorrect with single determinantal methods. Future work in this project will include computing the vibrational frequencies for the final complex. Vibrational frequencies computed to date are in good agreement with experiment. Subsequently, we plan to study compounds with three chromium atoms that form a Cr-Cr-Cr bond. Specifically, one compound has been shown switch from a symmetric to asymmetric bond (where one Cr-Cr distance is shorter than the other) when the apical ligand is modified. We are interested in determining if our approach can yield the correct geometry with the minimal active space or if a large active space required. An overarching goal of this project is to determine if small active spaces can give the correct geometry, therefore requiring less computational resources and making this approach more accessible for routine application.

Finally, copper corrole complexes are often used as catalysts in the hydrogen evolution reaction. The corrole can be redox active and a variety of ligand functionalizations have been synthesized to tune the properties of these catalysts. The unfunctionalized corrole has a characteristic saddling geometry and a multiconfigurational electronic structure. We are currently exploring how the electronic structure and geometry change if the ligand is functionalized. Comparisons with density functional theory will be made. Future work will extend this to include reaction profiles for the hydrogen evolution reaction and will be the focus of the graduate student in the upcoming year of the project.

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**DE-SC0019463 Controlling Molecular Structure and Spin with  
Multiconfigurational Quantum Chemistry**

**Postdoc(s):** Brian A. Finney

**Student(s):** Rina Bhowmick, Clara Kirkvold

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

1. J. W. Park, R. Al-Saadon, M. K. MacLeod, T. Shiozaki, and B. Vlasisavljevich “Multireference Electron Correlation Methods: Journeys Along Potential Energy Surfaces” *Chem. Rev.*, **2020**, Accepted.

# *Ab initio* geochemistry of hydrous phases(Award DE-SC0019759)

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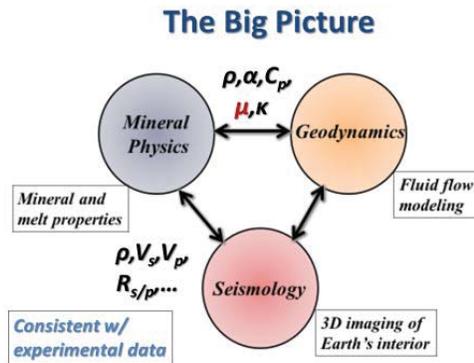
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## Abstract:

Our project aims to advance understanding of properties of Earth forming phases at high pressures and temperature ( $P$ - $T$ ) from an *ab initio* atomistic perspective. Hydrous and nominally anhydrous mineral (NAMs) phases are among the most challenging systems to investigate. In addition to the usual complexity posed by natural materials, hydrogen (proton) participates in complex processes, e.g., dehydration, water incorporation via substitutional defects, and exotic bonding phenomena, e.g., H-bond symmetrization and disordering (dynamic and static), superionic behavior, etc..



**Figure 1** – Mineral physics offers  $P$ - $T$  dependent density,  $\rho$ , shear,  $V_s$ , and compressional,  $V_p$ , velocities and velocity ratios  $R_{SP}$  for seismic tomography interpretation, and  $\rho$ , thermal expansion coefficient,  $\alpha$ , thermal conductivity,  $\kappa$ , and specific heat,  $C_p$ , for geodynamic modeling. Geodynamic simulations then attempt to provide plausible dynamical scenarios for the origin of tomographic images.

Our goal is to address the thermodynamic and thermoelastic properties of these materials to investigate equilibrium states and their properties, including seismic velocities. We have great expertise in such calculations but want to extend them to this more challenging class of problems. We cooperate with seismologists (Abers et al.) and geodynamicists (Yuen et al.) to use these results in Earth modeling. Fig.

1 indicates the close interaction and information flow between three research areas in geophysics. Today they are integrated owing to the availability of predictive thermodynamic and thermoelastic properties obtained with *ab initio* calculations and experimental data.

The complexity of Earth materials has pushed materials simulations to new frontiers. Structural complexity and disorder(solid-solutions), strong electronic correlation due to iron, high-temperature properties, thermoelasticity, multi-phase equilibrium, etc. are some of the challenges that need to be overcome to advance realistic modeling on Earth's internal processes illustrated in Fig. 1. The Wentzcovitch group has addressed and overcome most of these challenges in the past and now aims to tackle hydrous phases and NAMs. Such calculations need to provide results in a continuum of pressure, temperature, and composition ( $P$ - $T$ - $x$ ) to be useful. Therefore, they are demanding from the HPC perspective and are also high throughput (HTC).

## Accomplishments:

### Software and database development:

A wealth of computational methods data have been developed by our group in the past. This award supports further development and publication of such methods/codes. In 2019 we published two codes:

- 1) **qha**: A Python package for quasiharmonic free energy calculation of multi-configuration systems<sup>1</sup>- this

code computes thermodynamic properties of ordered and disordered solids using the quasiharmonic approximation (QHA) and complete statistical sampling of structures within a finite size supercell. The method was successfully used in the past to investigate the order/disorder transition from ice-VIII to ice-VII, and the equilibrium concentration of hydrous defects in forsterite, the main phase of the upper mantle.

- 2) **phq: A Fortran code to compute phonon quasiparticle properties and anharmonic phonon dispersions<sup>2</sup>** – In 2014, we proposed a method based on the concept of phonon quasiparticles (phq) to obtain temperature renormalized phonon dispersions and phonon lifetimes. It combines molecular dynamic (MD) simulations and phonon calculations. Such anharmonic phonon dispersions allow us to obtain anharmonic free energy and lattice thermal conductivity ( $\kappa_{lat}$ ) “in the thermodynamic limit ( $N \rightarrow \infty$ )” using relatively small size supercells. This year, this method has been used to compute  $\kappa_{lat}$  in cubic CaSiO<sub>3</sub>-perovskite, a highly anharmonic system<sup>3</sup> (see below).
- 3) **Abers database and software<sup>3</sup>**: Abers and Hacker have compiled a database of elastic properties of minerals for interpreting seismic tomography. The database was published along with Mathematica code. We developed a Web service to access the data and perform such calculations online, the “Rock property calculator.” This database will be upgraded in the next funding period (see below).

### Scientific papers:

- 4) **Thermal conductivity of cubic CaSiO<sub>3</sub>-perovskite (CaPv) at lower mantle conditions<sup>4</sup>** – CaPv is the third most abundant phase of the Earth's lower mantle (LM) (~7 vol%). It is strongly anharmonic and unquenchable below 600 K at all pressures. It is, therefore, very challenging to calculate or measure some properties of this phase. We used the phonon quasiparticle method (phq code) to obtain phonon lifetimes and velocities and computed  $\kappa_{lat}$  in this phase within Peierls-Boltzmann transport theory. We also offered consistent  $\kappa_{lat}$  values for MgSiO<sub>3</sub>-perovskite (MgPv) and MgO periclase, the first and second most abundant phases of the LM. We find CaPv's  $\kappa_{lat}$  to be ~three times greater than that of MgPv, a counterintuitive result. To validate this finding, we also measured CaPv's  $\kappa_{lat}$  in a diamond-anvil-cell. Measurements confirmed predictions. An in-depth analysis of this unexpected behavior indicated that the large CaPv's  $\kappa_{lat}$  originates in its higher symmetry. We concluded that, despite its small abundance in the LM, it could increase the LM's  $\kappa_{lat}$  by ~10% if accounted for.
- 5) **Post-perovskite transition in Al- and Fe-bearing bridgmanite<sup>5</sup>** – This work reported the phase diagram of the post-perovskite (PPv) transition in bridgmanite (MgSiO<sub>3</sub>-perovskite) containing up to 12.5 mol% of FeSiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, FeAlO<sub>3</sub>, or Fe<sub>2</sub>O<sub>3</sub>, in two- or three-component systems. This transition was discovered in 2004. We demonstrated in 2006 that the PPv transition in MgPv produces seismic discontinuities compatible with observed velocity jumps across the D” discontinuity. In 2019 we computed such seismic velocity discontinuities in solid-solutions. We concluded that Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, increase the transition pressure, produce narrow two-phase regions, and sharp seismic velocity discontinuities. FeSiO<sub>3</sub> and FeAlO<sub>3</sub>, on the other hand, lower the transition pressure, produces broad two-phase regions, and smooths velocity change profiles. These findings suggest that detailed regional tomographic images of the deep LM might offer insights into the redox state of the LM. These calculations were carried out using codes qha and code cij (see below).
- 6) **Velocity and density characteristics of subducted oceanic crust and the origin of seismic heterogeneities in the lower mantle<sup>6</sup>** – This work had been underway for a couple of years. Seismic heterogeneities detected in the LM were proposed to be related to subducted oceanic crust. However, the velocity and density of subducted oceanic crust at LM conditions remained unknown until this work. We report *ab initio* results for the elastic properties of calcium ferrite-type phases and determined the velocities and density of oceanic crust along different mantle geotherms. We found that the subducted oceanic crust shows a large negative shear velocity anomaly at the phase boundary between stishovite and CaCl<sub>2</sub>-type SiO<sub>2</sub>, which is highly consistent with this property of mid-mantle scatterers. After this phase transition in SiO<sub>2</sub>, subducted oceanic crust should be visible as high-velocity heterogeneities as imaged by seismic tomography. This study suggests that the presence of subducted oceanic crust could provide good explanations for some lower-mantle heterogeneities with different length scales except the large

low shear velocity provinces (LLSVPs). Calculations were carried out using codes `qha` and code `cij` (see below).

- 7) **Seismic detection of the iron spin transition in Earth's lower mantle**<sup>7</sup> - This work had been underway for a couple of years. (Mg,Fe)O-ferropericlase (Fp) and (Mg,Fe)SiO<sub>3</sub>- bridgmanite (Bm) comprise ~ 90 vol% of Earth's LM. Iron in Fp undergoes a high-spin to low-spin (HS-LS) crossover that influences density, viscosity, elasticity, thermal conductivity, and iron partitioning, however, the predicted effects of this transition are not apparent in global 1D seismic velocity profiles. This work consists of an analysis of shear (S-) and compressional (P-) tomographic models to address correlation/decorrelation of S- and P-velocity heterogeneities. Specifically, we searched for a decorrelation of velocity heterogeneities in S- and P-models between 1,400-2,000 km depth as predicted by *ab initio* calculations of seismic velocities in the presence of the spin crossover in Fp. We found clear signs of this decorrelation in fast velocity (cold) regions where subducted plates are expected to reside. We also observe a similar but subtler decorrelation in slow velocity (hot) regions below 1,800 km depth, consistent with *ab initio* predictions of a pressure increase and broadening of the Fp spin transition at higher temperatures. Our identification of the spin transition signal in seismically fast and slow regions indicates that the spin crossover can identify the presence of Fp in the LM. Predictions of the spin crossover signal were carried out using codes `qha` and code `cij` (see below).
- 8) **Phonons in (Mg,Fe)O ferropericlase throughout the iron spin crossover**<sup>8</sup> - Iron in Fp undergoes a high spin (HS), S=2, to low spin (LS), S=0, state change at LM *P-T* conditions. The nature of this phenomenon is quite well understood now, but there are still open questions regarding structural stability and the existence of soft phonon modes during this iron state change. Theories invoked to explain the volume reduction, thermo-elastic anomalies, and the broad nature of this HS-LS crossover make extensive use of the quasiharmonic approximation (QHA). Therefore, dynamical and structural stability is essential to their validity. We investigated the vibrational spectrum of Fp throughout this spin-crossover using *ab initio* DFT+Usc calculations. We addressed vibrational modes associated with isolated and (2<sup>nd</sup>) nearest neighbor iron ions undergoing the HS-LS state change. As expected, acoustic modes are resilient, while optical modes are the most affected by the HS-LS state change. We show that there are no soft phonon modes across this HS-LS crossover, and Fp is dynamically stable at all relevant pressures. The HS-LS transition resembles localized first-order transitions in individual iron.
- 9) **Phase stability of FeO polytypes from self-consistent LDA+U<sub>sc</sub> calculations**<sup>9</sup> - This work advances applications of the DFT+U method, an exceedingly important method in mineral physics. We carried out LDA+U<sub>sc</sub> calculations of the phase stability of iron monoxides with five polytypes in multiple spin-state configurations. The Hubbard parameter *U* was determined self-consistently simultaneously with the occupation matrix and structures at arbitrary pressures. *U* strongly depends on pressure, structure, and spin state. Comparison with experimental structural data indicates the LDA+U<sub>sc</sub> can predict structure, compression curves, phase relations, and transition pressures very well for the insulating B1 and iB8 phases. However, it requires additional calculations with thermally excited electrons using the Mermin functional to obtain an nB8 metallic state and a consistent iB8 to nB8 insulator-to-metal transition pressure.
- 10) **A Fresh Outlook on Numerical Methods for Geodynamics**<sup>4</sup> – David A. Yuen is a geodynamicist who has advanced the application of *ab initio* materials properties in geo-fluid flow simulations. This article covers Yuen's activities in geodynamics for the past five years. It is a review of geodynamic modeling numerical techniques, traditional ones, and recent ones based on data analytics that has emerged since 2015 and take advantage of machine learning, neural networks and deep learning, unsupervised learning and HPC.

#### **Planned research for 2020-21:**

#### **Software and database to be developed published and in 2020-21:**

Three new codes will be published in the next funding period:

- 1) **`cij`: A Python package to compute thermoelastic properties** - This will be an updated version of a semi-analytical-method to compute the *P-T*-dependent elastic tensor. It is an efficient semi-analytical method, ~10<sup>2</sup>-10<sup>3</sup>x faster than the numerical approach. Only our group and former group members have had this code.

- 2) **pgm: A Python code for anharmonic free energy** – This code combines features from 1) and 2) above. It offers thermodynamic properties for anharmonic systems, e.g., the pre-melting hcp→bcc transition in Be at 0 GPa.
- 3) **EXPRESS: non-stop calculations with the Quantum ESPRESSO** – This is a collection of HTC workflows in Julia to compute equations of state (EoS), static elasticity, vibrational and thermodynamic properties within the QHA, and thermoelasticity using the Quantum ESPRESSO software.
- 4) **Abers database update** - We will carry out *ab initio* calculations of thermodynamics and thermoelastic properties of many phases in the Abers database. We will also incorporate our results for iron bearing phases, including those undergoing a spin-state change in this database and in the Perple\_X database.
- 5) **Thermal conductivity of the LM** – The successes of the phonon quasiparticle method stimulates us to further explore  $\kappa_{lat}$  of mantle phases at extreme conditions. We will compute  $\kappa_{lat}$  of crust forming phases at deep LM conditions. In possession of these properties, we will address the  $\kappa_{lat}$  of (cold) crust accumulations at the core-mantle-boundary (CMB). Such regions should have greater temperature gradients at the CMB and extract the most heat from the core. Knowledge of  $\kappa_{lat}$  of different aggregates will allow us to constrain the CMB heat flow better.
- 6) **FTIR spectra of hydrous defects in olivine** – We will carry out a series of IR spectra calculations of hydrous defects in iron-bearing forsterite (olivine). This work will be a collaboration with Terry Plank’s team, who measure such spectra at Lamont-Doherty Observatory.
- 7) **Geodynamic simulations** – Yuen will conduct geodynamic simulations using new estimates of  $\kappa_{lat}$  of crust and pyrolytic mantle, i.e., including lateral variation in  $\kappa_{lat}$ .

**Wentzcovitch group members:**

- Jingyi Zhuan (student in DEES),
- Zhen Zhang, Qi Zhang, Cheanxing Luo, Tianqi Wan (students in APAM),
- Dr. Yang Sun (post-doc in APAM),
- Dr. Pedro da Silveira (part-time research scientist in APAM, 25% effort).

**Publications** (underlined names are present or former students or post-docs):

- 1) T. Qin, Q. Zhang, K. Umemoto, and R. M. Wentzcovitch, qha: A Python package for quasiharmonic free energy calculation for multi-configuration systems, *Comp. Phys. Comm.* 237, 199-207 (2019). DOI:10.1016/j.cpc.2018.11.003
- 2) Z. Zhang, D.-B. Zhang, T. Sun, and R. M. Wentzcovitch, phq: A Fortran code to compute phonon quasiparticle properties and anharmonic phonon dispersions, *Comp. Phys. Comm.* 243, 110-120 (2019). DOI:10.1016/j.cpc.2019.05.003
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- 5) G. Sheppard, C. Houser, J. Hernlund, T. Reidar, J. Valencia-Cardona, and R. M. Wentzcovitch, Seismic detection of the iron spin transition in Earth’s lower mantle, *Science*, under review (2020).
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## Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC)

SS Xantheas,<sup>1</sup> E Aprà,<sup>1</sup> A Chaka,<sup>1</sup> W de Jong,<sup>2</sup> TH Dunning, Jr.,<sup>3</sup> N Govind,<sup>1</sup> S Hirata,<sup>4</sup>  
S Krishnamoorthy,<sup>1</sup> K Kowalski,<sup>1</sup> X Li,<sup>3</sup> JJ Rehr,<sup>3</sup> C Yang,<sup>2</sup> D Zgid,<sup>5</sup> L Veis,<sup>6</sup> J Brabec,<sup>6</sup> O Legeza<sup>7</sup>

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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 and (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:** Details of development in the areas of Green's Function Coupled Cluster (GFCC) (*Kowalski/Krishnamoorthy/Li/Rehr*), Scalable Multi-Configurational and Multi-Reference Methods for Describing Quasi-Degenerate Molecular Systems (*Dunning/de Jong*) and Finite-temperature many-body perturbation theory for electrons & Grid-based diffusion Monte Carlo without fixed-node approximation & Monte Carlo Green's function methods (*Hirata*) are included in separate abstracts.

Below we highlight developments in using the GFCC as a general solver for embedding methods, recent developments in the area of Density Matrix Renormalization Group (DMRG) algorithms and associated development of a scalable library 4-component relativistic effects and the implementation of the GW Formalism in a Gaussian basis set for molecular systems.

• **Development of 1-particle Green's function (GF) from Coupled Cluster (CC) as a solver for general Green's function embedding methods:** We investigated the performance of GF Coupled Cluster Singles and Doubles (CCSD) method as a solver for GF embedding methods. To develop an efficient CC solver, we constructed the one-particle GF from the CC wave function based on a non-hermitian Lanczos algorithm. The major advantage of this method is that its scaling does not depend on the number of frequency points. We have tested the applicability of the GFCC solver in the weakly to strongly correlated regimes by employing it for a half-filled 1D Hubbard model projected onto a single site impurity problem and a half-filled 2D Hubbard model projected onto a 4-site impurity problem. For the 1D Hubbard model, for all interaction strengths, we observe an excellent agreement with the full configuration interaction (FCI) technique, both for the self-energy and spectral function. For the 2D Hubbard, we have employed an open-shell version of the current implementation and observed some discrepancies from FCI in the strongly correlated regime. Finally, in an example of a small ammonia cluster, we analyze the performance of the GFCCSD solver within the self-energy embedding theory (SEET) with Hartree-Fock (HF) and GF second order (GF2) for the treatment of the environment. The GFCCSD solver with the SEET scheme was subsequently applied to solids such as MnO and SrVO<sub>4</sub>.

• **Relativistic quantum chemical two- and four-component density matrix renormalization group (4c-DMRG) algorithms:** We have developed an efficient operator factorization and code structure of the relativistic quantum chemical two- and four-component density matrix renormalization group (4c-DMRG) algorithm, that includes a variational description of scalar-relativistic effects and spin-orbit coupling. The DMRG implementation of the four-component Dirac-Coulomb Hamiltonian has been

developed in a similar structure as has been done for the standard quantum chemistry package, which formed the basis of the MOLMPS code developments, thus it is also suitable for massive parallelization. In order to boost the performance of the DMRG, the dynamically extended active space (DEAS) procedure has also been generalized further and reorganized. A protocol to obtain configuration interaction (CI) coefficients and cluster amplitudes for the externally corrected relativistic versions of the coupled cluster (CC) method from the matrix product state (MPS) representation of the DMRG wave function has also been developed. These developments are crucial to treat numerically the heavier transition metal compounds, lanthanides, and actinides with open  $d$  or  $f$  shells. For such systems, sufficiently accurate numerical methods are not available, a fact that hinders applications in this field. As a benchmark study, we have presented the relativistic implementation of the coupled cluster method externally corrected by DMRG (4c-DMRG-TCC), to the best of our knowledge the first implementation of that kind, and applied it to TIH, AsH, and SbH. We have demonstrated that the new method brings a significant reduction of computational costs.

- **MOLMPS - A new scalable and highly flexible quantum chemistry DMRG code:** The recently developed MOLMPS program is designed to be a modern state-of-the-art highly scalable DMRG implementation capable of unprecedented large active space calculations and could be easily interface with any other quantum chemistry codes for post-DMRG calculations. Most recent tests show that MOLMPS scales up to 2,500 CPU cores and with over 70 active orbitals. In the recent work we focused on two areas: further optimization of the code, in order to minimize memory and CPU utilization, and on adding the new features. Specifically, we have modified the computation of the presumed operators, where newly created operators follow distribution pattern of the input operators. For the price of slightly increased memory imbalance we obtained a fully local algorithm requiring minimum communication resulting in up to 10x speed up. Further, we have introduced granularity for the most demanding parts involved in Davidson and renormalization algorithms. New important features include the implementation of one and two-site entropies, which are important for the selection of the active space or for the optimization of the active orbitals, the automatic optimization of the orbital ordering, the calculation of the one- and two-body reduced density matrices and their export for DMRG-CASSCF method and the extraction of the T1 and T2 cluster amplitudes from the matrix product states wave-function (needed for tailored CC method in the TAMM module of SPEC).

- **Gaussian Basis Set Implementation of the GW Formalism for Molecular 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. We are in the process of developing a scalable version of this development and integrate it higher-order method within an embedding framework.

- **Development of the Effective Stochastic Potential Configuration Interaction Singles (ESP-CIS) Method:** Obtaining excited states of large ensembles is computationally challenging because of the prohibitively high computational cost of performing first-principles quantum mechanical calculations. To address this challenge, we have developed a new approach, the effective stochastic potential configuration interaction singles (ESP-CIS) method. It uses random matrix theory for the construction

of an effective stochastic representation of the Fock operator and combines it with the CIS method. To illustrate this new method, we have performed excited state calculations of PbS quantum dots (0.75–1.75 nm) at temperatures of 10–400 K. Results from a total of 27 million excitation energy calculations reveal the distributions to be sub-Gaussian in nature with negative skewness, which progressively red-shift with increasing temperature. We plan to extend this method to excited state theories of increasing complexity.

- **Scalable Green’s Function Coupled Cluster Approaches** (see abstract by Kowalski/Krishnamoorthy/Li/Rehr)
  - Scalable and Efficient Green’s Function Coupled-Cluster Approach
  - Relativistic Real-Time Time-dependent Equation-of-Motion Coupled-Cluster Approach
  - Real-Time and Cumulant Green’s Function Coupled-Cluster Approach
- **Finite-temperature many-body perturbation theory for electrons & Grid-based diffusion Monte Carlo without fixed-node approximation & Monte Carlo Green’s function methods** (see abstract by Hirata)
  - Finite-temperature MBPT
  - Grid-based DMC
  - MC-GF2/GF3
- **Scalable Multi-Configurational and Multi-Reference Methods** (see abstract by Dunning/de Jong)
  - SCGVB-based Multiconfiguration Approaches for Describing Non-dynamical and Dynamical Correlation Calculations
  - Robust Selected Configuration Interaction Implementation for CASSCF Calculations for Describing Quasi-Degenerate Molecular Systems
- **Website: [spec.labworks.org](http://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:**

- Integration of the SEET(CCSD/GW) scheme with different GF variants. Public release of the SEET library is scheduled for FY2021.
- Implementation the DMRG-CASSCF method, which will be used for molecular orbitals optimization (important for studying multi-metallic complexes involved in many enzyme centers). We will also test the limits of the code on selected polycyclic aromatic systems involving up to 90 active orbitals.
- 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.
- 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.

- 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.

**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, C.-N. Yeh

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- 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", *J. Amer. Chem. Soc.* **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", *J. Chem. Phys.* **148** (9), 094104 (2018); <https://doi.org/10.1063/1.5010693>
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- 11) L. N. Koulias, D. B. Williams-Young, D. R. Nascimento, A. E. DePrince III, X. Li, "Relativistic Real-Time Time-Dependent Equation-of-Motion Coupled-Cluster," *J. Chem. Theory Comput.* **15**, 6617–6624 (2019).
- 12) J. A. Scher, N. Govind, A. Chakraborty, "Evidence of Skewness and Sub-Gaussian Character in Temperature-Dependent Distributions of One Million Electronic Excitation Energies in PbS Quantum Dots" *J. Phys. Chem. Lett.* **11**, 3, 986-992 (2020)
- 13) B. Peng, K. Kowalski, A. Panyala, S. Krishnamoorthy, "Green's function coupled cluster simulation of the near-valence ionizations of DNA-fragments," *J. Chem. Phys.*, **152** (1), 011101 (2020).
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## Scalable Green's Function Coupled Cluster Approaches

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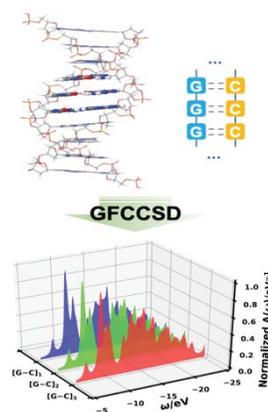
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**Program Scope:** We aim to develop novel scalable Green's Function Coupled-Cluster theoretical approaches and algorithms and associated software aimed at the efficient calculations of the excited states and x-ray spectra of large, complex molecular systems. Our development in this area is as follows:

### 1.1 Scalable and Efficient Green's Function Coupled-Cluster Approach

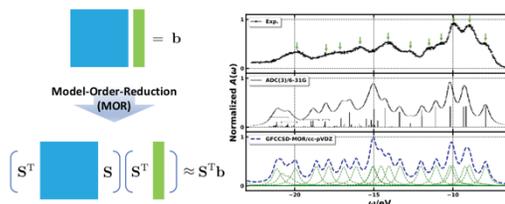
We have theoretically developed a new Green's function Coupled-Cluster (GFCC) approach and its several approximations, and computationally developed a new software library to make the GFCC approach more scalable and efficient for tackling the electronic structure problems of large molecular systems. In particular, we have theoretically demonstrated the analytical frequency-dependent coupled-cluster Green's function of a realistic molecular system can be obtained through solving shifted linear systems in complex space, and numerically calibrated the Green's function coupled-cluster with singles and doubles (GFCCSD) approach for a series of molecules ranging from small diatomic molecules to large DNA fragments with respect to other theories in terms of computing spectral functions including the satellites many-body states not only in the valence band but also in the core-level energy region.<sup>1,2</sup>



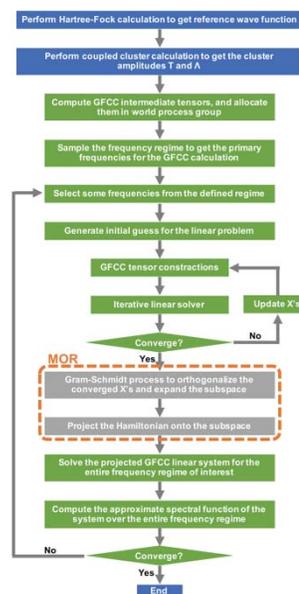
New approximations for the GFCC methods include:

- the GFCC- $i(n,m)$  method,<sup>3</sup> where the excitation level of the inner auxiliary operators ( $m$ ) used to describe the ionization potential and electron affinity effects in the  $(N-1)$ - and  $(N+1)$ -electron spaces is higher than the excitation level ( $n$ ) used to correlate the ground-state coupled cluster wave function for the  $N$ -electron system. Furthermore, in order to maintain size-extensivity of the GFCC matrix elements, we have revealed that  $m$  cannot exceed  $n+1$ . In particular, we have demonstrated the GFCC- $i(2,3)$  method as a new approximation to GFCCSDT, and the computed spectral functions from the GFCC- $i(2,3)$  method exhibit excellent agreement with the experimental results and other high-level theoretical results in terms of providing higher resolution of satellite peaks and more accurate relative positions of these satellite peaks with respect to the main peak positions.

b. the GFCC-MOR method,<sup>4</sup> where we have applied the model-order-reduction (MOR) techniques to form a reduced order model to approximate the original GFCC linear system to compute the spectral function in both interpolative and extrapolative spectral regions. The spectral functions computed from this approximation have been tested with respect to the conventional GFCC method exhibiting excellent agreement. To reach the same level of accuracy as that of the original GFCC method, the GFCC-MOR method is able to significantly lower the overhead of the original computational cost. As a byproduct, the extrapolation of the reduced order model is also able to provide a high-quality initial guess for the existing iterative linear solver to improve the convergence rate in the extrapolative spectral regions.

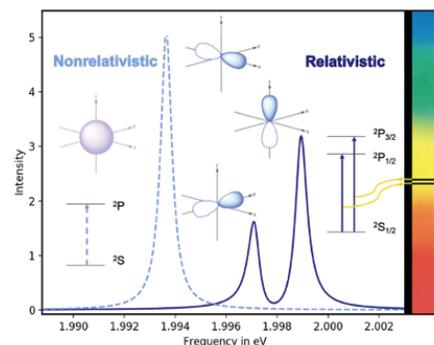


The above developments were incorporated in a scalable and efficient GFCC library.<sup>5</sup> In particular, our GFCC library has integrated and driven the development of a specific library for Tensor Algebra for Many-body Methods (TAMM) to properly treat the compute- and communication-intensive multi-dimensional tensor operations by using Global Arrays (GA) and MPI (involving multi-granular dependence analysis and task-based execution) for the scalable parallelization of tensor distribution, memory management, and scheduling of tensor operations on distributed memory platforms, and using optimized libraries for efficient intra-node execution of tensor operation kernels on CPUs and accelerators (including a GPU execution scheme using TALSH as the underlying GPU tensor algebra engine). For solving multiple frequency and orbital dependent linear equations, the task-based execution is also designed in our GFCC library to allow the process group that finishes the computation earlier to automatically pick another one to jeopardize load imbalance issue in the massive GFCC computations. We have released the GFCC library version 1.0 in September 2019.



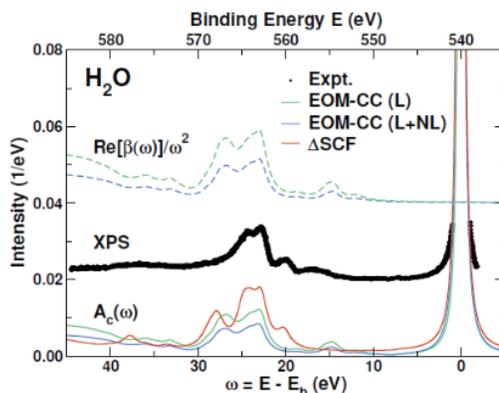
## 1.2 Relativistic Real-Time Time-dependent Equation-of-Motion Coupled-Cluster Approach

We have developed a relativistic time-dependent equation-of-motion coupled-cluster with single and double excitations (TD-EOM-CCSD) formalism.<sup>6</sup> Unlike other explicitly time-dependent quantum chemical methods, the present approach considers the time correlation function of the dipole operator, as opposed to the expectation value of the time-dependent dipole moment. We include both scalar relativistic effects and spin-orbit coupling variationally in this scheme via the use of the exact two-component (X2C) wave function as the reference that enters the coupled-cluster formalism. We show that zero-field splittings in atomic absorption spectra of open-shell systems computed using X2C-TD-EOM-CCSD are in excellent agreement with values obtained from experiment. In closed-shell species, we observe singlet triplet mixing in the X2C-TD-EOM-CC calculations, which results from the



use of the X2C reference. Compared to spectra obtained by X2C-TDDFT, X2C-TD-EOM-CCSD results are consistently in better agreement with experiments.

As the number of electrons in a system increases, one must make a compromise between cost and accuracy for the electronic structure method used, opening the door for quantum embedding methods. Embedding is often used as a tool to improve the electron-electron correlation of a subsystem by exploiting the locality of the interaction. Since relativistic effects, such as the scalar relativity and spin-orbit coupling, are more local than electron-electron correlation, embedding should be an effective tool for introducing new physics within the Dirac framework into the Hamiltonian of a quantum subsystem. We developed a relativistic quantum embedding formalism capable of variationally treating relativistic effects, including scalar-relativity and spin-orbit coupling. We extend DFT-in-DFT projection-based quantum embedding to a relativistic two-component formalism, where the full spin magnetization vector form is retained throughout the embedding treatment. To benchmark various relativistic embedding schemes, spin-orbit splitting of  $W(CO)_6$  and the dissociation potential curve of  $WF_6$  are investigated. The results computed using the relativistic embedding approach show an excellent agreement with the full relativistic calculations.



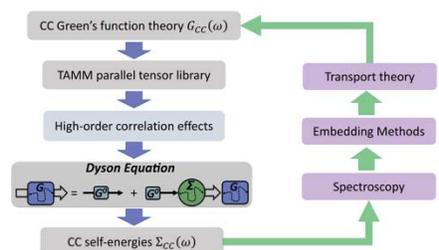
### 1.3 Real-Time and Cumulant Green's Function Coupled-Cluster Approach

*RT-EOM-CC*: A key theoretical development is the introduction of an EOM-CC cumulant Green's function approach. Instead of energy space, the method is based on an initial value problem with the time evolution of the Green's function governed by CC EOM.<sup>7</sup> The core-hole Green's function in the time-domain then has a cumulant representation, which simplifies both the calculations and analysis. The method is illustrated with calculations of intrinsic inelastic losses in x-ray spectra. Many-body contributions to x-ray spectra are calculated using an exact factorization of the transition amplitude, which leads to a convolution of an effective one-body absorption spectrum and the core-hole spectral function. The spectral function  $A(\omega)$  accounts for intrinsic inelastic losses that give rise to satellites in XPS and XAS, as illustrated in the figure.<sup>7</sup> Our current implementation uses an efficient real-time integrator limited to linearized singles. A manuscript describing an extension to the full singles EOM-CC equations is in preparation.<sup>8</sup> We now plan to implement the approach using the tensor contraction engine (TCE) formalism. This will also permit efficient calculations of double excitations arising from the  $T_2$  cluster operator. In related work, we developed a formal approach for going beyond the linear-response approximation to the cumulant Green's function based on the Kadanoff-Baym equation for the fully-interacting Green's function.<sup>11</sup> The theory leads to a compact formula which suggests how to calculate corrections to the cumulant using real-time TDDFT. The approach was tested on an exactly solvable model system, and the results suggest that linearization about the final state in the presence of the core-hole is a preferable starting point.

*Real-time linear and non-linear response software*: We are developing software to implement the previously developed theoretical and algorithmic advances.<sup>8</sup> In particular, we have developed a module for the real-time propagation of single-particle quantum states with a general, time-

dependent Hamiltonian. This module can be used, for example, to provide real-time capabilities such as real-time TDDFT to enable exascale capabilities in spectroscopy. Preliminary performance tests at National Energy Research Scientific Computing Center (NERSC) yield linear scaling up to thousands of processors.

**Future plans:** The GFCC infrastructure/library will enable quick deployment of hierarchical structure of GFCC approximations accounting for higher-rank excitations, which play an important role in identifying challenging satellite states. These unique features make the GFCC formalism competitive to existing Green's function approaches including family of GW and ADC(n) formalism. We believe that these formulations can coexist and be used to construct more accurate forms of quantum embedding formalism that can utilize GFCC and through Dyson equation CC self-energies as building blocks. A natural extension of GFCC will be core-level spectroscopy and transport theory.



Our implementation of the X2C-TD-EOM-CCSD approach sets the groundwork for simulations of electron dynamics in the presence of time-varying electromagnetic fields, so that non-equilibrium dynamics with a variational treatment of relativistic effects can be considered in the future. We further plan to apply the relativistic embedding formalism to the modeling of systems containing late transition metal, lanthanide, and actinide molecular complexes.

We plan to incorporate the platform-independent routines developed in Section 1.3 into a library, which can be used as a component of major electronic structure codes.

## Publications

1. B. Peng, K. Kowalski, "Green's function coupled cluster approach: Simulating photoelectron spectra for realistic molecular systems," *J. Chem. Theory Comput.*, **14** (8), 4335–4352 (2018).
2. B. Peng, K. Kowalski, A. Panyala, S. Krishnamoorthy, "Green's function coupled cluster simulation of the near-valence ionizations of DNA-fragments," *J. Chem. Phys.*, **152** (1), 011101 (2020).
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4. B. Peng, R. Beeumen, D. Williams-Young, K. Kowalski, C. Yang, "Approximate Green's function coupled cluster method employing effective dimension reduction," *J. Chem. Theory Comput.*, **15** (5), 3185–3196 (2019).
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**Scalable Multi-Configurational and Multi-Reference Methods  
for Describing Quasi-Degenerate Molecular Systems**

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**Program Scope:** Many molecular phenomena cannot be described with wave functions based on a single configuration. This includes the dissociation of molecules, diradicals, chemical reactions, many excited states, etc. The valence Complete Active Space Self-Consistent Field (CASSCF) wave function provides a versatile multiconfiguration description of a broad range of molecular phenomena. Unfortunately, as the number of active orbitals and electrons increases, the number of configurations in the CASSCF wave function explodes exponentially. This limits the range of applicability of CASSCF approaches. In this task we are developing more efficient, yet accurate approaches based on the construction of multiconfiguration wave functions with reduced complexity to address the exponential explosion in the number of configurations in CASSCF wave functions. In particular, we are developing a parallel MCSCF module for modeling the ground and excited states of molecular systems, utilizing two complementary approaches to reduce the exponential scaling of the CASSCF wave function:

- Multiconfiguration approaches based on Spin-Coupled Generalized Valence Bond (GVB) wave functions.
- Efficient selected CI approaches for CASSCF calculations that systematically eliminate the least important CASSCF configurations.

These multiconfiguration wave functions will set the foundation for economical, yet effective MRCI and MRCC formulations.

**Recent Progress:** Several new advances were made in both the methodological as well as the algorithmic / code development fronts. Below we summarize the most important developments:

**I. SCGVB-based Multiconfiguration Approaches for Describing Non-dynamical and Dynamical Correlation Calculations**

The spin-coupled generalized valence bond (SCGVB) wave function provides an efficient and effective description of molecular phenomena requiring a multiconfiguration wave function.<sup>1</sup> The SCGVB wave function (1) describes non-dynamical correlation effects in atoms and molecules, correcting the most serious limitation of single configuration wavefunctions; (2) contains only a subset of the CASSCF configurations, although these are usually the dominant CASSCF configurations; and (3) is an orbital wavefunction that provides insights into the electronic structure of both “normal” and “abnormal” molecules, e.g., hypervalent molecules, diradicals, etc.

Although the SCGVB wavefunction includes non-dynamical correlation effects, dynamical correlation effects must be included in the electronic wave function to make quantitative predictions of molecular energetics, structures and properties. To facilitate calculations that include the effects of dynamical correlation, the SCGVB wavefunction, in which the active orbitals ( $\varphi_{ai}$ ) are non-orthogonal, is recast as a multiconfiguration wavefunction in terms of orthogonal natural orbitals (NOs) and used in multireference MRCI.

**Table 1.** Comparison of the bond energies ( $D_e$ ) from  $c$ SCGVB(NO) and CASSCF calculations and  $c$ SCGVB(NO)+1+2 and CASSCF+1+2 calculations for a test set of molecules selected from the database of Peverati & Truhlar.<sup>4</sup>  $D_e$  and  $\Delta D_e$  are in kcal/mol.

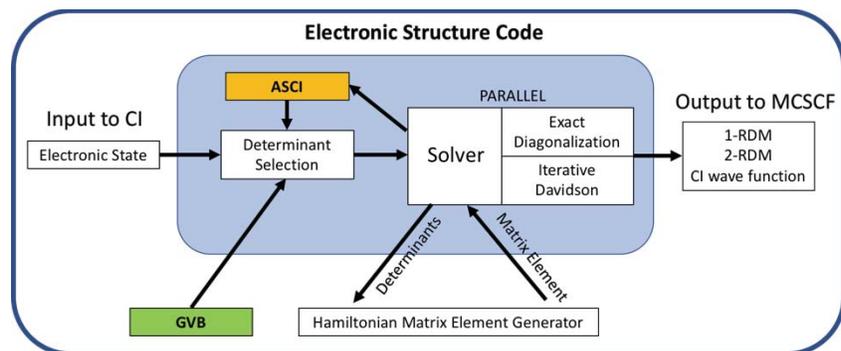
	Bond	$D_e$ (MC)			$D_e$ (MRCI)		
		$c$ SCGVB(NO)	CASSCF	$\Delta D_e$	$c$ SCGVB(NO)	CASSCF	$\Delta D_e$
<b>HF</b>	H-F	114.80	115.36	0.56	138.13	137.08	-1.05
<b>HCl</b>	H-Cl	90.87	91.73	0.86	104.74	105.36	0.62
<b>N<sub>2</sub></b>	N-N	204.40	205.35	0.95	223.37	223.60	0.23
<b>P<sub>2</sub></b>	P-P	89.07	89.74	0.67	109.48	109.79	0.31
<b>PN</b>	P-N	120.65	121.59	0.94	140.72	141.03	0.31
<b>F<sub>2</sub></b>	F-F	17.42	19.94	2.52	33.77	34.61	0.84
<b>NH<sub>3</sub></b>	H <sub>2</sub> N-H	102.81	102.83	0.02	113.91	111.50	-2.41
<b>PH<sub>3</sub></b>	H <sub>2</sub> P-H	75.89	75.93	0.04	86.00	86.05	0.05
<b>H<sub>2</sub>O</b>	HO-H	108.31	108.69	0.38	123.67	122.45	-1.22
<b>H<sub>2</sub>S</b>	HS-H	81.69	82.21	0.52	93.84	93.98	0.14
<b>HOCl</b>	HO-Cl	41.45	43.48	2.03	54.84	55.53	0.69
<b>C<sub>2</sub>H<sub>2</sub></b>	HC <sub>2</sub> -H	126.53	123.59	-2.94	137.54	137.16	-0.38
	HC-CH	221.17	225.62	4.45	232.84	233.19	0.34

We are assessing the accuracy of a version of the SCGVB(NO) wave function obtained by directly calculating the natural orbitals (NOs) in an approximate multiconfiguration version of the SCGVB wave function. This bypasses the need for computing the SCGVB wave function, techniques for which are still being actively developed.<sup>2</sup> This *constrained* SCGVB(NO) wave function was successfully used by Walch *et al.*<sup>3</sup> to study the bonding in V<sub>2</sub> and Cr<sub>2</sub>. We are systematically comparing the  $c$ SCGVB(NO)- and CASSCF-based approaches on a set of molecules selected from the database developed by Peverati and Truhlar.<sup>4</sup> These molecules cover a broad range of bond types—from diatomic to polyatomic molecules, from single bonds to multiple bonds, from strong bonds to weak bonds, from bond involving first and second row main group elements, *etc.* This set of molecules will provide a rigorous assessment of the  $c$ SCGVB(NO) approach for the main group elements. Selected preliminary results from this study are summarized in Table 1. As a result of this study we have found that, for some molecules, the CASSCF+1+2 energies are higher than the  $c$ SCGVB(NO)+1+2 energies (the CASSCF energies are always lower than the  $c$ SCGVB(NO) energies, as they must be). We are now investigating the cause of this unexpected behavior and its connection to the proper definition of non-dynamical and dynamical electron correlation.

## II. Robust Selected Configuration Interaction Implementation for CASSCF Calculations

The Adaptive Sampling Configuration Interaction (ASCI) code developed in collaboration with Tubman at NASA has been integrated into the NWChem MCSCF module, using its orbital solver (cf. Figure 1). This allows the simulation of systems that can be described effectively with 100,000s, possibly a million, determinants using serial solvers. Our target is to be able to study

active spaces in the order of (100, 100), which for strongly correlated systems will require tens or hundreds of millions of determinants. Although the ASCI algorithm aims to reduce the number



**Figure 1.** Architecture of the robust selected CI library.

determinants needed to describe the ground electronic state of complicated molecular systems, it is often the case that the number of determinants required for an accurate treatment grows  $>10^6$ , making dense solvers and serial sparse (Krylov) solvers impractical. As such, use

of efficient distributed memory Krylov solvers is necessary to further push the limits of the ASCI algorithm.

There are two primary challenges for an efficient distributed memory implementation of the ASCI, or any other selected CI algorithm: (1) the distributed formation of the sparse adjacency matrix for an arbitrary list of determinants with varying connectivity, and (2) optimization of the distributed memory sparse matrix vector product (SpMV) of the CI Hamiltonian onto trial vector spaces. For (1), we are developing efficient and scalable 1- and 2-dimensional distribution schemes for the determinant list which allow for reuse of highly efficient adjacency search algorithms previously developed for the ASCI method to search for determinant connections on a subset of the total determinants on each processor. For (2), we are examining the efficacy of distributed memory graph partitioning and reordering algorithms, such as those developed in the METIS and SCOTCH libraries, to optimize the distributed SpMV. In essence, graph partitioning allows for the reordering of the determinant list as to balance the non-zeros on each processor and minimize the communication incurred between processors in the distributed SpMV. Although graph partitioning poses a non-trivial upfront computational cost, the savings incurred by the resulting optimized SpMV will often amortize this cost over the remainder of the ASCI iterations. Once an efficient SpMV has been developed, it may be integrated with any number of distributed memory Krylov solvers, such as Lanczos, Davidson, etc.

Due to its stability, and its efficient utilization of level-3 BLAS primitives, we have examined the use of the LOBPCG algorithm, which will allow for the determination of multiple eigenstates in future work.

**Future plans:** We are currently investigating the underlying cause for the  $DD_e$ 's in excess of -1 kcal/mol in Table 1, which in all cases are a result of the  $D_e$ 's from the  $c$ SCGV(B(NO))+1+2 calculations being larger than those from the CASSCF+1+2 calculations. In the future we will extend the  $c$ SCGV(B(NO)) and  $c$ SCGV(B(NO))+1\_2 studies to molecules and molecular states of the main group elements not included in the Peverati and Truhlar database, e.g., hypervalent molecules, molecular excited states, diradicals, etc. In a corollary study prompted by the results of the  $c$ SCGV(B(NO)) and  $c$ SCGV(B(NO))+1+2 calculations, we will investigate non-dynamical and

dynamical correlation to gain insights into the impact of these two, long recognized, but still poorly defined contributions to electron correlation on molecular energetics and structures.

Although the developments in the Selected Configuration Interaction library have been focused on the distributed memory implementation of ASCI, each of them could be applied to other selected / truncated CI methods as well. As such, we plan on developing open source, modern C++ software with reusable interfaces such that it may be easily integrated into other selected CI codes in the future. In addition, we will be (1) integrating the spin-coupled generalized valence bond (cSCGVB) recipe developed by Dunning and coworkers into ASCI, which effectively means adding additional constraints on the selected determinants, and (2) develop a stand-alone C++ MCSCF module that couples the second-order orbital rotation with the ASCI routine. The goal is to release the software library in late FY2020. We are currently using the implementation in NWChem to continue the exploration of electronic state and spin behavior of larger iron-sulfur complexes in collaboration with Drs. S. Xantheas (PNNL) and Prof. D. Tzeli (Univ. of Athens, Greece).

**Supported personnel:** Jasper V. K. Thompson (Grad Student) and Lu T. Xu (Postdoctoral Fellow)

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## Polymers in deep eutectic solvents

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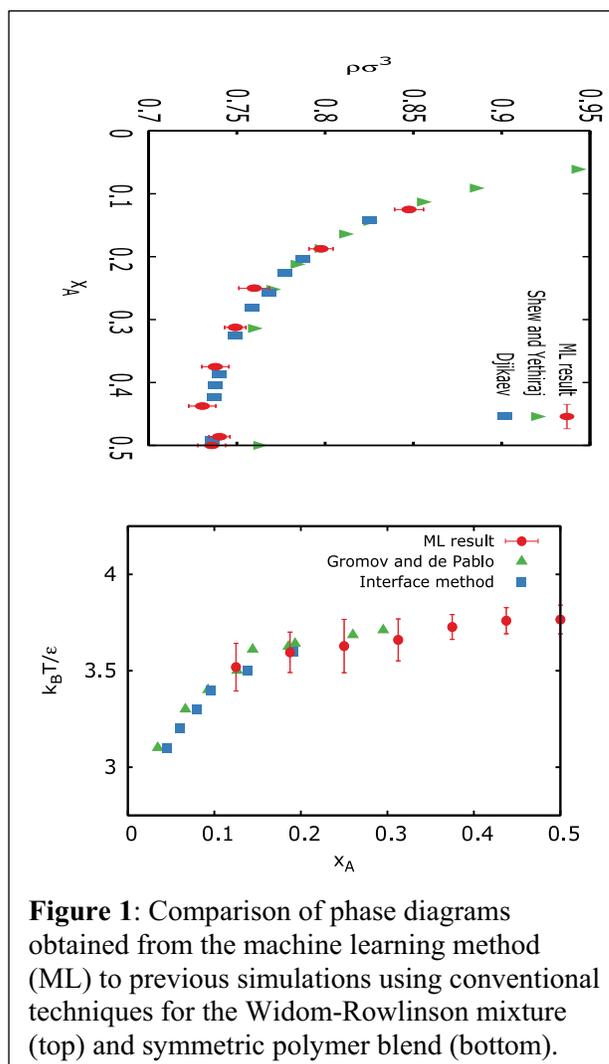
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### Abstract

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 developed machine learning methods to calculate the phase diagram of complex fluids. We tested these methods for two simple models and have then applied them to calculate the phase diagram of PEO in the ionic liquids [BMIM][BF<sub>4</sub>] and [BMMIM][BF<sub>4</sub>].

The phase behavior of complex fluids is a challenging problem for molecular simulations. Supervised machine learning (ML) methods have shown potential for identifying the phase boundaries of lattice models. We have extended these ML methods to continuous-space systems. We use a convolutional neural network (CNN) model that utilizes grid-interpolated coordinates of molecules as input data of ML, and optimizes the search for phase transitions with different filter sizes. The method is accurate for the phase separation boundaries of two off-lattice models; the Widom-Rowlinson model and a symmetric freely jointed polymer blend, for which results are available from standard molecular simulations techniques



**Figure 1:** Comparison of phase diagrams obtained from the machine learning method (ML) to previous simulations using conventional techniques for the Widom-Rowlinson mixture (top) and symmetric polymer blend (bottom).

(figure 1). The ML method has the added advantage that there is no critical slowing down. The long simulations required make the method challenging for systems (like ionic liquids) with slow dynamics.

We have developed a different deep neural network method that uses thermodynamic and structural descriptors instead of the grid interpolated positions as the training set. We apply this method to PEO in the ionic liquids [BMIM][BF<sub>4</sub>] and [BMMIM][BF<sub>4</sub>]. We are able to obtain the phase diagram near the critical point including the critical exponents, although we have no experimental or other data to test the method against.

We have developed ab initio force fields for choline chloride and urea. The resulting force fields are accurate for the properties of the urea-water system, and we are investigating the force fields for the DES.

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.

**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**

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3. C.-Y. Son, J. G. McDaniel, Q. Cui, and A. Yethiraj, "Conformational and Dynamic Properties of Poly(ethylene oxide) in [BMIM][BF<sub>4</sub>] : A Microsecond Computer Simulation Study Using First Principles-Based Force Fields, *Macromolecules* **51**, 5336-5345 (2018).
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## Incorporating long-range interactions for machine-learning potentials of water and electrolyte solutions

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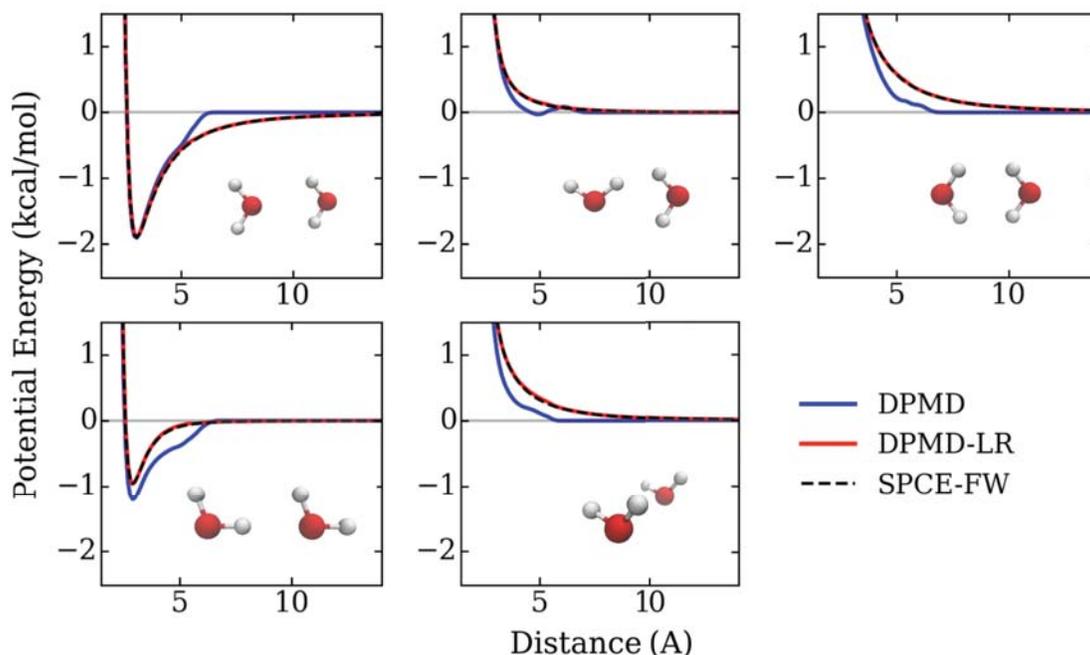
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### Abstract

Electrolyte solutions in water are important in many natural and industrial processes, such as CO<sub>2</sub> sequestration trapping mechanisms in brine solution, ion transfer in electrochemical systems, and specific ion effects in protein stability and activity. The vapor phase of water, specifically in liquid-vapor equilibrium, also has immense significance in industrial settings, since cavitation damage in pumps and turbines is a great concern. Many studies on both systems have turned to molecular simulations as a means to provide intuition regarding the underlying physics and chemistry. To obtain meaningful simulation studies of these systems, however, there is a need for molecular models that can provide necessary information on thermodynamic and dynamic information over a wide range of conditions and heterogeneous environments. In recent years, atomistic machine learning models [1] have become increasingly popular in molecular simulations, given their ability to combine the accuracy of *ab initio* representations with the speed and efficiency of classical models. These models are capable of learning highly complex and multi-dimensional interactions within a local environment; however, they face significant challenges in fully capturing long-range behavior which are critical in representing charged and heterogeneous systems.

In this work, we use the Deep Potential Molecular Dynamics (DPMD) [2,3] framework to train deep neural networks to interatomic Potential Energy Surfaces to construct many-body classical potentials that accurately represent the structure and dynamics of water and electrolyte systems. We introduce a formalism to represent long-range electrostatics by decomposition of the Coulombic Ewald energy from the local environment representation. We evaluate the approach by training a model to fit the simple classical water model SPC/E and demonstrate the effectiveness of our adapted model (DPMD-LR) in representing long range dimer potential energies, as shown below:



We further validate our approach by predicting accurate bulk water and electrolyte solution properties, such as equilibrium densities and transport coefficients, as well as vapor-liquid coexistence behavior and gas phase second virial coefficients. All together, these properties highlight the versatility of our model in representing heterogeneous and charged systems.

In the future, we will implement this long-range formalism to DPMD models trained from ab initio data. In this manner, we can perform a first principles investigation of these systems by combining the computational efficiency of classical methods with the complexity of ab initio descriptions brought by machine learning techniques.

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**Grant DE-SC001934: Chemistry in Solution and at Interfaces**

**Students:** Shuwen Yue, Maria Nicola Barbosa Muniz, Marcos F. Calegari Andrade,  
Linfeng Zhang

**ECC: EXASCALE COMPUTATIONAL CATALYSIS**

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**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<sub>2</sub> 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**

We have made important progress on the problem of optimizing saddle point structures. Our method,<sup>1</sup> which has been implemented in the Sella (<https://github.com/zadorlab/sella>) software package, bridges the gap between commonly-used saddle point optimization algorithms in both gas-phase molecular chemistry and condensed-phase or solid-state applications. Our approach is a strict improvement over methods which rely on iterative diagonalization of the Hessian matrix. The curvature calculated during iterative diagonalization is used to construct an approximate Hessian which approaches complete accuracy as the number of diagonalization iterations increases. In the limit of full diagonalization, our method becomes equivalent to saddle point optimization algorithms which involve full evaluation of the Hessian matrix. We have also implemented efficient minimization and saddle point refinement algorithms that use internal coordinates. In our approach, displacement vectors are realized in the redundant and coupled internal coordinate space as a geodesic on the manifold of physically meaningful internal coordinate vectors. This facilitates both geometry optimization and iterative diagonalization of the Hessian in the internal coordinate space. Furthermore, the machinery developed for internal coordinates can also be used to enforce constraints in both minimization and saddle point optimization through the sequential quadratic programming approach.

The combined groups of West and Goldsmith have made improvements to RMG-Cat. RMG-Cat was merged with the official master branch of RMG, so that it is now distributed to a much wider user base, has many more developers maintaining it, and will benefit from many new features being developed in RMG. Since the merge it is just called RMG, not RMG-Cat (although the latter name is still used in this project). A major development is the implementation of Linear Scaling Relations (LSRs) to predict adsorption energies of any adsorbate on a wide range of metals, parameterized by the binding energies of elemental atoms. This has allowed us to explore how reaction mechanisms change as a function of binding energies on arbitrary alloy surfaces. Coupled with sensitivity analyses to reveal the degree of rate control, one can explore not only the location of the optimal catalyst on a “map” of metals, but also the reasons for the shape of the map. We have demonstrated

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this with the catalytic partial oxidation of methane, and are very close to submitting a publication. The previous work on the catalytic combustion of methane on platinum has now been published.<sup>10</sup>

AutoTST, our code for automatically predicting transition state geometries and performing fully automated TST calculations of reaction rates, has been improved and is better tested. The code has been refactored, conformer searches are more robust, symmetry numbers are determined using RMG, and the workflow has been improved for deployment on larger computational clusters. Hindered rotor scans for 1D-HR corrections have also been implemented 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. We made significant progress in transforming Active Thermochemical Tables (ATcT) into a public interactive database allowing contributions from external collaborators by creating adjunct Django databases that not only contain all historical ATcT data over the last 15 years, but also new collaborator data. We have contributed substantial improvements to the public ATcT website including a new interactive search functionality and an API that provides direct access to the current ATcT through species name, SMILES, InChI, CASRN, and ATcTID. We have also extended the ATcT capabilities to enable the treatment of adsorbate thermochemistry.

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<sub>2</sub>OH 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).

We have begun development of AdTherm, a new code for computing the partition functions for adsorbates. A PhD student at Brown visited Sandia to collaborate on code development. The project focuses on the six degrees of freedom that correspond to the motion of the adsorbate relative to the surface. These degrees of freedom are anharmonic and coupled. The approach uses classical phase space representations. We are currently considering two means of generating a surrogate potential energy surface for use in the phase space integrals. One method utilizes artificial neural networks. The second method uses Bayesian compressed sensing. These two methods are currently being tested on DFT data for methanol on Cu(111). Our initial focus is on the 3 degrees of freedom that correspond to frustrated translation.

NWChem is an open source computational chemistry code developed at PNNL. 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, as well as several meta-GGAs include M06 and SCAN functionals. In addition, E. Bylaska and E. Hermes developed an i-PI interface in NWChem. This interface can be used with a variety of external packages such as ASE and the Sella optimizer which was developed in this project. To improve the efficiency of certain types of simulations with transition metals and larger surfaces we have implemented faster algorithms to compute 2-center Gaussian multipole integrals used by PAW potentials, implemented O(N) exact exchange algorithms based on the standard Wannier localization and Damle-Lin-Ying localization procedures, and we are completing a port of the PAW code to the band structure codes. We also updated fractional occupation optimizers and fixed various bugs for metallic systems. For the NWChemEx plane-wave code, we have completed an initial version of the code and we are working the Argonne researchers through the ALCF catalysis-esp project (led by D. Bross) to implement hybrid MPI-GPU algorithms into it (the non-local pseudopotential kernel has already been converted to SYCL and as a complement a HIP/CUDA version is also completed).

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 are currently using these interfaces and queues to carry out catalysis reaction simulations on 111 Cu surfaces using the Theta computer with the ALCF catalysis-ESP project at ANL. We also developed strategies for calculating first and second quantization of periodic 2-electron integrals. Our in-press paper<sup>2</sup> written by E. Bylaska includes E. Hermes and J. Zádor as co-authors describes the first quantization the strategy. This manuscript also highlighted the Sella program and its interface to NWChem to carry out several simulations validating the method. Several of the software developments were described in the just accepted J. Chem. Phys. publication, "NWChem: Past, Present, and Future". This manuscript includes team members E. Bylaska and E. Hermes as co-authors.

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. Current scalability tests for medium (tens of species) and large (hundreds of species) chemical kinetic models indicate a 10x speedup for GPU-enabled architectures compared to parallel model employing the CPU only resources. We have developed a parser for Chemkin-format surface kinetic model specifications, and have developed tools for handling micro-kinetic models necessary for heterogeneous catalysis models. These tools were validated against other libraries (Cantera) and we are not in the process to extent the heterogenous catalysis models to GPU-based architectures via Kokkos.

We have completed 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 both chemical systems and general dynamical systems governed by either ordinary differential equation (ODE) or differential algebraic equation (DAE) models. We have validated analysis results with both synthetic ODE/DAE model problems, and gas phase chemical kinetic ODE systems, using TChem and relying on legacy CSP-analysis codes in the latter context. We also worked on enhancing accuracy and robustness of our Kokkos batched eigensolver targeting mixed CPU/GPU architectures. The eigensolver is required for eigendecomposition of the Jacobian matrices for CSP analysis. We demonstrated up to 28x speedup with this eigensolver relative to unbatched CUDA eigensolvers running on an NVIDIA V100 GPU system, for Jacobian matrices resulting from 53-species chemical mechanisms for methane-air oxidation.

We developed and tested derivative-based extensions to sparse polynomial regression as well as to Gaussian process (GP) regression. Derivative-based GP has shown greater promise for PES approximation. Currently, we are implementing hierarchical GP approximation in an active learning setting for custom search tasks, such as PES minimization or saddle point discovery. Besides, we have implemented Bayesian optimization for hyperparameter (e.g., GP correlation length) selection in surrogate construction. Furthermore, we developed and tested multiple integration strategies, all surrogate-based, for efficient partition function computations aiming to minimize the number of DFT calculations.

## **FUTURE PLANS**

Sella's implementation of internal coordinate optimization struggles with certain systems, e.g. systems where three sequentially-bonded atoms become collinear. We are working on solutions for this problem, which may include the automatic on the fly addition of "dummy atom" sites or alternate definitions of internal coordinates which remain well-defined even for collinear systems. Furthermore, we intend to implement optimization in a mixed Cartesian/internal coordinate representation to more efficiently optimize systems relevant to heterogeneous catalysis, as the positions of atoms in the solid are most efficiently represented by Cartesian coordinates, whereas adsorbate atom positions can be effectively represented by internal coordinates.

We are also developing routines for generating realistic initial guess structures for saddle points on heterogeneous catalysts in order to avoid performing the large number of expensive nudged elastic band (NEB) calculations that would otherwise be required to find the relevant saddle points. In our approach we define penalty function as a harmonic potential acting on metal-adsorbate bond distances for various bidentate binding configurations. Then, we minimize the penalty function plus potential energy. We select all symmetry distinct structures, and Sella is used to optimize these unique guess structures to the first order saddle points. We are currently working on the work-flow which would automate the whole method.

At Brown we are continuing to develop AdTherm. Our next steps will be to incorporate the three degrees of freedom that correspond to frustrated rotation, and then to extend this approach to additional molecules. 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 adding new reaction families and data to RMG-Cat for Eley-Rideal reaction types, and reactions involving van-der-Waals adsorbates, and an ability to treat bidentate adsorbates.

We anticipate that coupling AutoTST 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, and have started exploring the use of graph neural networks to predict adsorbate properties.

PNNL and ANL are working together to test our newly developed the web-based periodic builder and queue system by running NWChem plane-wave simulations for simulations on the 111 Cu surface and Cu nanoparticles on ALCF machines at ANL. We will be working with SNL to make sure these workflows are able to work with the KinBot and Sella programs. Our implementation of RPA in NWChem is slightly behind schedule in order to focus on our recent developments for integrating the Brillouin zone with periodic many-body electronic structure methods. We are currently refocused on implementing RPA and other periodic many-body methods in NWChem. We have also been working on  $O(N)$  DFT solvers including  $O(N)$  exact exchange algorithms, and we are working with Argonne researchers through the ALCF catalysis-esp project (led by D. Bross) to implement hybrid MPI-GPU algorithms into NWChemEx.

In the near term we will be releasing the gas-phase component of TChem++ that employs Kokkos for many-core and GPU computing platforms. In parallel we will be extending the microkinetic model capability in TChem to handle multiple surface sites and expand its Kokkos implementation. We will augment the range of physical models with continuously stirred-tank reactor and plug-flow reactor models. In the near term these models will be implemented and tested in a serial mode. In the longer term, these models will be parallelized and tailored to run on heterogenous computing platforms.

We will also be working on a number of improvements in the CSP library pertaining to interfacing to TChem++ and the Kokkos batched eigensolver, the bulk efficient handling of large-scale chemical data bases, as well as general code housekeeping/cleanup, and documentation, prior to proceeding to open-source code release. We will also develop DAE interfaces to TChem++, with targeted demonstrations in surface catalysis.

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**Postdocs:** Eric Hermes (SNL), Oscar Diaz-Ibarra (SNL)

**Students:** Brown: Katrin Blondal, Northeastern: Emily Mazeau, Nate Harms, David Farina

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## Accurate Ab-Initio Methods for Correlated Surface Problems

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**Scope:** The ab-initio simulation of periodic surfaces and solids with strong correlations is an important problem in quantum chemistry and condensed matter physics. While reliable computational methods exist for weakly correlated solids, they tend to be less suitable where the underlying independent electron approximation fails, such as in systems with d-electrons. Where strong correlations are important, the community has historically resorted to the construction of low-energy effective models, such as single- or multi-orbital Hubbard models, in order to describe effective low-lying degrees of freedom. For systems where a treatment of the electronic structure in addition to strong correlation physics is desired, embedding methods such as a combination of the dynamical mean field theory (DMFT) with density functional theory (DFT) electronic structure codes, led to a combination of both approaches. These methods are very successful in their region of applicability. However, they suffer fundamentally from the need to determine free parameters, such as the double counting correction or the values of screened interaction parameters, at the interface between the electronic structure and strong correlation calculations. In this grant we focus on the development and assessment of a diagrammatic ab-initio embedding theory - the self-energy embedding theory (SEET). This theory that was developed by Zgid combines the GW approximation with the non-perturbative solution of quantum impurity models. SEET can be used to describe molecules, surfaces, and solids.

**Recent progress:** The accurate ab-initio simulation of periodic solids with strong correlations is one of the grand challenges of quantum chemistry and condensed matter. While relatively mature methods exist for weakly correlated solids, the ab-initio description of strongly correlated systems is an active field of research. In our recent work, we showed results for the single particle spectral function of the two correlated d-electron solids NiO and MnO from self-energy embedding theory (SEET) combined with finite temperature GW methodology. Unlike earlier work, our method does not use any adjustable parameters and is fully ab-initio, while being able to treat both the strong correlation and the nonlocal screening chemistry and physics of these materials. Fig 1 and 2 illustrate embedding and choices of physically important orbitals, and compare our results to x-ray and angle-resolved photoemission spectroscopy as well as bremsstrahlung-isochromat spectroscopy. We believe that these are very significant results and that these tools will allow us to routinely treat strongly correlated solids fully ab-initio at the post DFT level. The implications of this work are very significant for our fundamental understanding of the nature of strongly correlated solids as well as to new materials design and materials science.

**Future developments:** Investigation of SEET as applied to superconducting materials. Estimation of finite size effects in solids. Simulation of phononic spectra and phononic superconductivity.

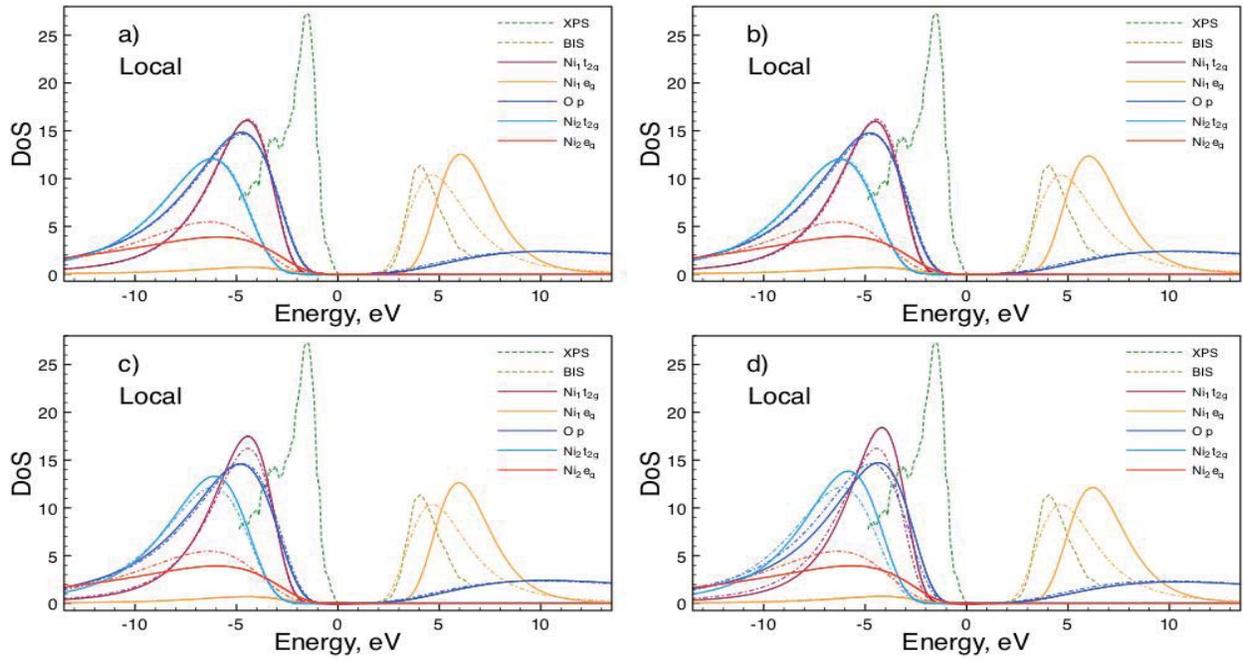


Fig. 1. Orbitally resolved SEET local spectral function for NiO solid. Panels in the plots correspond to impurity choices from Table I. (Specifically, the panel a) corresponds to an impurity choice a), etc.) Dash-dotted lines: GW, solid lines: SEET; Dashed lines: experimental data. For impurity choices see arXiv:2003.04440).

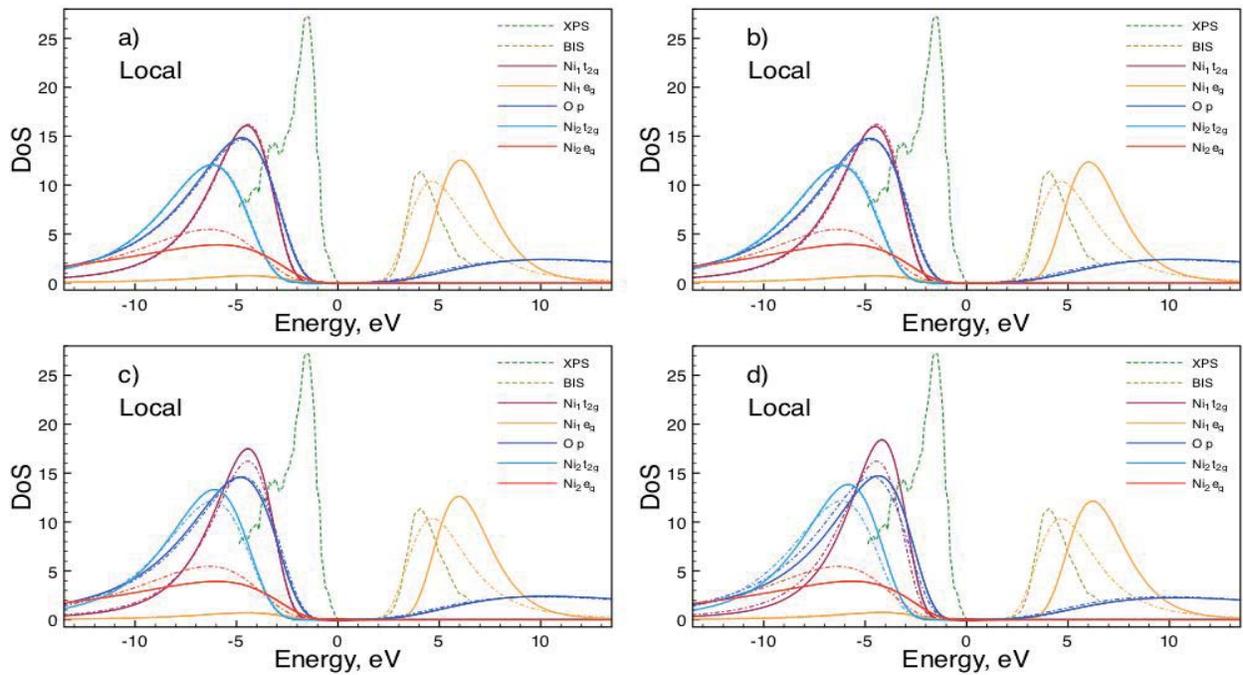


Fig. 2 Orbitally resolved SEET local spectral function for MnO solid with impurity choice of Table III. Panels in the plots correspond to impurity choices from Table III. (Specifically, the panel a) corresponds to impurity choice a), etc.) Dash-dotted

lines: GW, solid lines: SEET; Dashed lines: experimental data. For impurity choices see arXiv:2003.04440)

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# New Software Tools and HPC Implementation of DPMD

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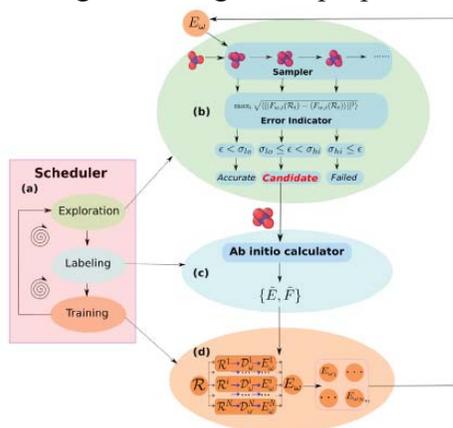
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## Abstract

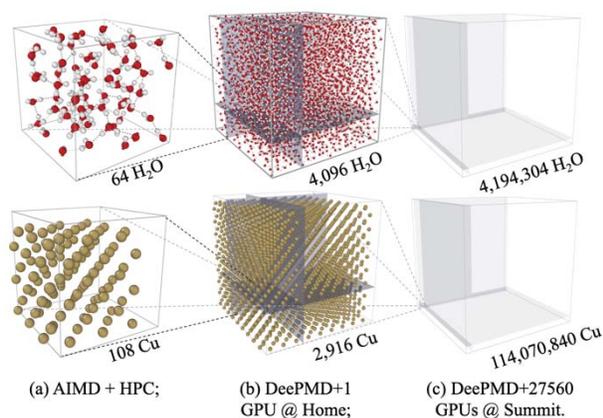
Harnessing the power of future exascale computer architectures is one of the goals of software development at our center. Equally important is the release of new open software tools to the computer simulation community. In this context, we have completed two projects: (1) we have implemented<sup>1</sup> and made available to users a tool called DP-GEN to construct deep potentials; (2) we have developed and optimized on Summit at ORNL a very efficient multi-GPU version of the DPMD software, which can simulate systems as large as 100 million atoms on Summit.

Deep learning-based models for the interatomic potential energy surface (PES) are very promising as they can make feasible large-scale molecular dynamics simulations of materials with quantum accuracy. However, making these models truly reliable and practically useful is still a non-trivial task. A key component to fulfill this task is the generation of the datasets for model training. In **project 1** we developed Deep Potential GENERator (DP-GEN), an open-source software platform that implements the "on-the-fly" learning procedure recently proposed<sup>2</sup> by our group, and is capable of generating uniformly accurate deep learning based PES models in a way that minimizes human intervention and computational cost for data generation and model training. DP-GEN automatically and iteratively performs three steps: exploration, labeling, and training. It supports various popular packages for these three steps: LAMMPS for exploration, Quantum Espresso, VASP, CP2K, etc. for labeling, and DeePMD-kit for training. It also allows automatic job submission and data collection on different platforms, including high-performance clusters and cloud machines, and supports different job management tools, including Slurm, PBS, and LSF. A tutorial, using metallic copper as an illustrative material example, provides a step by step guide on how to generate a general-purpose PES model using DP-GEN.

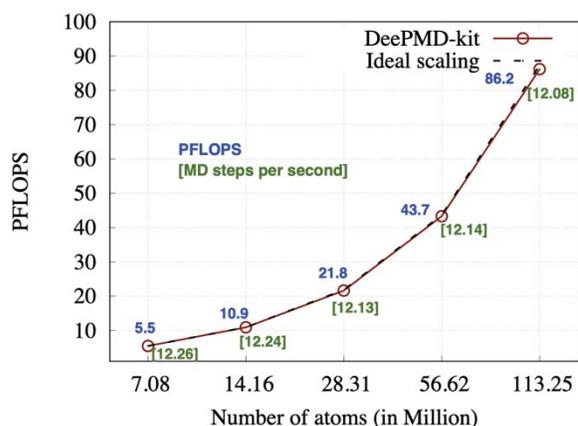


**Figure 1** Schematic illustration of the DP-GEN procedure: The scheduler (a) performs: (b) exploration with DPMD using an ensemble of DP models; (c) labelling based on the error indicator within the ensemble followed by collection of new DFT data; (d) a new ensemble of DP models is obtained and passed to the next iteration.

In **project 2** we developed an optimized GPU version of our open software package for DP molecular simulation, DeePMD-kit, which, upon training a deep neural network model using *ab initio* data, can drive extremely large-scale molecular dynamics simulation (MD) with *ab initio* accuracy. Our tests show that the GPU version is 7 times faster than the CPU version with the same power consumption. The code can scale up to the entire Summit supercomputer. For a copper system of 113,246,208 atoms, the code can perform one nanosecond MD simulation per day, reaching a peak performance of 86 PFLOPS (43% of the peak). Such unprecedented ability opens up the possibility of studying many interesting processes and phenomena in materials and molecules, such as heterogeneous catalysis, electrochemical cells, irradiation damage, crack propagation, and biochemical reactions, with *ab initio* accuracy. This work has been conducted in collaboration with professor **Lin Lin**, Department of Mathematics, University of California, Berkeley and Computational Research Division, Lawrence Berkeley National Laboratory, and postdoctoral associate **Weile Jia**, Department of Mathematics, University of California, Berkeley.



**Figure 2** Illustration of the vast increase in the system size made possible for specific systems (here liquid water and crystalline Cu) with DPMD. (a) typical sizes of AIMD simulations; (b) typical sizes of DPMD simulations with modest computational resources; (c) sizes of DPMD simulations possible with Summit.



**Figure 3** Weak scaling of DPMD for copper systems on Summit. Each GPU holds 4,139 atoms, and the corresponding number of nodes scales from 285 to 4,560 throughout the tests. Notice that the number of MD steps per second is held approximately constant. The simulation with ~ 113 million atoms was able to achieve ~ 86 PFLOPS performance on Summit, i.e. about 40 percent of the peak performance of the machine.

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**Grant DE-SC001934: Chemistry in Solution and at Interfaces**

**Students:** Linfeng Zhang

## Deep neural networks for the dielectric properties and vibrational spectroscopies of insulating materials

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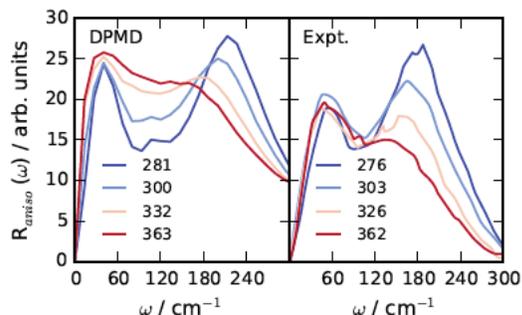
### Abstract

Vibrational spectroscopies, such as infrared (IR) absorption, Raman scattering (RS), and sum frequency generation (SFG) are important experimental tools to investigate the microscopic dynamics of materials, including bulk and interfacial liquid water. These spectroscopies probe the interaction of light with matter. The experimental observations can be modeled by calculating the time correlation functions of electronic properties like the polarization and/or the polarizability. These quantities are accessible in *ab-initio* molecular dynamics simulations (AIMD), but the computational cost of these simulations limits these studies to relatively small system sizes and short trajectories, which can affect the statistical accuracy of the calculated spectra. In some cases

Here we report on the development of a new methodology based on deep neural networks (DNN) to overcome the above limitations of direct AIMD studies. The DNN model is invariant for translations and permutations, and covariant for rotations. It extends the deep potential (DP) methodology, previously introduced by our group<sup>1,2,3</sup>, to make possible the representation of vectorial and tensorial quantities, like the polarization and the polarizability that are associated to the Wannier center positions and their derivatives with respect to atomic displacements. The model learns from *ab-initio* density functional theory calculations, wherein the electronic centers are uniquely specified by the maximally localized Wannier functions. When combined the DP model of the atomic potential energy surface, the scheme predicts accurately the dielectric properties of insulators for samples and trajectories inaccessible to direct *ab-initio* simulation. The scheme is non perturbative and can capture the dielectric changes in a mutating chemical environment.

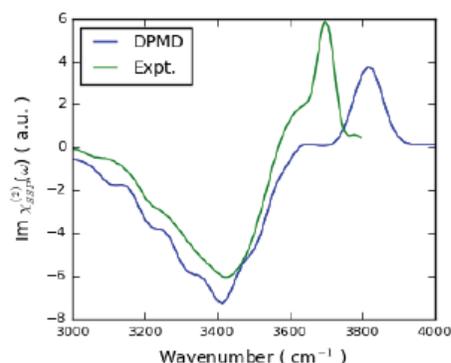
The above methodology was used to compute the IR spectra of liquid water (light and heavy) at standard conditions, as well as the IR absorption of ice undergoing a pressure induced transition from ice VII to ice X, as reported in ref. 4. The calculation on ice is particularly interesting because it shows that our DNN methodology can describe seamlessly the change in dielectric properties occurring when a molecular system (ice VII) transforms into an ionic system (ice X) under pressure. The DP methodology for the polarizability was used to calculate the Raman spectra of liquid water at different temperature conditions using 512-molecule cells and several 2ns long trajectories<sup>5</sup>. The agreement with experiment of the calculated Raman spectra is similar to that of direct *ab-initio* methods. However, the significant gains in efficiency provided by the

machine learning approach, enabled us to study the temperature dependence of the spectra and to obtain with good statistical errors the low frequency features whose intensity is more than one order of magnitude smaller than that of the stretching modes that dominate the spectra. We report in Fig.1 a comparison with experiment of the low frequency Raman spectra of liquid water calculated with our approach.



**Fig. 1** Reduced anisotropic Raman spectra of liquid water at different temperatures (Kelvin) as indicated by the colored lines. The two dominant features are due to H-bond network modes. The highest frequency mode, attributed to stretching, weakens considerably at higher temperature, an effect that we could attribute mostly to the reduction of intermolecular couplings with increasing temperature. The SCAN functional was used for the training data.

Using the DP methodology for the polarization and the polarizability we could compute the SFG spectra of the liquid water – air interface, which is reported in Fig. 2.



**Fig. 2** Sum frequency generation (SFG) spectra of the water air interface at 300 K. The simulation used a 5 ns long trajectory for a periodic cell containing 464 molecules plus vacuum. The calculation used the entire cell and was not restricted to the interfacial region, as typically done with AIMD to avoid the long simulation times required for the molecules in the bulk of the sample to experience, on average, an isotropic environment. The SCAN functional was used for the training data.

The liquid-air interface was chosen to validate our methodology because it has been studied extensively in experiments. In the future we intend to apply our methodology to compute SFG spectra for other interfaces of interest in the CSI project, with particular interest for reactive interfaces.

In the above calculations the atomic coordinates were treated as classical variables, neglecting nuclear quantum effects (NQE), which are small but not negligible in water. Work is in progress to include NQE in our spectral calculations with path integral methods, using a combination of approaches, from semi-classical approximations like linear semiclassical (LSC-IVR) dynamics to analytic continuation of imaginary time data with maximum entropy methods. These studies are greatly facilitated by the numerical efficiency of the DP methodology.

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