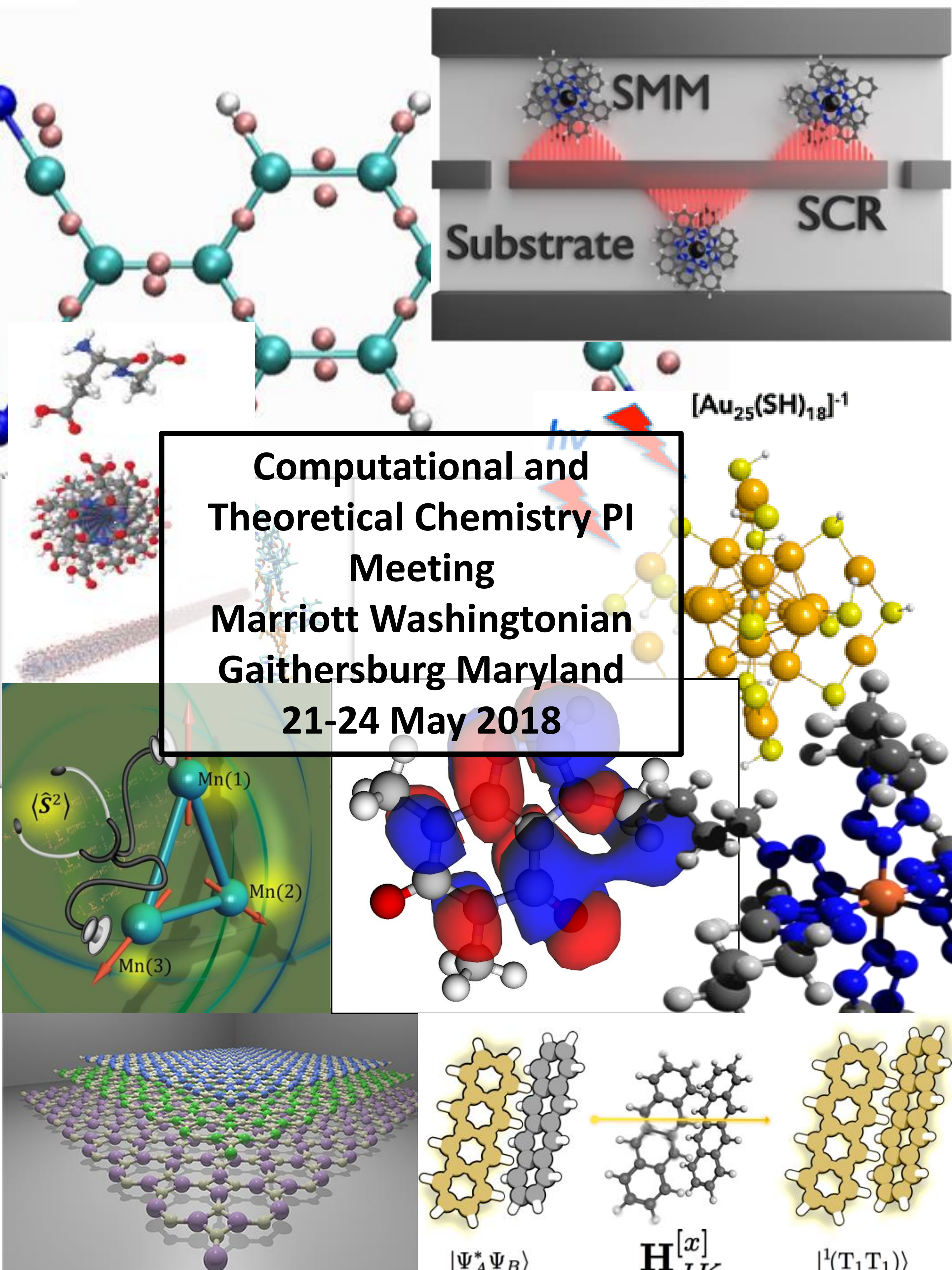

Computational and Theoretical Chemistry PI Meeting

Marriott Washingtonian
Gaithersburg Maryland
21-24 May 2018

FORWARD

This abstract booklet provides a record of the U.S. Department of Energy fourth annual PI meeting in Computational and Theoretical Chemistry [CTC]. This meeting is sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and includes invited speakers and participants from the core CTC program, Computational Chemical Science projects, Energy-Frontier Research Centers, and SciDAC efforts.

The objective of this meeting is to provide an interactive environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually complementary expertise, will identify needs of the research community, and will focus on opportunities for future research directions.

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

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

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

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

21-May 2018

SHORT AGENDA 2018 CTC PI Meeting
Marriott Washingtonian – Gaithersburg

9751 Washingtonian Boulevard Gaithersburg Maryland 20878 USA
For more information and registration: http://www.orau.gov/ctc2018/
Abstracts: http://science.energy.gov/bes/csgb/principal-investigators-meetings/

21 May 3-6 PM	**Registration**	
6:30-7:45	Conference Dinner at the Hotel – Everyone	
22 May 7:30AM	**Breakfast**	
8:15AM	**Welcome**	**Mark Pederson**
8:20AM	**BES/CSGB/CTC+CCS Update and Outlook**	**Bruce Garrett**
8:50 AM	**Modalities for Computational Chemical Research (Chair: George Schatz)**	
8:50	**Computational Catalysis - the Standard Model and Beyond**	**Joachim Sauer**
9:30	**How to Win Scientific Friends & Influence Frenemies: Team Science**	**Teresa Head-Gordon**
10:05	**Steering A SciDAC Towards Success: An After-Action Report**	**Christopher Cramer**
10:30AM	COFFEE	
	Excited-State and Mesh-Based Electronic Structure (Chair: Nick Mayhill)	
11:00	**Excited-States in Solution: Line Shapes, Ions, & NQEs**	**Christine Isborn**
11:25	**Variational Excited States, Quantum Monte Carlo, & Charge Transfer**	**Eric Neuscamman**
11:50	**Mesh-based Electronic Structure Methods**	**Vikram Gavini**
12:15PM	**Working Lunch**	Everyone
1:15PM	**Quantum Information Activities – ASCR/BES Viewpoints** **Chair: Alan Aspuru-Guzik**	**Ceren Susut** **Claire Cramer** **Mark Pederson**
	Seizing The Quantum Moment (Chair: Sophia Economou)	
1:45PM	**Molecular Magnets: Then (TM), Now (Ln), and Onward (QIS)**	**Kyungwha Park**
2:15PM	**Spin-Flip Methods for Massively Open Shell Molecules**	**Anna Krylov**
2:40PM	**Strong Correlation in Actinide-Based Single Molecule Magnets**	**Laura Gagliardi**
3:05PM	**Coffee**	Everyone
	Chemistry in Solution (Chair: Thanos Panagiotopoulos)	
3:30PM	**Modeling Challenges for Interfacial Phenomena & Nanostructures**	**Alenka Luzar**
3:55PM	**Fragment Calculations for Noncovalent Interactions & Energy Transfer**	**John Herbert**
4:20PM	**Restricted Light-Harvesting-Triad Conformers via Induced Polarization**	**Margaret Cheung**
8:00PM	**Poster Session (Moderated by Mark Pederson)** Your poster can be four feet high and should be less than four feet wide. Please advise if you would like to have your poster upgraded to a talk if there are cancellations.	**Baruah, Gopalakrishnan, Govind, Greeley, Hohenstein, Jang, Kao, Li, Markland, Najm, Niklasson, Sarupria, Schenter, Sides, Dunietz**

23 May 7:30	**Breakfast**	
	Complex Chemical Transformation (Chair: Juan Peralta)	
8:30 9:00 9:30	**ECC: Exascale Computational Catalysis** **SPEC: Predictive Methods for Excitations & Correlated Phenomena** **NMGC: Hierarchical Modeling of Chem. Separations/Transformations**	**Judit Zádor** **Sotiris Xantheas** **Ilja Siepmann**
10:00	**Coffee**	
	Functional Transition Metal Complexes (Chair: Dimitris Papaconstantopoulos)	
10:30 10:55 11:20 11:45	**FLOSIC: Density Functional Calculations without Self-Interaction** **Design of Quantum Molecular Magnets for Information Applications.** **Recovering exact conditions with DFT for Transition Metal Chemistry** **Light-Induced Spin Trapping in Transition Metal Compounds**	**Koblar Alan Jackson** **Ed Barnes** **Heather Kulik** **Angela Wilson**
12:10	**Lunch**	
	Photodriven Processes (Chair: Jerzy Leszczynski)	
1:30PM 1:55 2:20 2:45	**Interfacial Charge Transfer Dynamics** **Photochemistry of Molecules in Well-Defined Environments** **Electron & Optical Properties of Boron-Group V (4,8) Nanosheets** **Advanced Molecular ES Methods for Exciton and Spin Dynamics**	**Barry Dunietz** **Lasse Jensen** **Kevin Shuford** **Toru Shiozaki**
3:10	**Coffee**	
	Dynamics within Density Functional Theory (Chair: John Perdew)	
3:30PM 3:55 4:20 4:45	**Electron & Electron-Nuclear Dynamics in Open Quantum Subsystems** **Electron & Electron-Nuclear Dynamics in Au & Ag Nanoparticles** **Excited-State & Nonadiabatic MD Methods with Broad Applicability** **InterfaceCharacteristics of Organic Molecules on Metal Surfaces**	**Michele Pavanello** **Christine Aikens** **Filipp Furche** **Abdelkadar Kara**
23 May Evening	**DINNER ON YOUR OWN**	

24 May 7:30	**Breakfast**	
	Simulating Chemistry in Dielectric Media (Chair: Tom Markland)	
8:30AM	**Polymers in Deep Eutectic Solvents**	**Arun Yethiraj**
8:55AM	**Stat. Mechanics and Electronic Structure: Can They Co-exist?**	**Chris Mundy**
9:20AM	**Crystal Growth and Nucleation at MOF/Solution Interfaces**	**J.R. Schmidt**
9:45AM	**Projection-based Quantum Embedding for Large & Periodic systems**	**Jason Goodpaster**
10:10AM	**Coffee**	
	Non-Adiabatic Processes and Reaction Dynamics (Chair: Fritz Schaefer)	
10:30AM	**Non-Adiabatic Photo-dissociation**	**David Yarkony**
11:00AM	**Multiple Coupled Potential Energy Surfaces: Combustion Applications**	**Richard Dawes**
11:25AM	**Electron-Ion Dynamics w/ Time-Dependent Density Functional Theory**	**Neepa Maitra**
11:50AM	**Formation and Growth of Polycyclic Hydrocarbons**	**Alexander Mebel**
12:15	**Lunch**	
	Advances in High-Level Electronic Structure (Chair: Gustavo Scuseria)	
1:15PM	**SciDAC IV: Computational Catalysis**	**Martin Head-Gordon**
1:40	**Formulations of the Greens Function Formalism**	**Karol Kowalski**
2:05	**Coupled-Cluster Energetics by MC Sampling & Moment Expansions**	**Piotr Piecuch**
2:30	**Accurate Ab Initio Methods for Correlated Surface Chemistry**	**Dominika Zgid**
2:55PM	**Coffee**	
	Machine Learning in Complex Phenomena (Chair: James Lewis)	
3:30 PM	**More Efficient & Accurate DFT-based Dynamics via Machine Learning**	**Marivi Fernandez-Serra**
3:55 PM	**Open Chemistry: Interactive Data Analytics Platform**	**Marcus Hanwell**
4:30 PM	**Closing Remarks**	**Mark Pederson**

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

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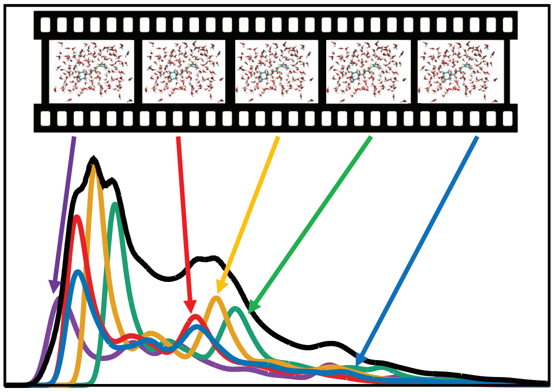
2. Washington State University, Email: auclark@wsu.edu
3. Stanford University, Email: tmarkland@stanford.edu

The development of next generation energy conversion and catalytic systems requires fundamental understanding of the interplay between photo-excitation and the resulting proton and electron transfer processes that occur in solution. To address these challenges requires accurate and efficient methods to compute ground and excited states, as well as the ability to treat the dynamics of energy transfer in the presence of solvent fluctuations. Our team is developing accurate and efficient theoretical models for solution phase reactions. These developments provide an improved understanding of photo-initiated excitations, electron transfer, and proton coupled electron transfer processes. Our research team brings together expertise in electron and nuclear dynamics (classical and quantum), electronic structure, and analysis of solvation networks. We are developing and validating techniques for modeling condensed phase reactions.

EXCITED STATES IN SOLUTION: One of the goals in our group is accurately modeling absorption spectra in solution. Reproducing experimental condensed phase spectra serves as a good way to validate the ground state sampling of solute-solvent configurations, the ground and excited state methodology, and the importance of what causes spectral broadening, including lifetime and vibronic effects. By gaining a better understanding of which effects are necessary to reproduce absorption spectra, we will know which effects are important for a correct model of condensed phase reactivity. We've explored the accuracy of both the ensemble and Franck-Condon approaches for modeling absorption spectra, and have found that neither approach accurately captures both the full inhomogeneous broadening due to the non-Gaussian solvent distributions along with the vibronic transitions. We have developed a combined approach to model the absorption spectrum of semi-flexible chromophores in solution that includes full sampling of solute-solvent degrees of freedom at the desired temperature using a large QM region for the calculation of vertical excitation energies, and then combines this ensemble sampling with the zero temperature Franck-Condon vibronic shape function to simulate the vibronic contributions to the spectrum at a particular solvent configuration. This combined approach models the full inhomogeneous broadening of the explicit solvent environment and is also able to reproduce the high-energy tail of the spectrum due to vibronic transitions. Our approach with no phenomenological broadening shows



Combined Ensemble Franck-Condon

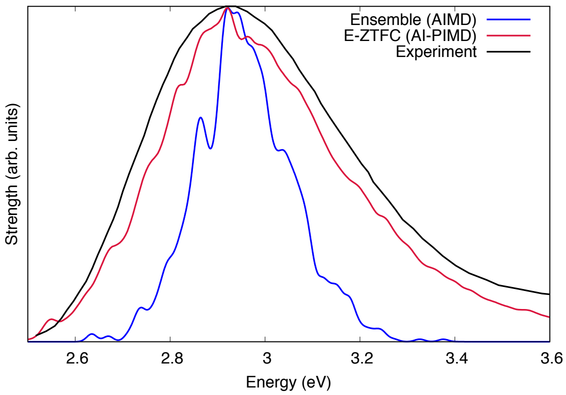


Figure 1: Comparison of the absorption spectra computed from the ensemble approach using AIMD configurations, and from our combined ensemble-zero-temperature Franck-Condon (E-ZTFC) approach using AI-PIMD configurations.

significant improvement in spectral shape compared to the ensemble approach with standard Gaussian broadening (see Figure 1). We are comparing absorption spectra computed from configurations ab initio density functional theory Born-Oppenheimer molecular dynamics (AIMD) that can simulate proton transfer to those including nuclear quantum effects via path integral molecular dynamics (PIMD). Future work includes inclusion of ionic effects and determining the best quantum correction factors for spectra computed from the energy gap autocorrelation function that includes full coupling of solute and solvent degrees of freedom.

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

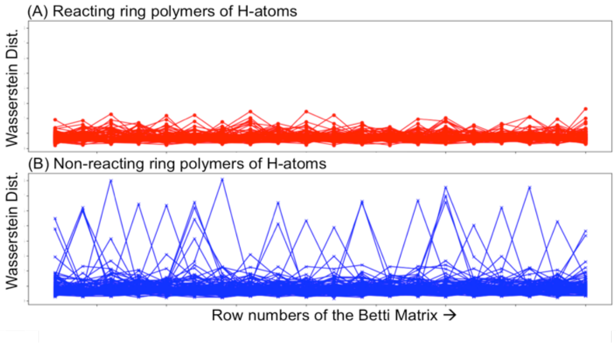
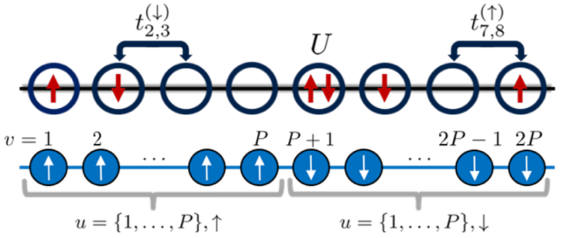


Figure 2: Comparison of the Wasserstein distances from the Betti numbers of the persistent homologies from reacting and non-reacting H-atoms via analysis of their ring-polymer shapes.

ON THE EXACT CARTESIAN MAPPING OF FERMIONS FOR INVESTIGATING ELECTRODE PROCESSES: The exact treatment of real time nonadiabatic quantum dynamics in condensed phase chemical systems remains a significant challenge that spurs the ongoing development of approximate methods that are accurate, efficient, and can treat large systems with a wide range of different forms of interactions. Quantum-classical (semiclassical) trajectory-based methods provide some of the most appealing solutions to this problem that offer a hierarchy of approaches with different balances between accuracy and computational cost. We have shown how quantum-classical approaches can be made both more accurate and efficient by combining them with the formally exact quantum master equation framework. This combination of quantum-classical theory and master equation (ME) techniques makes it possible to obtain the accuracy of much more computationally expensive approaches at a cost an order of magnitude lower than even the most efficient trajectory-based approaches, providing the ability to treat the quantum dynamics of atomistic condensed phase systems for long times.



$$\hat{H} = \sum_{u} U_u \hat{n}_{\uparrow,u} \hat{n}_{\downarrow,u} + \sum_{u,\lambda} t_{u,u+1}^{(\lambda)} \left[\hat{c}_{\lambda,u}^{\dagger} \hat{c}_{\lambda,u+1} + \hat{c}_{\lambda,u+1}^{\dagger} \hat{c}_{\lambda,u} \right]$$

$$\text{“} \mapsto \text{”} \sum_{u} U_u \hat{\eta}_{\uparrow,u} \hat{\eta}_{\downarrow,u} + \frac{1}{2} \sum_{u,\lambda} t_{u,u+1}^{(\lambda)} \left[\hat{x}_{\lambda,u} \hat{x}_{\lambda,u+1} + \hat{y}_{\lambda,u} \hat{y}_{\lambda,u+1} \right]$$

Figure 3: Mapping and index ordering for the 1D Hubbard model using our Cartesian mapping approach.

Our most recent work has focused on extending the developments of quantum-classical GQME-based dynamics to many-fermion problems where the discrete energy levels are so numerous as to create continua, as is the case for processes near metallic and semiconducting interfaces. To achieve the accuracy benefits from the GQME approach one must have a prescription to generate the initial conditions exactly. In cases where one can write the Hamiltonian in terms of Cartesian positions and momenta, this can usually be achieved straightforwardly using path integral approaches. For Hamiltonians containing discrete states, the Meyer-Miller-Stock-Thoss protocol can be used, however, for those that include fermionic creation and annihilation operators an exact Cartesian mapping has remained elusive. In our recent work, we have therefore derived a rigorous, quantum mechanical map of fermionic creation and annihilation operators to continuous Cartesian variables that exactly reproduces the matrix structure of the many-fermion problem. We have shown how our scheme can be used to map a general many-fermion Hamiltonian and then consider two specific models that encode the fundamental physics of many fermionic systems: the Anderson impurity and Hubbard models. We used these models to demonstrate how efficient mappings of these Hamiltonians can be constructed using a judicious choice of index ordering of the fermions. For example, Figure 3 shows how the 1D Hubbard Hamiltonian can be exactly mapped from its usual form in terms of fermionic creation and annihilation operators to an isomorphic form in terms of Cartesian positions and momenta. Most remarkably in this case, by using an appropriate choice of index ordering, one can eliminate the need to treat the nonlocal operator that imposes the fermionic anticommutivity. This development provides an alternative exact route to calculate the static and dynamical properties of fermionic systems and sets the stage to exploit the quantum-classical and semiclassical hierarchies to systematically derive methods offering a range of accuracies, thus enabling the study of problems where the fermionic degrees of freedom are coupled to complex anharmonic nuclear motion and spins which lie beyond the reach of most currently available methods. These extensions should now allow us to simulate the GQME dynamics using memory kernels generated from a wide variety of quantum-classical approaches for large quantum subsystems coupled to fully atomistic environments. These developments are essential for treating problems such as proton coupled electron transfer in solution and at interfaces.

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

Up to Ten Publications Acknowledging this Grant

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

2. On the exact continuous mapping of fermions. *A. Montoya-Castillo, T. E. Markland. arXiv:1803.05561 and Submitted to J. Chem. Phys. (2018)*

3. Combining the ensemble and Franck-Condon approaches for calculating spectral shapes of molecules in solution. *T. J. Zuehlsdorff and C. M. Isborn. J. Chem. Phys. 148, 024110 (2018)*

4. Nuclear quantum effects enter the mainstream. *T. E. Markland and M. Ceriotti. Nature Rev. Chem., 2, 0109 (2018)*

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

6. Electrostatic control of regioselectivity in Au(I)-catalyzed hydroarylation. *V. M. Lau, W. C. Pfalzgraff, T. E. Markland and M. W. Kanan J. Am. Chem. Soc., 139 (11), 4035-4041 (2017)*

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

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

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

10. Unraveling the dynamics and structure of functionalized self-assembled monolayers on gold using 2D IR spectroscopy and MD simulations. *Yan, R. Yuan, W. C. Pfalzgraff, J. Nishida, L. Wang, T. E. Markland, M. D. Fayer, Proc. Natl. Acad. Sci., 113 (18), 4929-4934 (2016)*

Variational Excited States, Quantum Monte Carlo, and Charge Transfer

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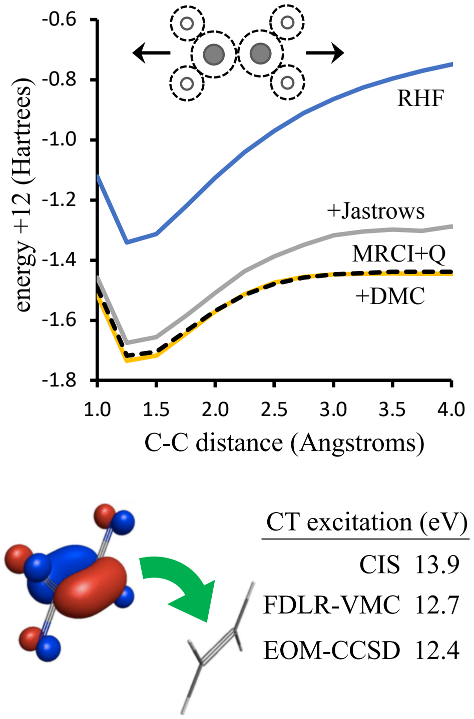

CT excitation (eV)	
CIS	13.9
FDLR-VMC	12.7
EOM-CCSD	12.4

This research program will explore the intersection of variational principles for excited states, quantum Monte Carlo (QMC) methods, and charge transfer processes. While the foundations for this research lie in our DOE-funded work over the past few years in the Gas Phase Chemical Physics program and the Computational Materials Science Program, funding from DOE's Early Career Research Program will now allow us to explore the exciting opportunities that lie at the intersection of these three topics. This will include the development of more efficient and black-box tools for QMC treatments of excited states and especially charge transfer excited states, improved QMC optimization algorithms to relieve the method's variable-number-bottleneck, and the use of high-level QMC benchmarks to guide the exploration of lower-cost alternatives in the area of variational excited states.

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 orbital basis, 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.

The other piece of recent progress that will support this new program is our recent development of efficient forms of 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, 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 results for the double bond dissociation of ethylene. Our early work within the Early Career Research Program has already resulted in a fundamental improvement in this area in which the user no longer needs to specify molecular sub-regions; instead, the introduction of cleanly-additive NCJFs allows the variational principle itself to choose in which regions it will control charge and to what degree. This feature marks a significant advance in comparison to the well-developed approach of constrained density functional theory, in which the charge density constraints that allow charge transfer states to be accessed must be imposed by the user.

Going forward, our research in this area will combine the advantages of NCJFs and the state-specific orbital optimization enabled by excited state variational principles in order to improve our predictive power of charge transfer excitations and foster the growth of lower-level but more computationally efficient approaches to variational excited states. In practice, the naturally large system sizes involved in charge transfer processes will necessitate further research in QMC optimization methods, where we suggest there are opportunities to combine the traditionally most successful QMC methods with noise-tolerant numerical optimization methods inspired by recent advances in neural-network training. In terms of high-accuracy charge-transfer, the combination of NCJFs with our orbital-relaxed variation-after-response wave functions and with the more systematically improvable multi-Slater Jastrow ansatz will deliver a type of ansatz flexibility that is especially propitious for charge transfer and that is simply not achievable in current wave function approximations.

An especially exciting opportunity in this line of development is the prospect of creating a black-box route to diffusion-Monte-Carlo-quality excited states in analogy with the present situation for ground states. For weakly correlated systems, DMC has been shown to typically produce results of CCSD(T) quality when given a single Slater determinant with which to construct the nodal surface. With our methods for reoptimizing orbitals for excited states, which can take as their initial guess the result of a CIS or TDDFT starting point, we expect to be able to provide excited state nodal surfaces for single excitations whose quality matches those that can be easily supplied today for ground states. If this can be achieved, the low cost-scaling of QMC could, with the help of production level parallelization, provide new benchmark-quality results in systems with 30 or more carbon atoms.

In summary, our work under the Early Career Research Program will leverage our recent progress in variational QMC excited state methods and correlation factors capable of controlling electron charge distributions to break new ground in the simulation of charge transfer excitations and in our understanding of what other methodologies may be applied to the variational evaluation of excited states.

Grant Numbers and Grant Titles:

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

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

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

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

Post-docs:
Nicholas Blunt

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

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

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

Zhao, L.; Neuscamman, E., Equation of Motion Theory for Excited States in Variational Monte Carlo and the Jastrow Antisymmetric Geminal Power in Hilbert Space. J. Chem. Theory Comput. 2016, 12 (8), 3719. DOI: 10.1021/acs.jctc.6b00480

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

Blunt, N. S.; Neuscamman, E., Charge-transfer Excited States: Seeking a Balanced and Efficient Wave Function Ansatz in Variational Monte Carlo. J. Chem. Phys. 2017, 147 (19), 194101. DOI: 10.1063/1.4998197

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

(continued on next page)

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

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

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. Thus, the objective of this work is to develop computationally efficient, systematically improvable and scalable large-scale real-scale all-electron Kohn-Sham (KS) DFT calculations.

This presentation discusses the main ideas being developed in this direction, which include: (i) development of an enriched finite element (FE) basis [1]; (ii) development of efficient computational algorithms for computing the electronic structure, which include reduced order scaling techniques [2,3]. The enriched finite-element basis is constructed by augmenting the finite-element basis with compactly supported atom-centered numerical basis functions that are constructed from the solution of the KS problem for single atoms. The compact support for the enrichment functions is obtained by using smooth cutoff functions, which enhances the conditioning and maintains the locality of the enriched finite element basis. The integrals involved in the evaluation of the discrete KS Hamiltonian and overlap matrix in the enriched finite element basis are computed using an adaptive quadrature grid that is constructed based on the characteristics of enrichment functions. Further, we propose an efficient scheme to invert the overlap matrix by using a blockwise matrix inversion in conjunction with special reduced-order quadrature rules, which is required to transform the discrete Kohn-Sham problem to a standard eigenvalue problem. Finally, we solve the resulting standard eigenvalue problem, in each self-consistent field iteration, by using a Chebyshev polynomial based filtering technique to compute the relevant eigenspectrum. The accuracy, efficiency, and parallel scalability of the proposed method is benchmarked on semiconducting and heavy-metallic systems of various sizes, with system sizes containing ~10,000 electrons. We obtain accuracies in the ground-state energies that are ~1 mHa with reference ground-state energies employing classical finite element as well as Gaussian basis sets. Using the proposed formulation based on enriched finite element basis, for accuracies commensurate with chemical accuracy, we observe a staggering 50–300-fold reduction in the overall computational time when compared to classical finite element basis. Further, we find a significant outperformance by the enriched finite element basis when compared to the Gaussian basis for the modest system sizes where we obtained convergence with Gaussian basis. We also observe good parallel scalability of the numerical implementation on representative benchmark systems.

Currently, extension of the enriched FE basis to periodic systems is ongoing. Further, we are extending our framework to compute configurational forces [4]—generalized forces corresponding to the inner variations of the Kohn-Sham energy functional with respect to spatial position, which result in a unified

formulation to compute both ionic forces as well as stresses—initially developed for classical FE basis to enriched FE basis. Other ongoing efforts include: (i) combining the developed framework for enriched FE basis with localization techniques [2,3] to realize reduced-order computational complexity in the solution of KS equations, (ii) developing a framework for conducting all-electron GW calculations, which will enable a systematic transferability study of the pseudopotential approximation in bandgap calculations.

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1. B. Kanungo, V. Gavini, Large-scale all-electron density functional theory calculations using an enriched finite element basis, *Phys. Rev. B* **95**, 035112 (2017).
2. P. Motamarri, V. Gavini, A subquadratic-scaling subspace projection method for large-scale Kohn-Sham DFT calculations using spectral finite element discretization, *Phys. Rev. B* **90**, 115127 (2014).
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4. P. Motamarri, V. Gavini, Configurational forces in electronic structure calculations using Kohn-Sham density functional theory, *Phys. Rev. B* **97**, 165132 (2018).

Grant Numbers and Grant Titles

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

Postdoc(s): None

Student(s): Nelson Rufus; Bikash Kanungo

DE-SC0008637: Software center for predictive theory and modelling

Postdoc(s): None

Student(s): Sambit Das

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

1. P. Motamarri, V. Gavini, A subquadratic-scaling subspace projection method for large-scale Kohn-Sham DFT calculations using spectral finite element discretization, Phys. Rev. B 90, 115127 (2014).
2. M. Iyer, B. Radhakrishnan, V. Gavini, Electronic structure of an edge dislocation in Aluminum and the role of macroscopic deformations on its energetics, J. Mech. Phys. Solids 76, 260-275 (2015).
3. S. Das, M. Iyer, V. Gavini, Real-space formulation of orbital-free density functional theory using finite-element discretization: The case for Al, Mg, and Al-Mg intermetallics, Phys. Rev. B 92, 014104 (2015).
4. S. Das, V. Gavini, Electronic structure study of screw dislocation core energetics in Aluminum and core energetics informed forces in a dislocation aggregate, J. Mech. Phys. Solids 104, 115-143 (2017).
5. P. Motamarri, V. Gavini, Configurational forces in electronic structure calculations using Kohn-Sham density functional theory, Phys. Rev. B 97, 165132 (2018).

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Lanthanide-based single-molecule magnets for quantum information applications

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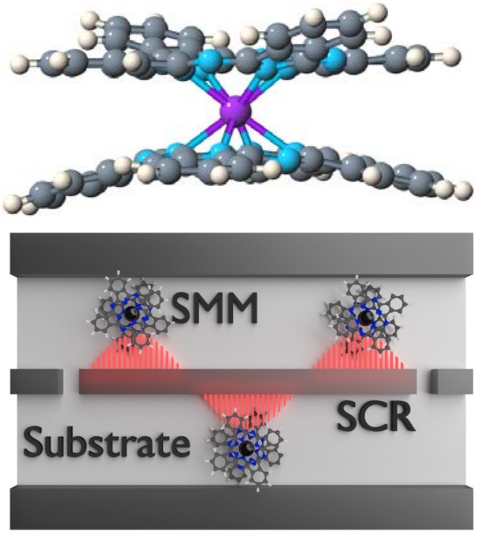

Nanoscale single-molecule magnets (SMMs) typically consist of a few to several tens of transition metal ions surrounded by ligands, where different metal ions interact with one another via neighboring anions through superexchange coupling. One crucial property that SMMs must carry is a zero-field splitting (ZFS) or magnetic anisotropy barrier (MAB) caused by spin-orbit coupling. This property lifts the degeneracy of the magnetic levels even in the absence of an external magnetic field. A large ZFS or MAB would lead to well-separated ground-state doublets or magnetic levels that can be used as two-level quantum bits (qubits) or as multilevel "qudits" which take advantage of d>2 levels for information storage.

The prototype SMMs are $Mn_{12}O_{12}$-acetate and their derivatives with a total ground-state spin S=10, which exhibit a MAB of 65 K. Since this discovery, there has been considerable effort to increase the ZFS or MAB by increasing the total magnetic moment or the number of transition metal ions. The idea is based on the apparent quadratic dependence of the MAB on the total magnetic moment. However, later, it was theoretically and experimentally found that this approach does not in fact yield an increase in the MAB since the magnetic anisotropy of individual magnetic ions decreases due to structural distortion. After this realization, research into SMMs was diversified into searching for either mononuclear or dinuclear SMMs with large orbital angular momentum.

For SMMs to be useful as molecular electronic or nuclear spin qubits or qudits, the following two conditions have to be satisfied in addition to the large ZFS or MAB. Firstly, the metal atom must carry a nuclear spin moment in at least one of its isotopes if one wishes to realize a nuclear spin qubit. Secondly, adsorption of SMMs on a surface must be stable, without forming aggregates or losing neighboring ligands, against thermal diffusion. Recently, Wolfgang Wernsdorfer's group experimentally demonstrated a qubit candidate with remarkable properties in the lanthanide-based SMM $TbPc_2$ (Pc= phthalocyanine), featuring a nuclear spin that can be used as either a qubit or qudit and which possesses 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 quantum-information processor (QIP) devices. Although these SMMs are promising, 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.

Our efforts to systematically design quantum information processors with SMMs by varying chemical and physical environmental factors using a multiscale model approach ranging from different levels of ab-initio quantum chemistry simulations to analytically solvable effective models and time-dependent external control will be discussed. Our work is predominantly focused on $TbPc_2$ due to its extremely attractive features, but the techniques we are developing will be general and transferable to other molecules and other qubits. The quantum chemistry methodologies and simulation codes we are developing will be tested, run, and adapted on one of the NERSC supercomputers for more efficient implementations for other large-scale correlated

In order to simulate the electronic structure of the relatively large and highly correlated character of the $TbPc_2$ molecule, we are developing methods which aim to achieve qualitative accuracy, while maintaining reasonable computational complexity. In this direction, we are exploring a combination of spin-flip (SF) methods with number changing electron-affinity (EA) methods to create a model chemistry which simultaneously addresses spin and Jahn-Teller-type degeneracies, which are present in the $TbPc_2$ complex. In order to provide insight into the development of this combined method, we will show our preliminary results on electronic structure and magnetic properties of a $TbPc_2$ molecule in a gas phase, within density-functional theory and multi-reference methods such as CASSCF (complete active space self-consistent field) with and without spin-orbit coupling. We will consider different charge states of the molecule and discuss the ground-state (pseudo)spin multiplets. We will also present their magnetic anisotropy in the different charge states.

Grant number and title: DE-SC0018326, Lanthanide-based single-molecule magnets for quantum information applications

Postdocs: Daniel Claudino, Khadijeh Najafi

Students: Shannon Houck, Ryan Pederson, Fei Zhang

Electronic structure methods for electronically excited and open-shell species: Theory and applications

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Summary of recent major accomplishments

During the past year, we conducted several computational studies of open-shell and electronically excited species. The common theme in these studies is interactions between states of different character and intersections between the corresponding potential energy surfaces. We also continued to develop and benchmark computational methods for modeling electronic structure and spectroscopy of open-shell species. The following representative publications supported by DOE highlight selected recent results.[1–8] The important accomplishments are:

- Developed formalism and computer code for non-adiabatic couplings within equation-of-motion coupled-cluster theory framework;[1]
- Developed and validated a new approach for computing core-level states in isolated and solvated species;[2]
- Developed new protocols for characterizing electronic structure of strongly correlated systems;[3]
- Contributed to interpretation of experimental studies of several open-shell and electronically excited systems relevant to combustion[5] and catalysis;[7,8]
- Investigated electronic structure in strongly correlated systems relevant to quantum materials.[4]

Highlight: Singlet-triplet energy gaps and the degree of diradical character in binuclear copper molecular magnets characterized by spin-flip density functional theory

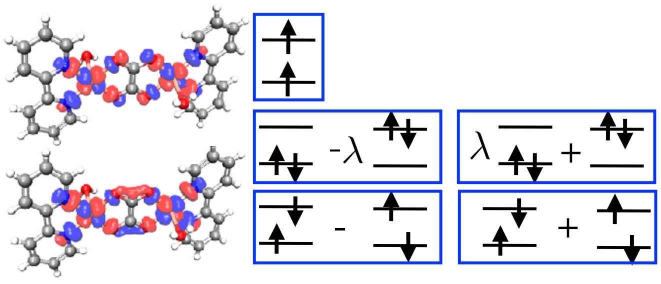

Figure 1: **Left:** Magnetic orbitals of a binuclear copper SMM (BISDOW complex). **Right:** Diradical wave functions. The top configuration corresponds to the high-spin $M_s = 1$ triplet state; the next four states correspond to the low-spin states: $M_s = 0$ singlets and a triplet. Due to orbital near-degeneracy, the coefficient λ is close to 1. Note that all $M_s = 0$ configurations can be formally generated by spin-flipping excitations of one electron from the high-spin $M_s = 1$ configuration.

We investigated the lowest spin states of several binuclear copper diradicals using spin-flip methods.[4] In contrast to previous studies, we considered not only the energetics of the low-lying states (which are related to the exchange-coupling parameter within the Heisenberg-Dirac-van-Vleck model), but also the character of the diradical states themselves. By using natural orbitals, their occupations, and the number of effectively unpaired electrons we were able to quantify bonding patterns in these systems and to map complicated many-body wave functions into a simple two-electrons-in-two orbitals picture, as shown in Figure 1. We compared the performance of spin-flip time-dependent density functional theory (SF-TDDFT) using various functionals and effective core potentials against the wave-function based approach, equation-of-motion spin-flip coupled-cluster method with single and double substitutions (EOM-SF-CCSD). We found that SF-TDDFT paired with the PBE50 and B5050LYP functionals performs comparably to EOM-SF-CCSD, with respect to both singlet-triplet gaps and states' characters. Visualization of frontier natural orbitals showed that the unpaired electrons are localized on copper centers, in some cases exhibiting slight through-bond interaction via copper *d*-orbitals and *p*-orbitals of neighboring ligand atoms. The analysis revealed considerable interactions between the formally unpaired electrons in the antiferromagnetic diradicaloids, meaning that they are poorly described by the Heisenberg-Dirac-van-Vleck model. Thus, for these systems the experimentally derived exchange-coupling parameters are not directly comparable with the singlet-triplet gaps. This explains systematic discrepancies between the computed singlet-triplet energy gaps and the exchange-coupling parameters extracted from experiment.

Current developments and future plans

In the near future, we plan to complete the following:
(i) extend our benchmark study of molecular magnets to systems with more than 2 unpaired electrons and different metal centers;
(ii) finalize the paper on electronic states of hydroxycarbenes (collaboration with Prof. H. Reisler);
(iii) finalize the paper on modeling arginine photoionization in the gas and condensed phase (collaboration with Dr. M. Ahmed).

Grant numbers and grant titles

Theoretical modeling of spin-forbidden channels in combustion reactions, DE-FG02-05ER15685.
Postdocs: Dr. Marwa Farag, Dr. Ilya Kaliman, Dr. Samer Gozem.
Students: Anastasia Gunina, Arman Sadybekov, Natalie Orms.

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Strong electron correlation in uranium- and plutonium-based single molecule magnets

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I will describe our latest developments of multireference methods with special focus on multiconfiguration pair-density functional theory (MC-PDFT) [1], which combines mutireference wave functions and density functional theory methods to treat strongly correlated systems. I will illustrate how to explore the electronic structure of single molecule magnets containing actinides [2], by means of multiconfigurational electronic structure theory including spin-orbit coupling effects. Finally I will discuss our latest extension of multireference methods to complex systems using density matrix embedding theory [3].

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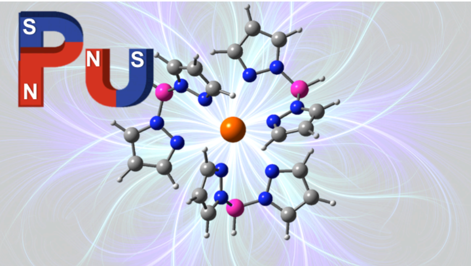

Challenges in Molecular Modeling of Interfacial Phenomena and Nanostructured Materials

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Presentation Abstract

Interfacial phenomena play the determining role in macroscopic behavior of complex materials systems and in a variety of energy applications. Interfacial properties can often be manipulated by the application of external fields. Conversely, internal fields can be exploited to control the structure, wetting and aggregation of nanoparticle. We will discuss our recent simulation advances toward molecular understanding of wetting, partitioning and dynamic responses in electrically controlled interfacial systems, and the impact of surface modification on dispersion behavior of nanoparticles.

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

Postdoc(s): B. Shadrack Jabes
Graduate Student(s): Serban Zamfir (summer)

Program scope

The project is advancing molecular level understanding of nanoscale hydration in ionic solutions with emphasis on the influences of electric stimuli and ionic patterning. It relies on the development of novel simulation algorithms in statistical mechanics to capture complex processes in open systems under electric control. Parallel studies of wetting and dispersibility of ionizing particles aim to uncover predictive relations between electrowetting, chemical functionalization, and geometry of nanomaterial particles. Open Ensemble Monte Carlo simulations with fractional ion-exchanges enable studies of permeation in nanoporous electrodes at imposed voltage, a phenomenon critical for the function of ultracapacitors. Transitory regulation of wetting in nanoporous media by electric field spans an array of applications in materials, energy storage, and separation sciences. The physically related modulation of nanoparticle solubility by fixed or pH-dependent surface charges can significantly extend the range of the nanomaterial applications, improve processing techniques, and potentially alleviate environmental concerns.

Recent progress

Nanoconfined solution modeling in open ensemble in the presence of multibody polarizability effects. Electrolyte absorption in porous materials is of essential importance in a range of energy applications from high contact-area electrodes in batteries and supercapacitors to surface-energy absorption or energy storage in form of liquid springs. Computational predictions of solution uptake require the use of open ensembles, i.e. the Grand Canonical and Gibbs Ensemble, which can be implemented in a rigorous way in Monte Carlo simulations. To extend these methods to confined saline solutions, we have been developing novel algorithms with fractional particle exchanges that mitigate prohibitive energy differences upon exchanges of ionic species or hydration water. In recent stages of the project, we have been addressing the role of molecular polarizabilities whose importance increases with focus on heterogeneous systems, the presence of charges, and strong external electric fields. The incorporation of multi-body interactions, which are well suited for Molecular Dynamics simulations, requires profound changes in the implemantation of Monte Carlo algorithms. As the iterative energy computations in principle involve all molecules in the system, we replace the standard single particle moves by the force-biased multi-particle-move Monte Carlo with acceptance corrections offsetting the bias effects. Our results for the polarizable Gaussian charge-on-spring (BK3) model in neat aqueous systems capture the ~10% reduction of molecular dipoles within the interfacial layer near the hydrophobic pore walls. While we observe only moderate changes in overall thermodynamic properties and atom and charged site spatial distributions, the Gaussian distribution of atom charges blurs the charge-layering effects associated with increased ion absorption in point-charge models. The double layer distribution show increased sensitivity to external field when including molecular polarizabilities. When comparing the polarizable and nonpolarizable force fields in modeling electrokinetic effects in hydrophilic silica nanochannels, we observe dramatic changes in ion-silica binding that appears exaggerated in the nonpolarizable model. Remarkably, separate inclusions of ion and solvent polarizabilities prove the polarizability of the *solvent alone* has a major effect on ion binding.

Modulation of nanoparticle interactions by polar functionalities. Numerous applications, as well as processing of graphitic nanoparticles depend on successful tailoring of particle solubility in aqueous media. *In silico* predictions for optimal particle functionalization rely on realistic modeling of hydration forces and Coulombic interactions among dissolved particles. Our atomistic simulations reveal two major sources of nonlinear dependences of interparticle interactions on the composition of surface coating. The conversion from hydrophobic to weakly polar, electrically neutral, coatings involves a qualitative change in interparticle forces by averting the collective dehydration transitions between apolar particles brought to small separations; surface repulsion intensifies near linearly with further addition of the polar surface component. When solubilization is achieved by gradual ionic functionalization, we observe a strongly nonmonotonic increase in interparticle repulsion with particle charge. Following a rapid initial increase, at a critical charge density, the repulsion shows saturation indicative of ion condensation effects. A new molecular picture uncovered by our recent analysis, however, augments this interpretation by showing the saturation also coincides with completing the hydrophilic hydration of the particles' coating as the uptake of water molecules reaches a limit imposed by steric effects *unrelated* to ion condensation. The saturation in both, the Coulombic and hydration contributions to solute repulsion manifests a strong dependence on particle curvature, with initial sensitivity of *both* terms to ionic functionalization increasing, and the saturation limit decreasing from spherical to cylindrical to planar geometry of the solutes. The same order therefore applies to the strength, and to the ease of overturning the hydrophobic attraction by polar functionalization (Fig. 1).

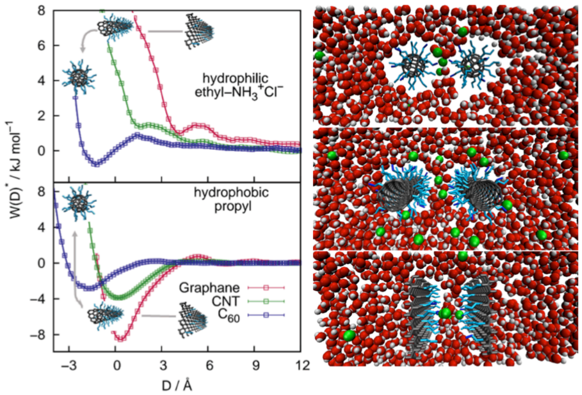

Fig.1 The sensitivity of interparticle potential *W*(*D*)* to ionic functionalization increases with the curvature in identical order as the original strength of hydrophobic attraction.

Dynamics in ionic liquids. In view of broad electrochemical window and high conductivity ionic liquids (IL) represent a superior medium in capacitors and electric double layer (EDL) supercapacitors. While the structure of ionic liquids has been well characterized both experimentally and computationally in many studies, *dynamic responses in ionic liquids* remain to be determined at a comparable level of accuracy. An objective of this study was to evaluate the timescales of elementary dynamic events that underlie ion motion, from the processes of forming and breaking hydrogen bonds within IL ion pairs (Fig.2) to ion pair formation to entrapments in and escapes from ion cages. The succession of these events ultimately determines the dynamic response of the medium and hence the AC conductance and EDL charge/discharge rates during capacitor operation. We studied structural and dynamic properties of ionic liquids and their mixtures with water, evaluating the requirements of system conditions on characteristic timescales of the above processes, which were estimated from pertinent time correlation functions and the reactive flux formalism. The main results of the study concern relative rates of hydrogen bonding in IL ion pairs, ion-pair and ion-cage formations and their dependences on the temperature, extend of mixing with water, and the form of the force field. The lifetimes of the three forms of localization span a broad range from O(10^2) ps for IL hydrogen bonds to O(10^3) ps for ion cage events. The influence of polarizable vs. non-polarizable force fields (applicable via charge renormalization) was tested on the example of 1-butyl-3-methylimidazolium bromide and chloride. Reduced coordination numbers, larger mean separations, and significantly accelerated dynamics are observed when the polarizable force field is applied. A domain analysis showed that the nonpolar parts of the ions are dispersed and when more water is added the water clusters increase in size. The dynamics accelerate in general upon addition of water. In ionic liquids with a mixture of chloride and bromide anions, the coordination of the cation depends on the anion type and the ion-pair dynamics slows down with increasing content of chloride ions.

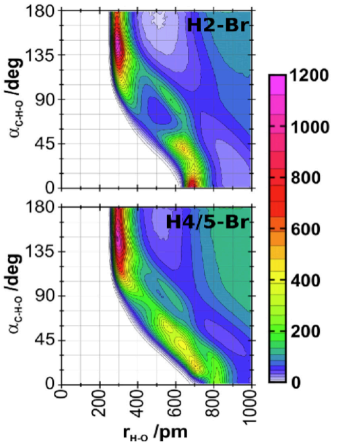

Fig. 2 Geometry distributions in H-bonded 1-methyl 3-butyl imidazolium bromide ion-pair in polarizable force field for distinct H-donor positions.

Future plans

To enable predictions of electrolyte absorption in nanopores, underlying the optimal electrode function in electric storage devices, we continue developing Fractional Exchange Monte Carlo techniques (FE-GCMC) for electrolyte solutions. To enable studies of nanopore surface-energy storage we also envisage extension to highly compressed conditions, including characterizations of bulk solutions. To model the function of porous-electrode supercapacitors, we will be implementing a Gibbs-like ensemble with separate anode and cathode compartments at controlled voltage difference. To characterize molecular polarization effects in aqueous confinements requires improved algorithms to achieve viable efficiency of FE-GCMC simulations for ionic solutions with polarizable force fields, which become especially significant near interfaces and under external electric perturbation.

Publications Acknowledging the Award DE-SC-0004406 from 2014 – 2017:

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

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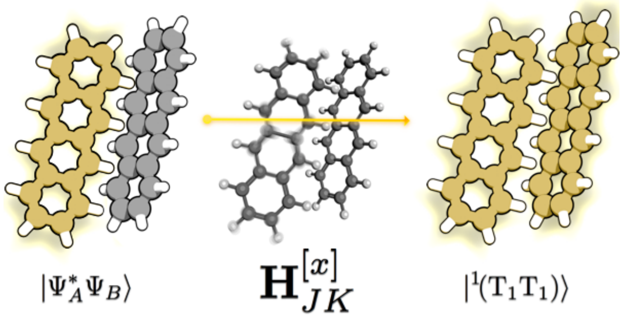
Abstract

Project Scope



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

Recent Progress

Over the past several years we have developed a fully *ab initio* version of the old Frenkel-Davydov exciton model, in which a collective excitation in a molecular crystal, aggregate, or other multi-chromophore system is described using an *ansatz* consisting of a linear combination of excitations that are localized on individual chromophores. Chromophore wave functions can be computed in a distributed way, as can the coupling matrix elements between these basis states. Notably, we do not introduce common approximations such as dipole coupling or neglect of exchange interactions, both of which are dubious in closely-packed crystals. Using this model, we have simulated exciton transport in models of an organic semiconductor nanotube, finding that very different dynamics are obtained in small model systems as compared to larger ones containing 50–100 chromophores. Smaller models suffer from an artificial heterogeneity in the site energies due to "edge effects". In larger collections of chromophores, our approach predicts coherences lasting several hundred femtoseconds that are not seen in smaller model systems.

Recently, we have derived and implemented analytic derivative couplings ($\partial H_{JK}/\partial x$) for this model, which express how the matrix elements of the exciton Hamiltonian change with respect to the nuclear coordinates. These derivative couplings provide *ab initio* values for electron/phonon couplings that can be used to parameterize a model vibronic Hamiltonian of Holstein-Peierls type. We have used this approach to study the mysterious problem of singlet fission in crystalline pentacene, a process that is known to be fast and efficient despite being ostensibly endothermic. We showed that only when vibronic coupling is included does the singlet fission pathway become feasible. The endothermicity is only illusory; in a vibronic basis, the process is exothermic and driven by *intra*molecular vibrational modes. This may provide insight for design of new singlet fission materials since previous discussion in the literature has focused on the role of *inter*molecular vibronic coherence.

On the intermolecular interactions front, we have spent several years characterizing the convergence, or lack thereof, in the many-body (monomer, dimer, trimer, …) expansion. Most applications of this approach benchmark against supersystem results for rather small systems and then assume that these accuracy estimates hold equally well for large systems. This assumption is false, and as such much of the conventional wisdom regarding the behavior of the many-body expansion (MBE) is simply wrong. Four-body (tetramer) terms are absolutely required, the overall accuracy is quite sensitive to numerical thresholds, basis-set superposition effects are not negligible, and charge embedding makes very little difference in accelerating the convergence of the expansion. Together, these considerations render the MBE much less attractive, but we have recently shown that they can be overcome through the use of many-body counterpoise corrections and through judicious screening of the subsystem calculations. The result is a version of the MBE where up to 2/3 of the subsystem calculations can be discarded *a priori* while maintaining good accuracy. However, distance-based thresholds become awkward and inefficient for fragmenting macromolecular systems, and in preliminary calculations we achieve good success with screening the interactions in energy space, using low-level quantum methods or force fields. Only pairwise terms need to be treated at a high level of theory in this approach, which is therefore applicable to very large systems.

Future Plans

We are working on the periodic boundary conditions necessary to apply fragment-based methods to molecular crystals and liquids. The goal is twofold: (1) to apply our many-body version of symmetry-adapted perturbation theory (XSAPT) to compute cohesive energies of crystals; and (2) to use the many-body expansion to perform *ab initio* molecular dynamics calculations in liquid water using methods other than density functional theory. In the context of the exciton model, we continue to explore the interplay between vibrational and electronic degrees of freedom for charge-carrier generation (via singlet fission) and transport, in crystalline acenes.

Grant Numbers and Grant Titles

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

Postdoc(s): Jie Liu

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

Publications

1. K. U. Lao and J. M. Herbert, *Atomic orbital implementation of extended symmetry-adapted perturbation theory (XSAPT) and benchmark calculations for large supramolecular complexes.* Journal of Chemical Theory and Computation (in press).
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Induced Polarization Restricts Conformational Distribution of a Light-Harvesting Molecular Triad in the Ground State

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Abstract

A light-harvesting molecular triad, consisting of carotenoid, porphyrin, and fullerene, is one of the biological inspired materials that possibly impact the way we utilize the solar energy. This promising material, unlike a conventional solid-state matter, is structurally flexible at room temperature that hinders its efficiency of photo-induced charge transfer (CT); thus, the molecular triad is still far from real-world application. We characterize the relationship between the charge-transfer rates and the varying structures of the triad by means of quantum calculations and molecular dynamics simulations. The linearly extended conformation has the fastest rate of charge transfer, but it is the least populated conformation in a distribution of structures that bend and rotate around covalent bonds between the subunit of the triad in solution.

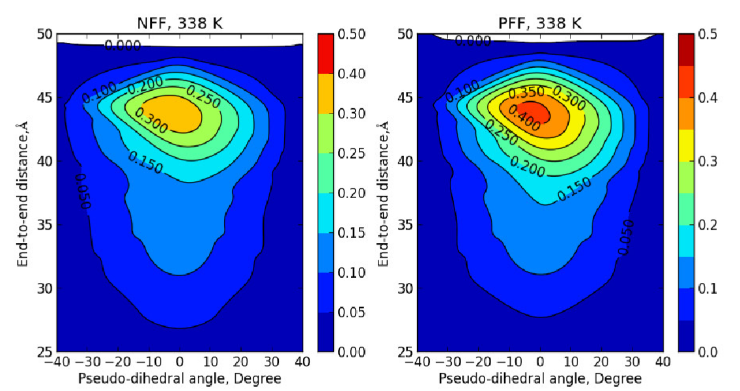

Figure 1. 2-D probability contour plots as a function of end-to-end distance and pseudo-dihedral angle of molecular triad for (left) non-polarizable force fields (NFF) and (right) polarizable force field (PFF).

Our group has employed molecular dynamics simulations with non-polarizable force fields to show the distribution of the molecular triad in solutions for the ground or the excited states [1-3]. Although the simulations with non-polarizable force fields describe the thermodynamics and structural properties of the triad well, the force field lack the effect of an induced polarization that is critical to the charge transfer properties of organic photovoltaic (OPV) materials. This past year, we have parameterized the polarizable force fields[4] for the individual component of the molecular triad as well as the THF solvent by matching their ensemble properties from simulations against the experimental measurements. We employed the Replica Exchange Molecular Dynamics simulations (REMD) to enhance the sampling of the simulations with explicit solvents. We plotted the 2-D distribution plot with the end-to-end distance and the pseudo-dihedral angle of a molecular triad in Figure 1. The distribution of the triad from the simulations using the polarizable force fields is noticeably sharper than the non-polarizable ones. After the structural analysis, we found that the induced polarization stabilizes the rotational isomerization of the polyene chain that gives a sharp peak in Fig1.

We have been developing polarizable models for the excited states that dictate the efficiency or pathways of charge transfer. In collaboration with Profs Barry Dunietz and Eitan Geva under a new award, we will investigate the effect of the induced polarization and solvent chemical structure on the triad conformational landscape in details. We have computed the triad's I amide stretch frequency of a linearly extended conformation and a bent one[5]. They are highly sensitive to the electronic states. In this coming year, my group will explore a new organic photovoltaic system made of C_{60} and SubPC. We will quantify the structural characteristics of a molecular junction made of these materials with molecular dynamics simulations. We have also made progress in developing portable molecular dynamics simulation software for heterogeneous computing systems including graphic processing units. One of the challenges in heterogeneous computing is about the cumbersome data transfer between stakeholders. The data transfer from the host to the device mandates the transfer of the main data structure and its children data structure, which impedes parallelization. We have created ACCHelper that reduces the size of an assembly code and effectively extracts the final address of a pointer in a data structure.[6] This prototype has worked on a proxy molecular dynamics code. Our next step is to implement it into popular community software such as Gromacs and LAMMPS.

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Grant Numbers and Grant Titles

DE-SC0016501 Title: Post-Marcus Theory and Simulation of Interfacial Charge Transfer Dynamics in Organic Semiconducting Materials (PI, Barry Dunietz. CoPIs: M.S. Cheung, E. Geva)

UH Postdoc: Oleg Starovoytov (2015-2017), Pengzhi Zhang (2017)

UH Graduate student: Jacob Tinnin (2017-current)

Publications acknowledging the grant:

1. A. K. Manna, D. Balamurugan, M. S. Cheung, B. D. Dunietz, "Unraveling the mechanism of photo-induced charge-transfer in carotenoid-porphyrin-C60 molecular triad", Journal of Physical Chemistry Letters, **6**, 1231-1237 (2015).
2. O. N. Starovoytov, P. Zhang, M. Cieplak and M. S. Cheung, Phys. Chem. Chem. Phys. **19**, 22969-22980 (2017).
3. X. Sun, P. Zhang, Y. Lai, K. L. Williams, M. S. Cheung, B. D. Dunietz and E. Geva, submitted (2018).
4. M. Ghane, M. S. Cheung and S. Chandrasekaran, submitted (2018).

ECC: Exascale Computational Catalysis

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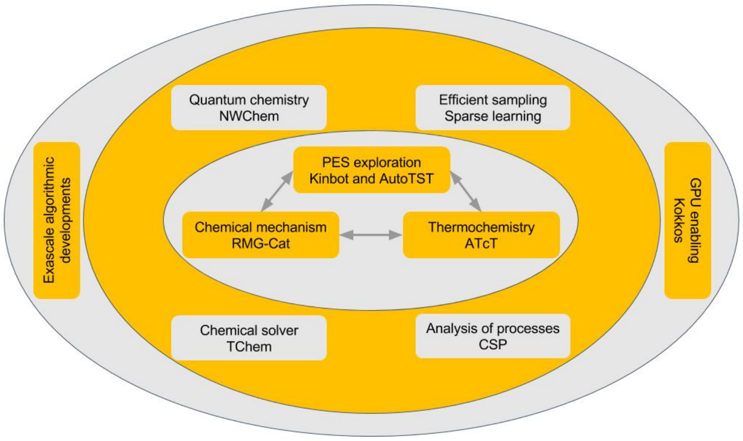
Program Scope

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_2 or methane, into larger and more valuable compounds. To achieve these goals most efficiently and selectively it is necessary to design and fine-tune catalysts and operating conditions through a combination of theory and modeling. Our work provides the necessary molecular-level understanding and quantitative description of chemical processes at the catalyst surface and in the gas phase above it to create an exascale enabled toolset for the broad research community to help design catalytic systems that can answer challenges of the 21st century, such as energy security and curbing global warming.

Our goal in this project is to create a computational framework that accelerates discovery and characterization of complex molecular systems. We are targeting coupled heterogeneous/gas-phase reactions and reaction mechanisms with relevance to catalytic conversion of hydrocarbons, oxygenates, and small molecules. We capitalize on recent improvements in theoretical chemistry, combined with improved mathematical software for solving complex problems, and with exascale-size supercomputers to develop a uniquely powerful chemical computational toolset for the research community.

We conduct three major thrusts of research supported by a diverse array of mathematical, software, and algorithmic tools. The hierarchy of the parts of the work is shown on the right. We define the three main areas as follows:

Automated reaction path exploration on multidimensional potential energy surfaces. Using advanced machine learning algorithms coupled to quantum chemistry code suitable for heterogeneous exascale architectures we develop codes that explore reaction pathways for elementary reactions. These algorithms automatically discover previously unknown elementary reaction classes and produce calculations on a large number of homologous systems to build up minable reaction databases.



Automated reaction mechanism generation for heterogeneous catalysis. We develop a complete computational infrastructure that generates reaction mechanisms for heterogeneous catalysis. This stores and recalls reactions and builds

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them into a mechanism that is able to predict macroscopic observables. Moreover, we solve the underlying kinetic equations efficiently, so that they allow for advanced mechanism analysis, reduction, and uncertainty quantification.

Advanced thermochemistry database. We create a modern, intelligent, user-friendly, and accurate thermodynamic database that is self-consistent and can be grown by us and the broader scientific community. For gas-phase systems we incorporate automatic state-of-the-art energy evaluations and anharmonic corrections and generate thermodynamic properties directly applicable in common kinetics codes, including ours. For heterogeneous systems, we implement methods beyond DFT to calculate energies, and novel approaches for entropy terms.

Recent Progress

The exhaustive exploration and characterization of the relevant elementary chemical pathways on the underlying potential energy surface is an extremely hard problem. Our main goals are to automate the discovery of new reactions pathways for catalytic reactions and generalize them into reaction families, and to rapidly evaluate reaction properties (barrier heights, transition state structures, etc.) for many homologous reactions and cast the resulting information into mineable data.

Our related goals at Sandia for Year 1 are to implement multimodal search algorithms, based on evolutionary or annealing algorithms, for gas-phase reactions, including search acceleration with sparse learning techniques demonstrated on small, gas-phase molecules. We have thus far implemented various established optimization algorithms for low-rank tensor approximations and tested them on simple molecular potential energy surfaces. We are working on extracting analytical Hessians and gradients from these approximations. We also tested several multimodal search algorithms, such as genetic algorithms and simulated annealing for critical point search, as well as implemented targeted saddle point search algorithms (e.g., dimer method), and worked on the parallelization of these codes. We coupled our codes to NWChem for scalability, but via the Atomic Simulation Environment (ASE) we will be able to couple with other electronic structure codes as well. We are also working on coupling these approaches with our heuristic KinBot code in order to further accelerate the search. The related work from Northeastern is described under 'Future Plans'.

A major goal in catalysis is to predict the performance of novel materials. Accurate prediction of the reactivity and selectivity of catalytic materials requires a detailed list of elementary surface reactions, or a microkinetic mechanism. To this end, we want to enhance and extend RMG-Cat (Reaction Mechanism Generator for Heterogeneous Catalysis), recently developed at Northeastern and Brown, which builds microkinetic models for catalysis in an automated manner and couple RMG-Cat to our other software tools and databases. The immediate goals are outlined under 'Future Plans.'

Thermochemistry is central to predicting and modeling the properties and behavior of matter. Some current challenges for accurate prediction are creating thermodynamically consistent datasets for a large number of chemical species and incorporating sufficiently rigorous calculations for entropy to allow reliable application of thermodynamic data under a wide temperature range. Over the course of the project we want to develop our Active Thermochemical Tables (ATcT) into a public and interactive database while preserving a strict control over accuracy, and incorporate into automated chemical mechanism calculations, enable the routine inclusion of anharmonic effects for gas-phase species, crucial for accurate entropy and create a suite of methods implemented into ASE to compute the partition function for the coupled, anharmonic motion of adsorbates relative to the catalyst surface.

Our Year 1 goals at Argonne are to create SQL databases for thermochemical networks and design a Non-Rigid Rotor Anharmonic Oscillator (NRRAO) code. Reference data was generated for small, three-atom systems to enable benchmarking of approximate methods of calculating anharmonic partition functions. The reference data for H_2O, HO_2, and $^3CH_2$ was created in collaboration with the Gas Phase Chemical Dynamics group at Argonne (Ruscic, Jasper, Wagner, Harding) from high accuracy potential energy surfaces that were solved using fully variational approaches methods to yield the vibrational energy levels and their computed partition functions. The reference partition functions generated in this work were well converged (~.1%) below 3000 K. The SQL database is being developed. The related planned work on adsorbate thermochemistry is outlined under 'Future Plans.'

NWChem is an open source computational chemistry code developed at PNNL. This is our main electronic structure code in this this project. Over the course of the project we want to create modern interfaces (e.g. web APIs) between NWChem and KinBot and ATcT, fully taking advantage of the GPU and MIC capabilities of NWChem and implement methods beyond DFT to treat heterogeneous catalytic systems.

Our Year 1 goals at PNNL is to add pathways optimization algorithms to NWChem Arrows, implement method of increments and dispersion corrections for surfaces. We created a molecular orbital viewing to EMSL Arrows and other, user-friendly web APIs (https://arrows.emsl.pnnl.gov/api/). Specifically, we added an automatic input generation capability in arrows that demonstrates the use of the bonding penalty function for mapping out reaction pathways or for getting initial pathway structures. We are currently working on implementing BEEF-vdW functional and testing it on molecules and surfaces.

At Sandia we are also developing a GPU-accelerated flexible chemical solver, called TChem++, applicable for catalysis and gas-phase chemistry, including a range of physical embeddings of the solver, e.g., plug flow reactor. Our Year 1 goals are to convert existing C utilities to C++ and add functionality for heterogeneous microkinetic models. Thus far we reviewed the sequence of computations and typical dimensions for various thermodynamic properties and reaction rate computations and added doxygen to the current C++ version. Currently we are working on the implementation of Kokkos structures to C++ class handling thermodynamic properties. In this context, we are exploring the efficiency of several memory layout models for a range of kinetic model sizes, from o(10) to o(10^3) species, and for both OpenMP and GPU-based computations.

Computational predictions from chemical systems computations are difficult to analyze, e.g. to assign cause-and-effect relationships and advance understanding, given the nonlinearity, stiffness, and intricate coupling among reaction processes. This is particularly so in results from large-scale computations with complex chemical systems. Accordingly, there is a strong need for analysis software tools that offer fast and effective capabilities tailored to the analysis of chemical systems. Our goals are to (a) build a GPU-enabled C++ chemical analysis software toolkit tailored for exascale architectures using Computational Singular Perturbation (CSP) and usable for analyzing both gas phase and catalytic chemical models (b) demonstrate effective performance on heterogeneous architectures and large scale chemical data, with both gas phase and catalytic chemical problems.

Our Year 1 goals are to develop the core C++ CSP library classes, providing a basic kernel of CSP operations. We have so far designed the high-level software architecture, defining essential classes and their key functionalities and extended the mathematical formulation of CSP analysis, beyond ODE/PDE systems to include DAE systems of relevance in catalytic systems. We are currently testing the CPU-GPU linear algebra package MAGMA eigensolvers on test matrices. The eigensolution of Jacobian matrices is the most computationally intensive element of the CSP analysis computational budget.

Future Plans

At Northeastern and Brown we had not received funding by the time of this abstract submission. However, we have a detailed plan for contributions as soon as the funds are received.

At Northeastern the goal for Year 1 in the first thrust of research is to improve, accelerate, and generalize the saddle point searches in our AutoTST code. We will create Python classes for molecules and transition states that allow the translation between RMG objects, RDKit objects, and ASE objects, with relative ease (e.g., preserving atom labeling), so that we can use RMG's graph methods and reaction generation, RDKit's distance geometry conformer embedding, and ASE's interface to electronic structure codes. Conformer generation via ASE in AutoTST will be tested, both with a brute force (rotate all the torsions in every combination) and some evolutionary strategies. We will also work on techniques using vibrational mode analysis instead of IRC for saddle point verification. Meanwhile, we will rewrite AutoTST as an independent project (that uses some RMG modules and classes) rather than being part of the core RMG codebase.

Our goals for Year 1 in the second thrust of research at Northeastern and Brown are to implement linear scaling relationships (LSR) and add reaction families, such as Eley-Rideal or bidentate, to RMG-Cat. We will implement LSR in RMG-Cat for binding energy estimation on a range of metals. We will test this on the catalytic combustion of methanol and generate new kinetic models for a range of metal surfaces. This reaction system will eventually be one of our test cases for the other tools; the catalytic partial oxidation of methane and natural gas coupled with gas phase chemistry will be the other one.

At Brown we will work on the theoretical aspects of adsorbate thermochemistry (third research thrust). The traditional approach to estimating the thermochemistry of adsorbates is to use the harmonic oscillator model. For each adsorbate, our new approach will separate the 6 modes of relative motion from the $3N$-6 internal vibrational modes in the partition function. The resulting $3N$-6 new vibrational modes will continue to be calculated using the quantum harmonic oscillator model, while the partition function for the remaining 6 degrees of freedom will be computed directly using classical statistical mechanics. At Brown the dynamics code originating from Argonne, called rotd (Klippenstein, Georgievskii) will be tested and adapted to calculate adsorbate thermochemistry and eventually to predict sticking coefficients. A major challenge is likely the calculation of the accurate energies during the sampling of the PES.

Our goals for the whole team are outlined in our original proposal, and are summarized below in the form of milestones.

	End of Year 1	End of Year 2	End of Year 3	End of Year 4
Automated reaction path exploration	Calculate reaction pathways for highly unsaturated on in other ways challenging gas-phase systems automatically and demonstrate generalization of search	Demonstrate capabilities on known heterogeneous reactions	Generate microkinetic model automatically where all tools demonstrate their individual capabilities as well as their coupling, performance, and scalability on heterogeneous architectures. Mechanism is generated with RMG-Cat, parameters are incorporated from KinBot, AutoTST, and ATcT, which drive NWChem directly or via Arrows. The kinetic ODE is solved with TChem and analyzed by CSP. Target test catalytic systems with coupled gas-phase and heterogeneous chemistry.	Create the ability to generate the building blocks of a kinetic Monte Carlo model of a heterogeneous catalytic system with the synchronized effort of the developed tools. Demonstrate ability on the same systems as listed in Year 3.
RMG-Cat	Generate model with linear scaling and gas-adsorbate reactions	Perform mechanism creation coupled to KinBot and AutoTST		
Thermochemistry	Release beta ATcT web version	Release beta version of ATcT on the web with thermo for high temperatures based on NRRAO		
NWChem	Arrows has new functionalities, and method of increments and dispersion corrections are functional	RPA is functional and surface interactions work in Arrows		
TChem	TChem can run RMG-Cat generated mechanisms off-line	Demonstrate direct coupling to RMG-Cat and ATcT and feasability on heterogeneous architectures		
CSP	Develop core CSP code classes	Develop full suite of CSP classes and batched mixed architecture eigensolver		

Grant Numbers and Grant Titles

Exascale-enabled computational tools for complex chemical systems

Postdoc(s): Eric Hermes (Sandia), Fazle Rob (Sandia), Rai Prashant (SNL, partial support)
Student(s): none currently

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

None so far, project started September 2017

Center for Scalable Predictive methods for Excitations and Correlated Phenomena (SPEC)

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Abstract

The Center for Scalable Predictive methods for Excitations and Correlated Phenomena (SPEC) aims at capitalizing on DOE's investments in experimental light source facilities (APS, ALS, LCLS, and NSLS) and national leadership computing facilities. The scientific vision of SPEC is to

- develop state-of-the-art, many-body electronic structure methodologies for excited state complex systems,
- implement these methods on leadership class computer architectures,
- deliver scalable, open-source electronic structure software libraries that are interoperable with community electronic structure software,
- address challenges in excited-state and correlated phenomena in complex chemical systems.

SPEC is comprised of team members with expertise in the domain science, computer science and applied mathematics fields (Figure 1). The goal is to deliver scalable software that is appropriate to make efficient use of DOE's leadership class computer architectures in support of the mission of DOE's Office of Basic Energy Sciences (BES). The currently existing knowledge and capability gaps in the area of highly-accurate, exited-state electronic structure methods, and their efficient implementation on leadership class computer architectures, define scientific and methodological challenges to address in order to advance our ability to model, understand, predict, control and design the properties of complex molecules and molecular assemblies. This will be achieved via the following 3 research goals (G1 – G3):

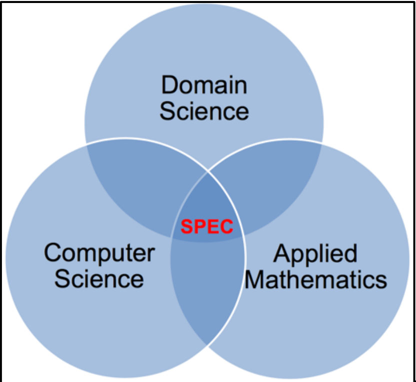

Figure 1. SPEC includes expertise from Domain Science, Computer Science & Applied Mathematics.

G1. ***Develop theoretical approaches that provide an accurate description of valence- and core level excited states of molecules in their local environment.***

The proposed methods consist of:

(*i*) Equation-Of-Motion Coupled Cluster (EOMCC) based on standard excited-state extension of the ground-state CC formalism that includes a hierarchical structure of approximations (singles, doubles, triples, …) and includes relativistic EOMCC formulations.

(*ii*) Multi-Reference (MR) Methods, which include Multi-Reference Coupled Cluster (MRCC), novel selected Configuration Interaction (CI) in Complete Active Space SCF (CASSCF), heat-bath and Adapted Sampling CI (ASCI) integrated with CASSCF, core-hole and excited states as well as spin-orbit coupling.

(*iii*) Hierarchical Green's Function (GF) Methods including Green's Function Bethe Salpeter Equation (GW-BSE), Cumulant expansions, GF2 (second order self-energy), Green's function Perturbation Theory (GFPT), Green's function Coupled Cluster (GFCC) and relativistic formulations.

G2. ***Develop methodologies to model excited state potential energy surfaces with an accuracy and consistency well beyond that provided by standard DFT-based methods.***

The goal is to develop robust, first principles-based protocols that are able to model excited state processes in realistic systems (i.e. systems beyond simple models), which will include the effect of the system's environment. This will be achieved via the coupling of the developed hierarchical methods (higher level) with the Self-Energy Embedding Theory (SEET, lower level) that allows the quantitative account for the system's environment. In addition, EOMCC excited state gradients will offer the capability to obtain geometries, transition states and the location of conical intersections on excited state potential energy surfaces.

G3. ***Develop scalable implementations that take full advantage of leadership class petascale computing facilities and establish a path towards future exascale computers.***

The goal is to reduce the computational cost of calculations and deliver sustainable performance that exceeds current levels by at least an order of magnitude to enable calculations to be extended to real systems. This will be achieved by the development of Tensor Algebra library for Many-body Methods (TAMM) targeting the efficient implementation of EOMCC, GFCC, Many Body Perturbation Theory (MBPT) and Many Body Green's Function (MBGF), and MRCC methods, the use of Model Order Reduction (MOR) method for core excitations with Green's Function approaches and the development of efficient and robust optimization algorithms for Multi Configurational SCF (MCSCF) iterations.

The research strategy for fulfilling the above research goals consists of the breakdown of the effort into 6 Tasks (T1 – T6), shown in Figure 2.

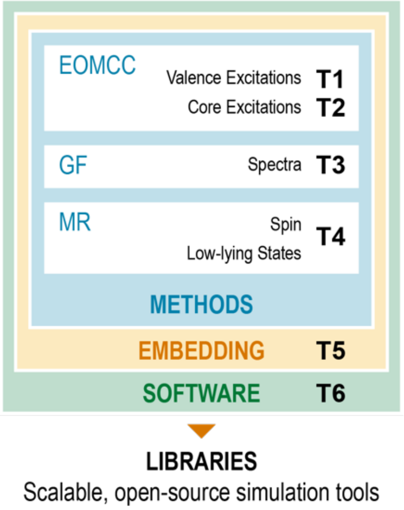

Figure 2. An integrated approach combining method development, computer tools and optimization (T1–T6) that will deliver scalable open-source libraries.

T1 Accurate Equation-of-Motion Coupled Cluster Formalisms for Valence Excited States (G1, G2)
T2 Accurate Equation-of-Motion Coupled Cluster Formalisms for Core Excited States (G1)
T3 Hierarchical Green's Function Formulations (G1, G2)
T4 Scalable Multi-Configurational and Multi-Reference Methods for Quasi-Degenerate Molecular Systems (G1, G2)
T5 Self-Energy Embedding Approaches (G1, G2)
T6 Programming Models, Computer Science Tools, and Optimization for Many-Body Methods (G3)

Grant Numbers and Grant Titles

This work was supported as part of the Computational Chemical Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division in the Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC) at Pacific Northwest National Laboratory.

Publications in the last year (2018)

1. Bo Peng, Karol Kowalski, "Green's function coupled-cluster approach: simulating spectral functions for molecular systems," *J. Chem. Theory Comput*. (submitted, 2018)
2. Karol Kowalski, "Properties of coupled-cluster equations originating in excitation sub-algebras," *J. Chem. Phys*. **148**, 094104 (2018).

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) will develop computational/theoretical chemistry methods and data-driven science approaches with the aims of (i) de-novo design of novel functional nanoporous materials, (ii) discovery and selection of the most promising functional nanoporous materials from databases of synthesized and hypothetical framework structures, and (iii) microscopic-level understanding of the fundamental interactions underlying the function of nanoporous materials. A pivotal part of NMGC's success is a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups that allows for iterative feedback.

Building upon prior NMGC research focused mostly on gas capture, separation and catalysis in crystalline nanoporous materials, the team will work on the development and application of a predictive hierarchical chemical modeling toolbox that can tackle increasingly complex chemical separations and transformations in complex nanoporous materials, including metal-organic frameworks, zeolites, and polymers with intrinsic microporosity. Research will be directed toward liquid-phase adsorption and catalysis in multi-component mixtures. The nanoporous materials will include hierarchical architectures, responsive frameworks that may undergo phase transitions or post-synthetic modifications, and may contain defects, partial disorder, interfaces or be a composite material. Tunable electronic properties of nanoporous materials, including luminescence and magnetic coupling and anisotropy, will be addressed Another major aspect of the proposed research is the development and application of data-driven science approaches that will lead to advances in machine learning for the discovery of optimally-performing materials, in genetic algorithms for the tailored design of nanoporous materials, and in computational methods to systematically identify and to characterize metal-organic frameworks and other nanoporous materials. The team will also work on the development of data repositories for nanoporous materials that add value by providing structures optimized via electronic structure calculations, along with their energetics for solvent removal, pore characteristics, and their adsorption and transport properties. Data management and computing will primarily use current petascale and future exascale capabilities at the Argonne Leadership Computing Facility, as well as NERSC.

The collaborative NMGC activities will also contribute to the training of graduate students and postdoctoral researchers with broad expertise in data-driven science approaches and computational chemistry methods, in addition to the skills to thrive in an integrated experimental and computational research environment.

This talk will highlight recent developments enabling first principles Monte Carlo (FPMC) simulations for which the potential energy is calculated on-the-fly using Kohn-Sham density functional theory. Applications of FPMC to the prediction of (a) unary and binary adsorption isotherms for gas molecules in metal-organic frameworks with under-coordinated metal nodes and (b) reaction equilibria in cation-exchanged zeolites (see **Figure 1**). Emphasis will be given to simulation methodologies and microscopic-level origins of the observed thermodynamic behavior.

Over the next year, the NMGC team will continue its collaborative endeavors to discover functional nanoporous materials and to use an integrated computational/data science/experimental approach for unraveling structure/chemistry/function relationships.

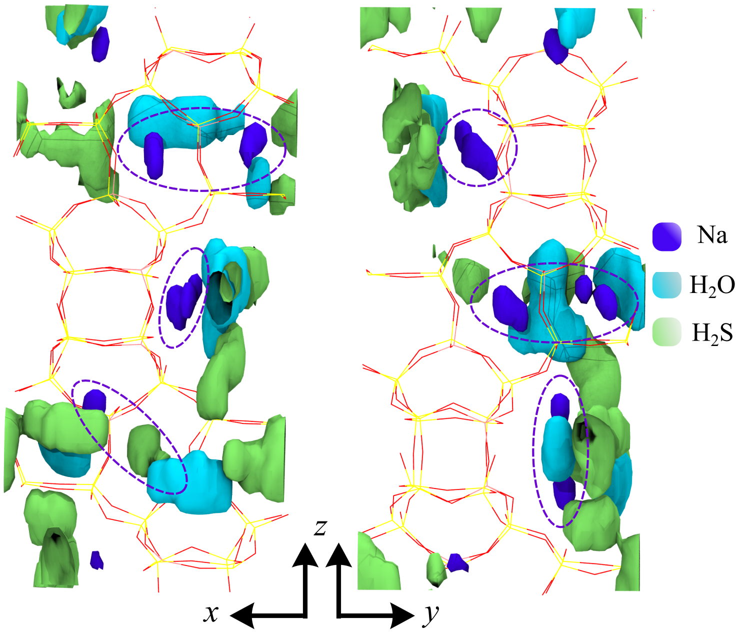

Figure 1: Spatial Distribution Spatial distributions of sodium cations, H_2O and H_2S molecules in Na-BEA. The isosurfaces indicate regions with densities larger than twice the corresponding average densities in the micropore. The dashed ellipses highlight the locations of Na+ pairs.

Grant Number and Grant Title

DE-FG02-17ER16362

Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

Postdoc(s): Peng Bai (UMN), S. Bobbitt (NU), Dhabib Chulhai (UMN), Hakan Demir (UMN), Subhadip Goswami (NU), Wooseok Jeong (UMN), Britta Johnson (Cornell), Ping Lin (UF), Andreas Mavrantonakis (UMN), Mohammad Momeni (UMN), Manuel Ortuno (UMN), David Presti (UMN), Saied Pratik (UMN), Dai Tang (GA Tech), Raghuram Thyagarajan (UMN), Pragya Verma (UMN), Jenny Vitillo (UMN), Xinping Wu (UMN), Zhenpeng Yao (UT), Mike Ziebel (UCB)

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P. Verma, Z. Varga, and **D. G. Truhlar**, "Hyper Open-Shell Excited Spin States of Transition-Metal Compounds: FeF_2, $FeF_2\cdots$ethane, and $FeF_2\cdots$ethylene," *J. Phys. Chem. A* **122**, 2563-2579 (2018).

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M. E. Ziebel, L. E. Darago, and **J. R. Long**, "Control of Electronic Structure and Conductivity in Two-Dimensional Metal–Semiquinoid Frameworks of Titanium, Vanadium, and Chromium," *J. Am. Chem. Soc.* **140***,* 3040–3051 (2018).

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

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Abstract

The over-arching goal of this project is to develop, test, and validate a user-friendly, open source software package that implements the Fermi-Löwdin orbital self-interaction-correction (FLO-SIC) to density functional theory (DFT). Self-interaction error (SIE) is an undesirable, but avoidable feature of semilocal DFT approximations that can poison DFT-based calculations in materials science and chemistry, most remarkably when electrons are shared over stretched bonds, as in the transition states of chemical reactions, and in strongly-correlated systems such as transition metal complexes, even near equilibrium geometries. Attempts to remove the SIE indicate that the Perdew-Zunger self-interaction correction (PZ-SIC) can largely eliminate these problems, but traditional implementations are too computationally demanding to be practical for general use or even to perform tests on large systems. Formulating the theory in terms of localized Fermi orbitals circumvents the main bottleneck and makes the FLO-SIC approach both unitary invariant and size-extensive.

The project integrates code development activities with theoretical research and two validation thrusts, one focused on MOF-based transition metal chemistry and the other on molecular magnets. The ultimate objective of the code development is to produce efficient software that can be used to study materials with 0-, 1-, 2-, and 3-dimensional periodicity and including atoms from across the periodic table. Initial priorities involve both algorithmic improvements to the FLO-SIC methodology and code optimization. The code development team is also carrying out proof of concept studies to demonstrate that FLO-SIC successfully eliminates SIE in practice.

The theoretical research involves investigating the use of FLO-SIC with sophisticated semilocal density functionals like the SCAN meta-GGA and testing different schemes for implementing self-interaction corrections within the FLO-SIC framework. The aim is to discover a way to limit the effects of the corrections to situations where they are needed without degrading the performance where existing functionals already work well. A second component is merging self-interaction corrections into a linear response, time-dependent DFT formalism. Here the aim is to improve the description of phenomena such as photoinduced charge transfer that are critical in novel photovoltaic applications.

The transition metal-based catalysis thrust involves coordinated synthesis, characterization, and computational research aimed at validating the success of the FLO-SIC method for describing important transition metal chemistry. Metal organic framework (MOFs) materials will be

synthesized with selected open metal sites. Samples of these materials will then be used in experimental reaction studies featuring a number of different adsorbate species. The focus will be to determine adsorbate energies for a set of metal-molecule interactions that are differentially affected by self-interaction effects. FLO-SIC calculations modeling these reactions will be carried out and the results compared directly with the experimental results and with results of other computational methods. Once validated, FLO-SIC calculations will be used to aid the search for MOF catalyst materials that can achieve the conversion of CO_2 to methanol or related reactions.

The magnetic molecule thrust also aims at validating the FLO-SIC method. Experimentally determined data for quantities such as magnetic exchange couplings and magnetic anisotropy energies (MAE) will be compared with the results of corresponding FLO-SIC calculations. Subsequent FLO-SIC calculations will then be used to guide the development of novel *3d-4d* molecular magnet compounds that are expected to have large MAE and could therefore be used for high density magnetic storage or in quantum computing applications.

In this talk, I will present the overall vision and structure of the project and give a brief report of initial results stemming from this research.

DoE Award: #DE-SC0018331 (start: 10/1/2017)

Post-docs: Kai Trepte, Kamal Sharkas, Yoh Yamamoto, Hamanadhan Myneni, Lin Li, Mona Mohamed

Graduate students: Yahui Yang, Rajendra Joshi, Kushantha Withanage,

Publications acknowledging this grant:

1. Der-you Kao, Kushantha Withanage, Torsten Hahn, Javaria Batool, Jens Kortus, and Koblar Jackson, “Self-consistent self-interaction corrected density functional theory calculations for atoms using Fermi-Löwdin orbitals: Optimized Fermi-orbital descriptors for Li–Kr”, J. Chem. Phys. **147**, 164107 (2017).
2. Kushantha Withanage, Kai Trepte, Juan E. Peralta, Tunna Baruah, Rajendra Zope, and Koblar A. Jackson, “On the question of the total energy in the Fermi-Löwdin orbital self-interaction correction method”, *submitted*.

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Ab initio design of quantum molecular magnets for information applications

Edwin Barnes, Sophia Economou, Nicholas Mayhall, Kyungwha Park
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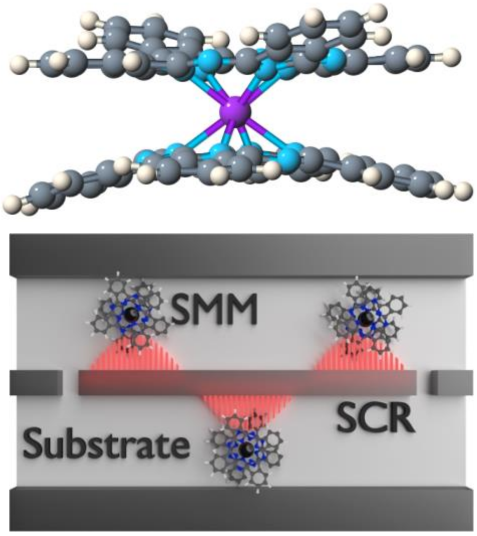

The demand for greater computing power to solve challenging problems in science, medicine, and economics continues to rise at a rapid pace. This need has fueled large investments from both government and industry in an approach to enhance computational power that exploits the principles of quantum mechanics. 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. The most well-known such problem is Shor's algorithm, which, if implemented in a large quantum computer, would be able to break the RSA cryptosystem, which is currently the predominant system for securely transmitting information. While the requirements for Shor's algorithm are formidable in terms of the necessary number of qubits and level of control precision, there also exist important near-term applications that can be implemented with a more modestly sized quantum computer. A notable application is quantum simulation, which would enable the computational modeling of large-scale strongly correlated quantum systems, with applications in quantum chemistry and medicine.

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. In 2001, Leuenberger and Loss proposed to use the spin of the nanoscale single-molecule magnet (SMM) Mn_{12} as a qubit, with the control achieved via electron spin resonance pulses. Since then, plausible setups and architectures for quantum computing with SMMs have been proposed by several groups. A majority of the 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 field control also limits the potential of SMMs for device integration and scalability, as it is extremely challenging to focus on a specific qubit.

Recently, a qubit candidate with remarkable properties was experimentally demonstrated by Wolfgang Wernsdorfer: the SMM $TbPc_2$, 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. 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.

Our efforts to systematically design quantum information processors with SMMs by varying chemical and physical environmental factors using a multiscale model approach ranging from different levels of ab-initio quantum chemistry simulations to analytically solvable effective models and time-dependent external control will be discussed. Our work is predominantly focused on $TbPc_2$ due to its extremely attractive features, but the techniques we are developing will be general and transferable to other molecules and other qubits. The quantum chemistry methodologies and simulation codes we are developing will be tested, run, and adapted on one of the NERSC supercomputers for more efficient implementations for other large-scale correlated quantum systems.

In order to simulate the electronic structure of the relatively large and highly correlated character of the $TbPc_2$ molecule, we are developing methods which aim to achieve qualitative accuracy, while maintaining reasonable computational complexity. In this direction, we are exploring a combination of spin-flip (SF) methods with number changing electron-affinity (EA) methods to create a model chemistry which simultaneously addresses spin and Jahn-Teller-type degeneracies, which are present in the $TbPc_2$ complex. We will discuss preliminary results on test systems, focusing on an analysis of the importance of including orbital relaxing during the number changing excitations. We will also show preliminary results on neutral $TbPc_2$ in a gas phase, using different exchange-correlation functionals within DFT and using a multireference method such as CASSCF. This result will be used to develop the aforementioned new method.

To advance possible quantum information applications of devices based on the $TbPc_2$ molecule, it is imperative to achieve high-precision control of this system. In particular, single-qubit gates and entangling two-qubit gates are needed for universal quantum computation. One of the challenges in doing so involves the more complex spectrum of the molecule (featuring four energy levels instead of two) and the anisotropic nature of the hyperfine interaction, which will also introduce an anisotropic nature to the Jaynes-Cummings Hamiltonian (the coupling between each molecule and the resonator). We will discuss our preliminary results in designing single-qubit gates by incorporating coherent errors into our designs, and also present our vision of the multi-qubit system and its operation.

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

Postdocs: Daniel Claudino, Khadijeh Najafi

Students: Shannon Houck, Ryan Pederson, Fei Zhang

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

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

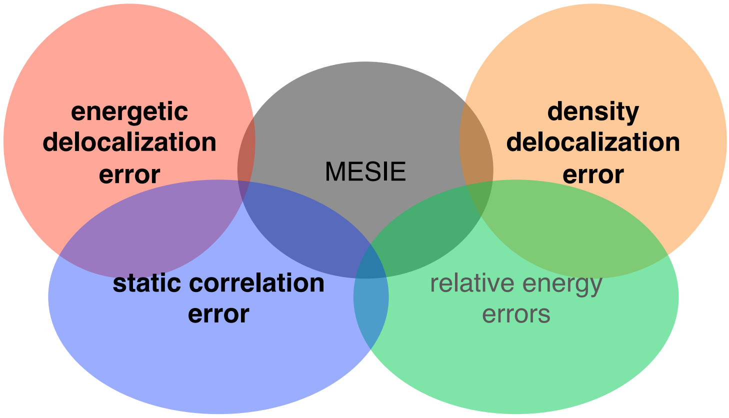

Figure 1. Range of coupled errors present in approximate density functional theory studied in this work.

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

i) We have examined how common approximations to recover the derivative discontinuity (i.e., DFT+U and global or range separated hybrids) affect the density properties of transition metal complexes and correlated solids in a counterintuitive manner with respect to near-exact, self-interaction-error-free references (i.e., multi-reference perturbation theory, CASPT2). Using real-space Bader charges, we have identified that across all octahedral inorganic complexes, regardless of ligand field strength and metal identity, oxidation state, or spin state, incorporation of Hartree-Fock (HF) exchange or inclusion of DFT+U universally localizes density away from the metal and onto ligand atoms. Such an observation runs counter to expectations about the nature of density errors in transition metal chemistry arising due to the uniquely localized orbitals of metal ions. We showed that altering the diffuseness of the surrounding ligand atoms does not change this trend. We then investigate trends in the solid state and instead observe divergent charge localization: consistent in hybrid tuning but periodic-table dependent trends are observed with DFT+U. Such an observation is critical owing to the frequent replacement of computationally demanding hybrid functionals with DFT+U in the solid state. Furthermore, we aimed to understand these

two differing conclusions by studying open-framework solids in which a molecular-like ligand field environment can be extracted (Figure 2). We observed that these solids behave similar to bulk transition metal oxides, but extraction of molecular complexes from these solids frozen in their solid-state geometries reverses solid-state trends. *These observations highlight that molecular analogues of solid-state crystal fields differ significantly, and methods demonstrated on molecules should not be expected to perform equivalently in the solid state.*

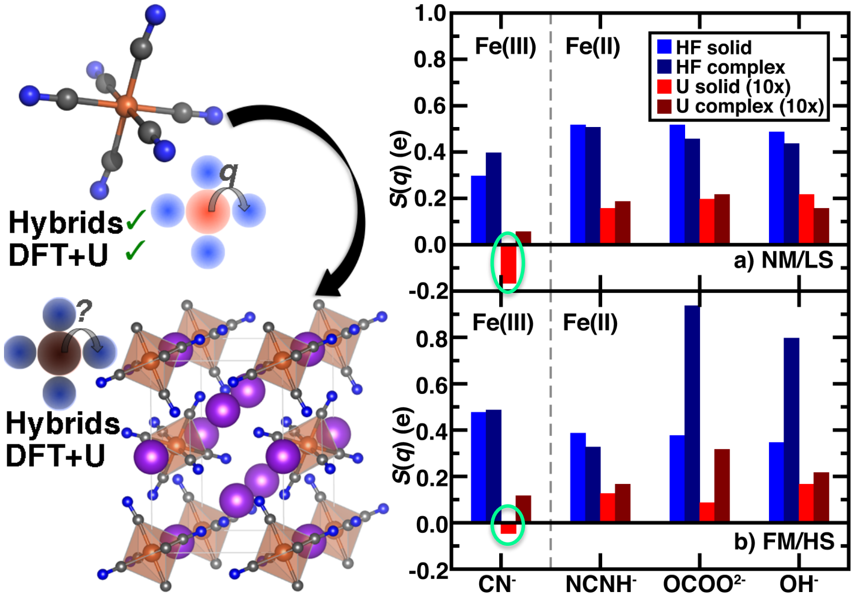

Figure 2. (Left) Example relationships for change in density properties with incorporation of exact exchange or DFT+U: consistent density accumulation on ligands (blue) and away from the metal (red) in molecules, but paradoxical behavior is observed in solids. (Right) Quantitative examples from open framework solids and extracted complexes, with paradoxical solid behavior circled in green.

ii) We demonstrate recovery of the flat-plane condition that is a union of the requirement of piecewise linearity with electron removal or addition as well as unchanged energy when changing the spin of an electron in isoenergetic orbitals. We accomplish this at no computational cost over semi-local DFT by building from scratch our judiciously-modified DFT (jmDFT) functionals designed to oppose errors inherent in semi-local functionals. Such an approach reduces fractional spin line errors (i.e., static correlation errors) while improving deviations from piecewise linearity at no computational cost (Figure 3). We show the connection to but divergence of these functional forms from hybrid expressions and standard DFT+U. This helps to explain why both common approximations increase static correlation errors. We also present fundamental expressions for determining these parameters, mitigating empiricism in the method. iii) Finally, we make efforts to overcome approximate DFT errors through the development of data-driven structure-method relationships, including in artificial neural networks that can predict sensitivity of spin-state ordering in transition metal complexes to changes in the exchange-correlation functional. These data-driven models have allowed us to design new spin crossover complexes in regions of chemical space where sensitivity to functional choice is lowest.

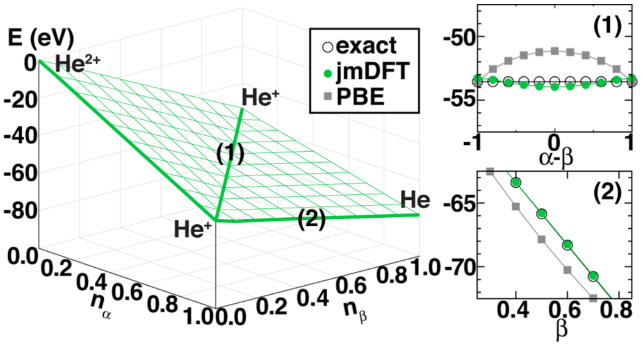

Figure 3. (Left) jmDFT energies annotated (1, fractional spin line or FSL and 2, the N to N+1 electron fractional charge line or FCL0) for insets on the right. (Right) The FSL (top) and FCL0 (bottom) for jmDFT (green circles), PBE (gray squares), and exact result (open circles), with the legend shown on the left.

Future Plans: We are developing accurate reference densities and constrained DFT functional forms that can allow us to selectively eliminate density or delocalization errors and measure baseline, residual errors in semi-local DFT functionals. We are also using these same tools to develop structure-method relationships and understand differences in functional performance across a range of chemical bonding environments in transition metal chemistry.

DE-SC-0018096: "Simultaneous mitigation of density and energy errors in approximate DFT for transition metal chemistry"
Postdoc: Fang Liu
Ph.D. Student: Akash Bajaj

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

1. A. Bajaj, J. P. Janet, and H. J. Kulik "Communication: Recovering the flat-plane condition in electronic structure theory at semi-local DFT cost", *Journal of Chemical Physics*, **147**, 191101 (2017). http://dx.doi.org/10.1063/1.5008981
2. Q. Zhao and H. J. Kulik "Where Does the Density Localize in the Solid State? Divergent Behavior for Hybrids and DFT+U", *Journal of Chemical Theory and Computation*, **14**, 670-683 (2018). http://dx.doi.org/10.1021/acs.jctc.7b01061
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3. J. P. Janet, L. Chan, and H. J. Kulik "Accelerating Chemical Discovery with Machine Learning: Simulated Evolution of Spin Crossover Complexes with an Artificial Neural Network", *The Journal of Physical Chemistry Letters,* **9**, 1064-1071 (2018). http://dx.doi.org/10.1021/acs.jpclett.8b00170
   Featured in Chemical & Engineering News February 19, 2018
   https://cen.acs.org/articles/96/i8/Machine-learning-identifies-potential-inorganic.html

Light-Induced Spin Trapping in Transition Metal Compounds

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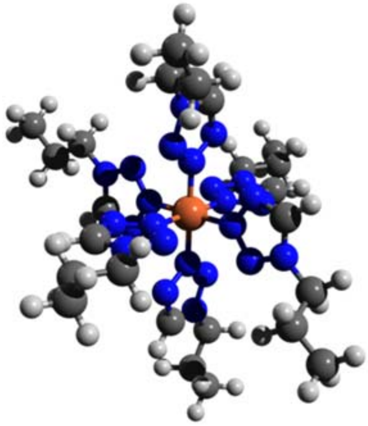
Spin-crossover (SCO) complexes can undergo a transition from a low-spin (LS) to a high-spin (HS) state and vice versa through irradiation with light, pressure or temperature changes. The most prominent SCO complexes contain Fe(II) metal ions connected to ligands through nitrogen atoms. LS and HS states of SCO compounds have strikingly different structural, magnetic, and electronic properties, and a controlled switching between these states is interesting for a multitude of applications in energy conversion, pressure-sensitive devices, data processing and information storage.



$[Fe^{II}(ptz)_6]^{2+}$ SCO complex

The theoretical study of SCO complexes has been hindered by the size and complexity of the compounds. Initial studies focused on density functional theory (DFT) as the only viable method, but with the development of more efficient algorithms in wavefunction based theories, and advances in computer architectures, SCO compounds can now also be studied using configuration interaction (CI) or complete active space (CAS) methodologies. Of all the different characteristics of SCO compounds, light-induced excited state spin trapping (LIESST) is of special interest due to its potential application in energy and information storage and conversion. In LIESST, a (typically octahedral) SCO compound is excited from the $^1A_1$ ground state into a metal to ligand charge transfer (MLCT) state by irradiation. From this state, the system can undergo intersystem crossing (ISC) to a triplet and through another ISC to the HS metastable $^5T_2$ state. The system is trapped in the HS state, since a direct conversion from HS to LS is only possible through tunneling; these metastable states can be very long-lived, with lifetimes of up to several days at low temperatures. Fe(II) compounds exhibiting LIESST are replacement candidates for the expensive Ru-based complexes in dye-sensitized solar cells.

In this project, advanced wave-function based methods such as CI are used to model several exemplary SCO compounds. CI methods are generally capable of a highly accurate description of SCO compounds, however the level of truncation, core-correlation effects and the quality of the electronic basis largely influence the level of accuracy. We have recently devised a routine by which the convergence of the CI wave function can be estimated, based on its representation in length and velocity gauge[1]. One advantage of CI methods is that they can be improved systematically, and that the inclusion of spin-orbit coupling (SOC) is fairly straightforward through the Breit-Pauli spin orbit coupling (SOC) Hamiltonian as in standard SO-CI (spin-orbit CI) implementations. So far, we have addressed the project from different angles. Several Fe(II) compounds have been optimized using DFT methods, to obtain a good structure for the subsequent SO-CI calculations. As starting point, $[Fe(CN)_6]^{4-}$, $[Fe(NH_3)_6]^{2+}$, $[Fe[bpy]_3]^{2+}$ (bpy – bipyridyl), and the largest compound, $[Fe(ptz)_6]^{2+}$ (ptz – propyl-tetrazol), have been selected, as these exhibit energetic differences of varying degree between LS and HS. The compounds have been optimized in the LS and HS spin states, using the TPSS functional and with basis sets up to the TZVP basis set. We have implemented the time-dependent SO-CI method (TD-SOCI) into our in-home time-dependent CI (TDCI) program. As test cases, we have selected several small molecules, such as LiH, CO^{2+}, and $Fe^{II}CO$ that exhibit varying strengths of SOC. For the implementation, modifications to the GAMESS-US program package were required to obtain not only the CI wave function and integrals, but also the SOC Hamiltonian. The TD-SOCI calculation is carried out in the spin-mixed SOC eigenfunctions, while a transformation to the spin-pure CI eigenstates is possible at all times. During the propagation, not only the population of SO-CI and CI states, but also of configuration state functions (CSFs) and molecular orbitals (MOs) are being monitored. With this information, (de-)excitation pathways upon irradiation with light are obtained, and electronic charge density and flux can be calculated at all time steps. We are currently connecting our TD-(SO)CI code to a program that generates such current maps (detCI/ORBKIT). Furthermore, we have nearly completed a manuscript in which the TD-SOCI method is described and applied[2].

Building upon our recent progress, we will apply the TD-SOCI to the larger Fe(II) compounds, and investigate how the spin trapping in these compounds is triggered. (De-)Excitation pathways, time-dependent populations of spin-mixed and spin-pure states, and lifetimes/transition rates will be obtained. We are extending the TD-SOCI methodology to a reduced density matrix representation, in which effects of the environment such as spontaneous emission, and the presence of a solvent or a metallic surface influence the electronic pathways. In the final phase, a set of design parameters is being developed which will aid the experimental design of promising SCO candidates.

[1] Inga S. Ulusoy, Zachary Stewart, Angela K. Wilson, "The Role of the CI Expansion Length in Time-Dependent Studies", *J. Chem. Phys.* **148**, 014107 (2018)
[2] Inga S. Ulusoy, Angela K. Wilson, "Time-Dependent Configuration Interaction for Multiple Spin States", *to be submitted*

DE-SC0017889, "Light-Induced Spin Trapping in Transition Metal Compounds"

Student: Zachary J. Stewart

Barry D. Dunietz

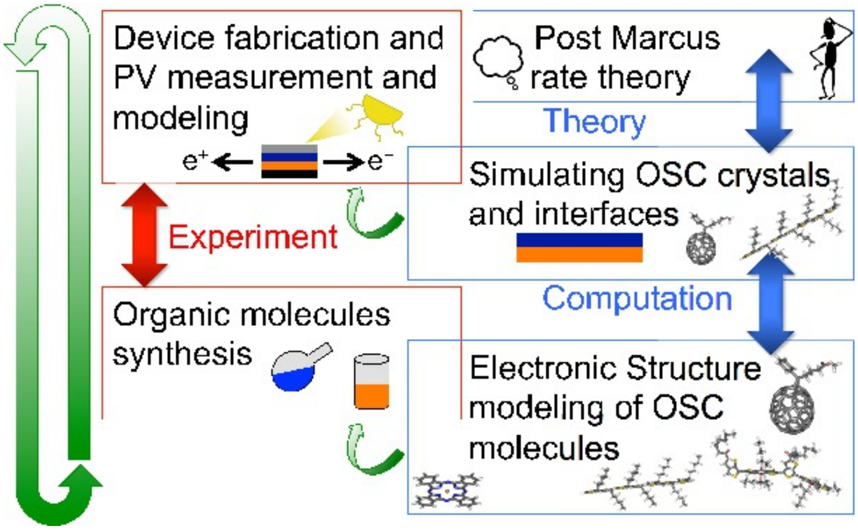
Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials

Margaret Cheung, Barry D. Dunietz, Eitan Geva
University of Houston, TX; Kent State University, OH; University of Michigan, MI

Abstract

The goal of the research program is to understand charge transfer (CT) and transpprt processes, which is key to improve alternative energy applications. In particular we are concerned with CT across interfaces related to organic photqovoltaics systems. We develop a transformative computational scheme, where we do not resort to otherwise widely used simplifications to achieve realistic descriptions of CT processes. We provide unique insight, where the molecular environment is properly addressed and that will benefit relevant experimental efforts.

Since the underlying challenges are substantial we pursue a comprehensive approach based on diverse expertise. Our collaboration brings together three principal investigators with expertise in molecular dynamics simulations (Cheung), electronic structure calculations (Dunietz), and quantum dynamics theories of the condensed phase (Geva).



We first introduce our comprehensive approach to calculate of photoinduced electron transfer and transport kinetics and benchmark against available measurements. We then use our approach to gain unique insight on OPV-related processes. We will also describe our studies of a large molecular triad demonstrating the effect of conformational flexibility on photoinduced charge transfer. We also present a novel density functional that combined screended range separated DFT with polarized continuum model in a fully consistent fashion and which is shown to achieve highly accurate orbital gaps and optical and CT excitation energies.

In particular the triad system is used to demonstrate our linearized semi-classical approach that opens the door to develop a hierarchy of methodologies of a range of approximations with a semi-classical limit (Marcus approach) to a Fermi-Golden rule level where the molecular environment is represented using molecular dynamics simulations. Our approach combines all-atom molecular dynamics simulations with an 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 constants, is established by comparing the rate constants calculated with and without resorting to this approximation.

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

Student(s): Srijana Bhandari

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

- A Computational Study of Charge Transfer Dynamics in The Carotenoid-Porphyrin-C60 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.* **Just Accepted** (2018).

- A Comparative Study of Different Methods for Calculating Electronic Transition Rates
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- Ultrafast Charge-Transfer Dynamics at the Boron Subphthalocyanine Chloride/C60 Heterojunction: Comparison between Experiment and Theory

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- Charge-transfer rate constants in Zinc-Porphyrin-Porphyrin-derived dyads: A Fermi golden rule first-principles-based study
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- Molecular structure, spectroscopy and photo induced kinetics in tri-nuclear cyanide bridged complex in solution: A first principle perspective
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A Polarizable Frozen-Density Embedding Method for Excited States

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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.

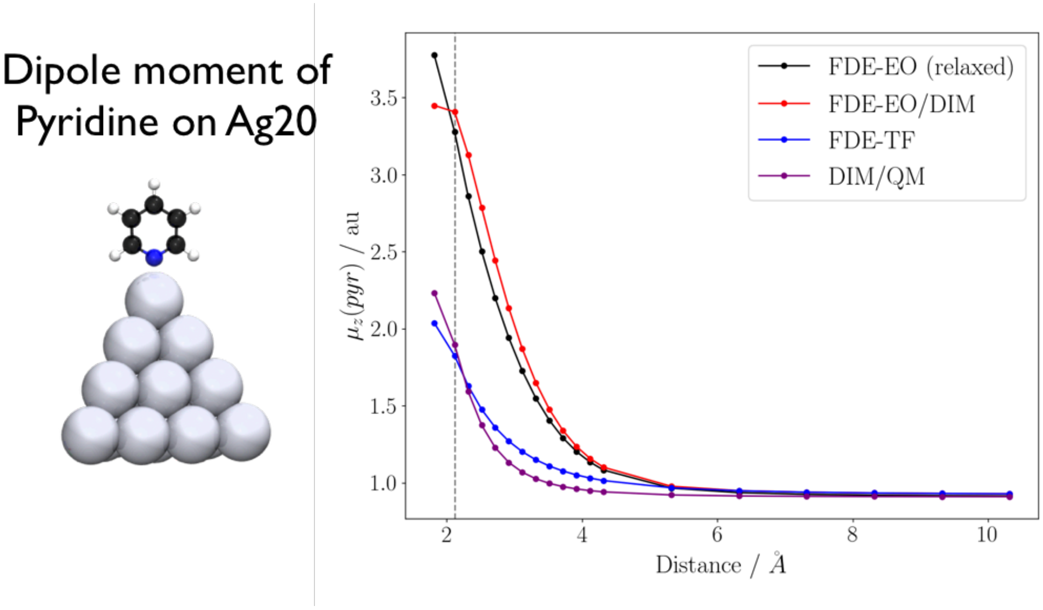

Fig 1: Dipole moment of pyridine on a small silver cluster as calculated using several different embedding methods.

Recent progress

We have developed a polarizable frozen-density embedding (FDE) method for describing molecules adsorbed on metal clusters. The FDE method incorporates external orthogonality (EO) through the use of a level-shift projection operator to avoid the non-additive kinetic energy functional (KEDF). This is essential as current KEDFs tend to fail drastically for strongly overlapping systems. However, the FDE-EO method is computational very expensive due to freeze-and-thaw cycles needed for the method to reproduce the super-molecular DFT results. However, FDE-EO constitutes an exact embedding method at the DFT level of theory and thus can be used to benchmark the quality of approximate embedding methods. We have found that the expensive freeze-and-thaw cycles needed in the FDE-EO method can largely be eliminated through polarization embedding (DIM). The method is found to reproduce the ground-state density and dipole moment of small molecules interacting with metal clusters. For these systems there is significant charge-transfer between the molecule and the surface and thus represents a challenge for embedding methods. This is illustrated in Fig. 1 where we plot the dipole moment of pyridine interaction with an Ag20 cluster. FDE-EO/DIM is shown to reproduce the fully relaxed FDE-EO result. Current efforts are focused on extending the FDE-EO/DIM method to describe excited states of molecules using time-dependent density functional theory (TDDFT). FDE-EO has been extended to TDDFT and thus can serve as a benchmark for FDE-EO/DIM.

Grant Numbers and Grant Titles

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

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

N/A

Kevin L. Shuford

Electronic and Optical Properties of (4,8) Boron-Group V Nanosheets

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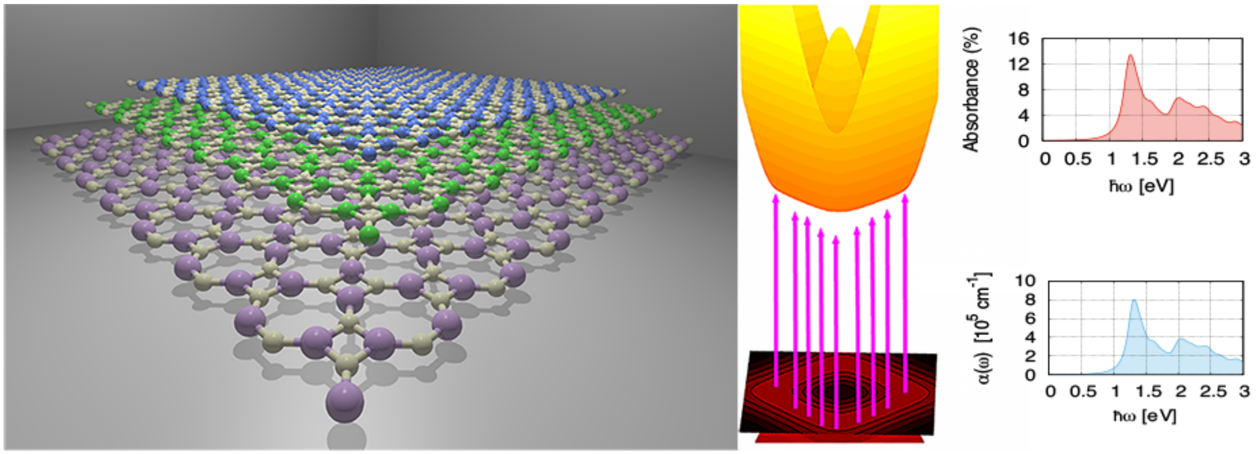
Abstract

The ascendancy of ultrathin films has emerged as a boon for 21st century nanotechnologies that rely on flexibility, tunable properties, and active surface area. We explore uncharted configurations with (4,8) lattice tessellations that exhibit exceptional light–matter interactions. We find that planar monolayers of boron-pnictogen binary materials possess strong interband absorbance and absorption coefficients that rival existing ultrathin films. These observables were found to occur in the ultraviolet for the boron-nitride nanosheet and in the infrared region of the electromagnetic spectrum for heavier pnictogens, suggesting a route for photocapture of high density solar photons. Moreover, we find the buckled boron arsenide supports a similar, yet slightly decreased, optical response that is blue-shifted from its planar configuration. The strong optical response of these ultrathin films emerges from their unique bandstructures, localization of π-electrons in the ground state, Van Hove singularities at band extrema, and complementary elemental properties. Consequently, the (4,8) motif demonstrates that many 2D films with distinctly different lattice tessellations from that of established ultrathin materials could have a significant impact on the field.



Theoretical Studies of Photovoltaic Interfaces (Grant Number DE-SC0010212)

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Postdoc(s): Alessia Polemi, Chengyong Xu, Olga Samoylova
Student(s): Paul A. Brown, Andrew G. Smith, Emvia I. Calixte

Program Scope: An overarching project goal is to determine how energy and charge move through material assemblies, such as those composed of wide bandgap semiconductors, strongly absorbing dye molecules, and plasmonic nanoparticles. The former two are relevant for current photovoltaic devices and the latter are known to have unique optical properties resulting from surface plasmon excitations. We want to determine the extent metal plasmon modes can be utilized to enhance chemical/physical processes at material interfaces relevant for photovoltaics, optoelectronics, and catalysis.

Recent Progress: We have made significant progress toward achieving this goal. Energy and charge transfer in multicomponent nanomaterials have been investigated using a variety of modeling and simulation techniques, including classical electrodynamics, density functional theory, and classical molecular dynamics. Our previous studies examined the electronic properties of a several different two-dimensional materials upon selective doping, molecular surface adsorption and application of mechanical strain. All of these stimuli alter the bonding structure at the interface and provide an avenue toward controlling the properties of these materials. This inspired us to explore the role that unusual lattice arrangements play in dictating electronic structure. In particular, we have examined ultrathin nanosheets with a (4,8)-tessellation composed of Boron and Group-V elements. This combination results in unique electronic properties and strong optical response at frequencies relevant for solar applications. We also studied the electronic effects of heteroatom substitution in the π-bridge of donor-π-acceptor organic sensitizer molecules. Lastly, we completed related studies on selective ion transport in functionalized carbon nanotubes and optical properties of multicomponent, asymmetric nanocrescents, which resulted in recent publications.

Publications Acknowledging this Grant in the Last 4 Years

1. Paul A. Brown and Kevin L. Shuford, "Exceptional Optical Response of Archimedean Boron and Group-V Ultrathin Nanosheets," J. Phys. Chem. C **121**, 24489-24494 (2017).
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6. Chengyong Xu, Paul A. Brown, and Kevin L. Shuford, "Strain-Induced Semiconductor-to-Semimetal Phase Transition and Indirect-to-Direct Band Gap Transition in Monolayer 1T-TiS_2: A First-Principles Study," RSC Adv. **5**, 83876-83879 (2015).

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Advanced Molecular Electronic Structure Methods for Exciton and Spin Dynamics

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Program Scope and Definition:

The objective of this research program is to develop fundamentally novel electronic structure theory that accurately describes dynamical processes in molecules and materials, such as exciton dynamics in organic semiconductors and spin dynamics in inorganic molecules and magnetic materials. Our approach is based on the so-called **active space decomposition (ASD)**, the theory that we have developed under the sole support by the DOE CTC program in the previous funding period. The ASD method compresses many-body wave functions into a sum of products of fragment wave functions, allowing us to apply multireference electronic structure theory to systems of unprecedented size. In addition, using ASD, one can obtain the diabatic model Hamiltonians for such dynamical processes. We have demonstrated the applicability of the method by partially addressing the mechanistic questions on the so-called singlet-fission dynamics, which is relevant to next-generation photovoltaics. Furthermore, we have shown that the ASD method has an interesting connection to tensor-network methods in condensed matter physics; it has been demonstrated that the ASD method can benefit from the density matrix renormalization group (DMRG) algorithm for optimizing the wave functions for linear chains of chromophores (or chemical units).

In this funding period, we seek to generalize the theory to higher-order tensor networks states to allow for simulating, for instance, chemical dynamics in two-dimensional networks such as organic crystals and porous magnets.

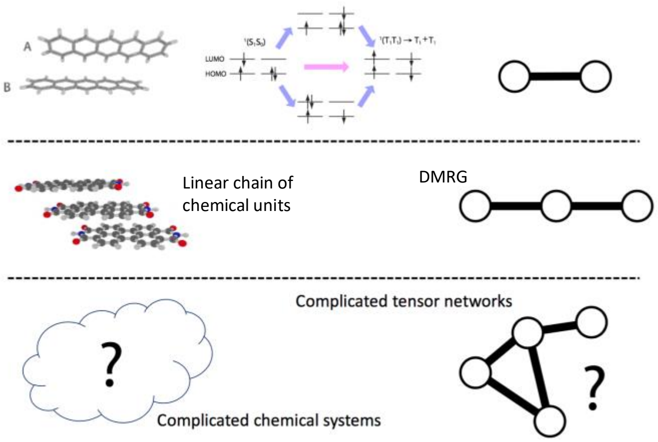

Figure 1: Relationship between chemical systems and tensor network states revealed by ASD.

Recent Progress: Efficient optimization of PEPS wave functions

In the past year, we have made several important progresses in realizing ASD with higher-order tensor network states. As a first step in this direction, we have developed an efficient and stable algorithm for solving finite projected entangled pair states (PEPS) problems. It has long been recognized in the condensed matter physics community that optimization of higher-dimensional tensor networks, such as PEPS, is numerically unstable because of the existence of the gauge degrees of freedom, which is inherent in the non-linear wave function ansätze. Even the optimization of PEPS wave functions for finite Hubbard models has never been performed prior to this research, mainly owing to numerical and algorithmic complexities.

D	3 × 5	4 × 4
4	−6.015	−6.601
6	−6.177	−6.710
7	−6.220	−6.779
9	−6.233	−6.788
Exact	−6.247	−6.808

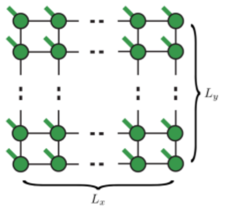

Figure 2: Preliminary results for application of PEPS to the finite Hubbard model with open boundary conditions.

To address this challenge, we developed a way to numerically stabilize the PEPS solver by introducing the 'quasi-normalized' tensor networks. In addition, we showed that the fermionization of the PEPS wave functions leads to efficient optimization. The results for small finite Hubbard lattice (U/t = 8) is shown in Figure 2. Currently we are working on further improving the algorithm in terms of computational efficiency and convergence behavior. We will then use this algorithm in conjunction with the ASD methodology to realize, for the first time, the application of PEPS in first principles simulations.

Program development:

We have been developing an electronic structure program package BAGEL under the support by this DOE program. BAGEL is a full-fledged package designed for modern parallel computer hardware. It implements various advanced multireference electronic structure theory including those described above. The source code is distributed under the GNU General Public License Version 3+ and openly available to fellow theoretical chemists and end users at http://www.nubakery.org. The initial official release was in September 2017, and since then, we have attracted more than 20 research groups worldwide as users (the number is based on private communications; it may be larger because it is hard to track who is using our software)

Grant Number and Grant Title

DE-SC0010265 Advanced Molecular Electronic Structure Methods for Exciton and Spin Dynamics

Postdoc(s) supported: n/a

Student(s) supported: Jheng-Wei Li and Yiqun Wang (2017–2018)

Currently actively recruiting a student or a postdoc to fill in the position.

Publications Acknowledging these Grant:

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

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

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BAGEL: Brilliantly Advanced General Electronic-structure Library. http://www.nubakery.org under the GNU General Public License. The user manual is available now.

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Electron and Electron-Nuclear Dynamics of Open Quantum Subsystems

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Abstract

Leveraging an open-subsystem formulation of Density Functional Theory (DFT) we aim at describing periodic and molecular systems alike, including their electronic and nuclear dynamics. Subsystem DFT enables first principles simulations to approach realistic time- and length-scales, and most importantly sheds light on the dynamical behavior of complex systems. Taking subsystem DFT to the time domain allows us to inspect the electron dynamics of condensed-phase systems in real time. In liquids and interfaces, we observe all the relevant regimes proper of non-Markovian open quantum system dynamics, such as electronic energy transfer, and screening. In addition, the *ab-initio* modeling of system-bath interactions brought us to observe and justify the holographic time-dependent electron density theorem. Contrary to interactions between molecular (finite) systems, when molecules interact with metal or semiconductor surfaces the electron dynamics is strongly non-Markovian with dramatic repercussions to the molecule's response to external perturbations. Metals and semiconductors typically have large polarizabilities, and even in a regime of low coupling their effect on impinging molecular species is significant–line broadening, peak shift, and intensity borrowing are observed, characterized, and explained in terms of inter-subsystem dynamical interactions and a many-body decomposition of the system's density-density response function in a way that transcends the canons of Fermi Golden Rule.

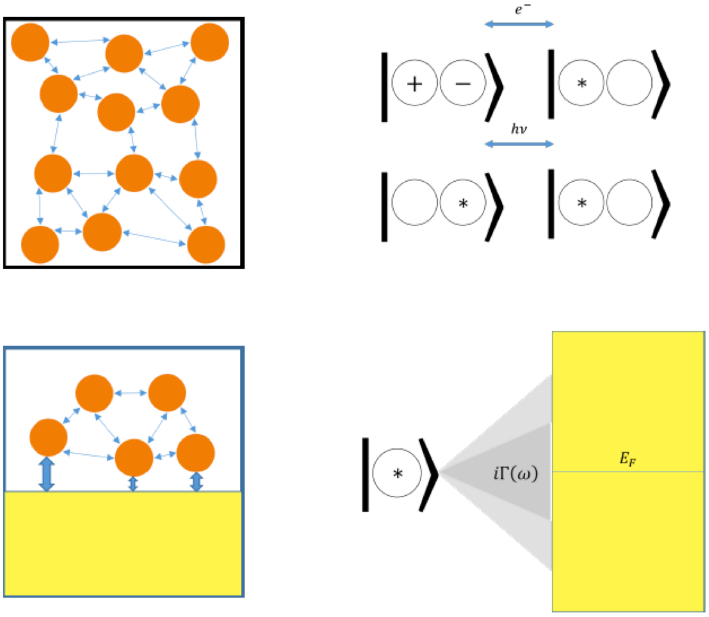

Figure 1: Open subsystems and their interactions. Upper left: collection of molecular subsystems; upper right: typical avenues of exchange of energy and electrons between open subsystems; lower left: interface between a set of molecular subsystems and an extended subsystem; lower right: depiction of the coupling between a finite subsystem having a discrete energy spectrum and an extended system having a dense energy spectrum.

To approach the nonadiabatic dynamics of condensed-phase systems, our research has focused on finding methods for computing excited states that are as balanced as possible with ground state calculations and that can be seamlessly extended to a subsystem formulation. Along this avenue, and exploiting the machinery of Constrained Density Functional Theory, we have recently proposed [3] a variational method for calculating low-lying excited states of molecular systems which we dub eXcited Constrained DFT (XCDFT). Excited states are obtained by self-consistently constraining a user-defined population of electrons, N_c, in the virtual space of a reference set of occupied orbitals. By imposing this population to be $N_c = 1$, we computed the first excited state of 15 molecules from a test set. Our results show that XCDFT achieves an accuracy in the predicted excitation energy only slightly worse than linear-response time-dependent DFT (TDDFT), but without incurring into problems of variational collapse typical of the more commonly adopted ΔSCF method. In addition, we selected a few challenging processes to test the limits of applicability of XCDFT. We find that in contrast to TDDFT, XCDFT is capable of reproducing energy surfaces featuring conical intersections (azobenzene and H_3) with correct topology and correct overall energetics also away from the intersection. Venturing to condensed-phase systems, XCDFT reproduces the TDDFT solvatochromic shift of benzaldehyde when it is embedded by a cluster of water molecules.

Future developments will involve implementation of Ehrenfest dynamics in a subsystem real-time TDDFT software that is currently developed by the PI and maintained by the students and postdocs supported by this grant. Additionally to the Ehrenfest dynamics, we plan to explore way of coupling subsystem TDDFT with time-dependent Thomas-Fermi theory for metal surfaces. We expect the latter to yield fast and still accurate models of the dynamics of molecule-metal interfaces which is still largely uncharted due to the large computational cost of modeling the metallic system.

Grant Number: DE-SC0018343.

Students: Sudheer Kumar P. (graduate student)

Postdoc: Dr. Pablo Ramos

Publications Acknowledging the Grant

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

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

3. Alina Umerbekova, Shou-Feng Zhang, Sudheer Kumar P. and Michele Pavanello
   Dissecting Energy Level Renormalization and Polarizability Enhancement of Molecules at Surfaces with Subsystem TDDFT
   Eur. Phys. J. B, submitted, Hardy Gross special issue (2018)

4. Johannes Tolle, Andre Gomes, Pablo Ramos and Michele Pavanello
   Charged-cell Periodic DFT Simulations Via an Impurity Model Based on Density Embedding: Application to the ionization potential of liquid water
   Int. J. Quantum Chem., submitted, Advances in Simulating Solvation special issue (2018)

Electron and Electron-Nuclear Dynamics in Gold and Silver Nanoparticles

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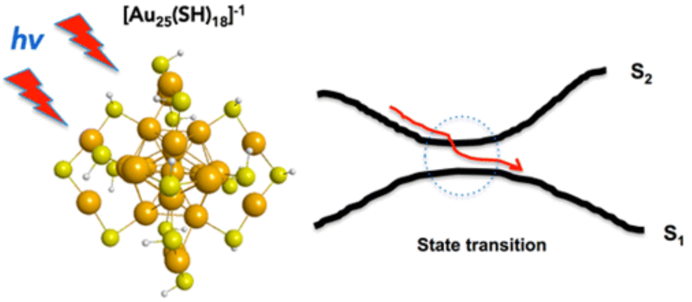
Abstract

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.

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. The presence of the silver nanoparticle enhances excitation into the antibonding orbital of N_2.

Recently, thiolate-stabilized gold nanoparticles with 1-2 nm diameters have been employed to yield increased photocatalytic efficiencies in metal-semiconductor composite materials. However, very little is known yet about the changes that occur within a nanoparticle upon photoexcitation. In this work, photoexcitation in the $Au_{25}(SR)_{18}^-$, $Au_{38}(SR)_{24}$, and $Au_{18}(SR)_{14}$ nanoparticles has been examined using time-dependent density functional theory methods. Nonadiabatic (NA) calculations on the $Au_{25}(SH)_{18}^-$ nanoparticle (shown at right) have been performed, and the time scales for electron dynamics are in good agreement with experiment. Recently, NA calculations on $Au_{25}(SR)_{18}^-$ (SR = SCH_3, SCH_2CH_3, and MPA (mercaptopropionic acid)) have also been computed, and small differences in the time scales for the observed electron dynamics are observed for MPA. Relaxation mechanisms are found to involve semiring-to-core charge transfer excitations for $Au_{18}(SR)_{14}$, whereas $Au_{25}(SR)_{18}^-$ and $Au_{38}(SR)_{24}$ involve core-to-core processes.



Geometrical relaxation in the excited states of the $Au_{25}(SR)_{18}^-$ nanoparticle have been determined to be responsible for the large Stokes shift observed for this system. Similar geometrical and electronic changes are also predicted for other nanoparticles including $Au_{22}(SR)_{16}$ and $Au_{38}(SR)_{24}$. Of the systems examined in this work, the $Au_{22}(SR)_{16}$ nanoparticle has the largest degree of structural flexibility and the largest Stokes shifts. This nanoparticle is known to have the strongest luminescence quantum yields. Poor spatial overlap between the occupied and unoccupied orbitals are suggested to contribute to its quantum yield. In contrast, the $Au_{38}(SR)_{24}$ system has small geometrical changes that result in a small Stokes shift.

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

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

Publications

- Theoretical Investigation of Relaxation Dynamics in $Au_{38}(SH)_{24}$ Thiolate-Protected Gold Nanocluster. R. D. Senanayake, E. B. Guidez, A. J. Neukirch, O. V. Prezhdo, C. M. Aikens, submitted to *J. Phys. Chem. C*
- Anisotropic Polarizability Induced Plasmon Transfer. G. Donati, D. B. Lingerfelt, C. M. Aikens, X. Li, submitted to *J. Phys. Chem. C*
- Molecular Vibration Induced Plasmon Decay. G. Donati, D. B. Lingerfelt, C. M. Aikens, X. Li, *J. Phys. Chem. C*, **2017**, *121*, 15368-15374.
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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.

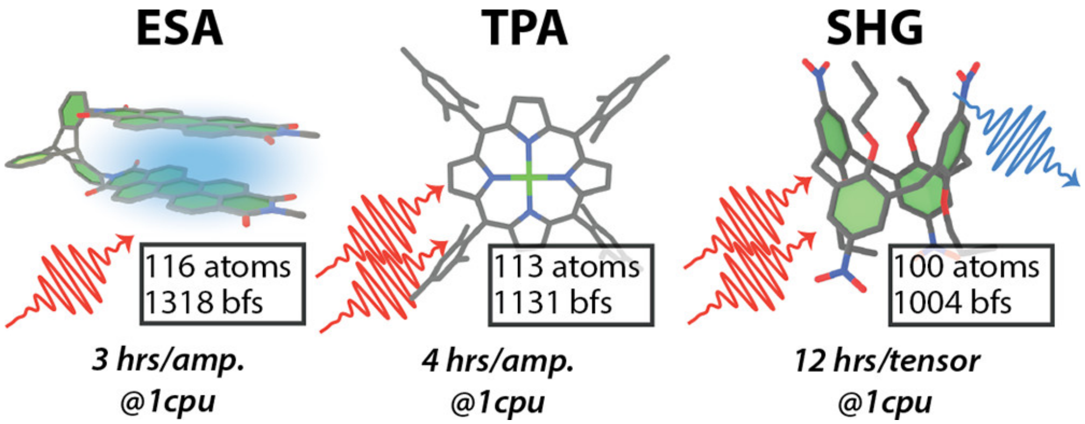

Figure 1: Typical resource requirements for TDDFT quadratic response calculations on perylene diimide dimers, twisted porphyrin and octupolar calix[4]arene systems using the PBE0 hybrid functional [1].

With previous DOE support, we devised, built, and deployed the first general-purpose NAMD implementation using time-dependent hybrid density functional theory (TDDFT) [2] during the past five years. This enabled the identification of nonadiabatic effects in acetaldehyde photodissociation [3] and elucidation of the mechanism of excited-state photocatalytic reactivity in TiO_2 nanoclusters[4]. However, our work also revealed spectacular unphysical divergences in conventional time-dependent response theory underlying most present-day excited-state computations [5, 6]. A key goal of the current project is to developed orbital-optimized ensemble TDDFT (oe-TDDFT) approach to address key remaining limitations in excited-state methodology: (i) Remove the need for divergent orbital-relaxation contributions in response theory; (ii) reduce self-interaction error without constructing new functionals; (iii) correctly describe conical intersections between all states with non-zero ensemble weight with correct dimensionality; (iv) retain computational efficiency to enable resource-efficient NAMD simulations for systems with 50-100 atoms on a single compute node. We further aim to develop a consistent approach to tackle fast intersystem crossing in NAMD simulations by including spin-orbit coupling (SOC) into our methods.

After the start of the new funding period in September 2017, we completed an implementation of quadratic response properties in the hybrid TDDFT framework [1], including static and dynamic dipole hyperpolarizabilities, ground-to-excited-state two-photon absorption amplitudes (through a single residue) and state-to-state one-photon absorption amplitudes (through a double residue). We showed that excited-state absorption spectra computed within the pseudowavefunction approach contain the qualitative features of transient absorption spectra tracking excimer formation in perylene diimide dimers, two-photon absorption cross sections for a series of highly twisted fused porphyrin chains are semiquantitatively reproduced, and the computed dynamic hyperpolarizability of several calix[4]arene stereoisomers yield simulated hyper-Raleigh scattering signals consistent with experiment. In addition, we were able to demonstrate the impact of the incorrect pole structure of adiabatic TDDFT response properties on excited-state absorption spectra and hyperpolarizabilities for experimentally relevant systems.

Taking a first important step towards oe-TDDFT, we gathered theoretical and numerical evidence that the ensemble extension of ground-state density functional theory correctly describes conical intersections between nearly degenerate ground and excited states. In addition, we completed an illustrative application of our methodology to light-activated *in vivo* chemical probes of nucleobase solvent accessibility [7].

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: Mikko Muuronen, Shane M. Parker, Gregory D. Bellchambers, Enrico Tapavicza
Graduate Students: Luke Nambi Mohanam, Saswata Roy, Jordan C. Vincent, Brandon T. Krull
Undergraduate Students: Alan Robledo, Jake Kwon, Alexander Le, Jason M. Yu, Brian D. Nguyen, Kirk C. Pearce

Publications (out of 16)

[1] S. M. Parker, D. Rappoport, and F. Furche: Quadratic Response Properties from TDDFT: Trials and Tribulations, *J. Chem. Theory Comput.* **14**, 807–819, 2018.

[2] E. Tapavicza, G. D. Bellchambers, J. C. Vincent, and F. Furche: Ab initio non-adiabatic molecular dynamics, *Phys. Chem. Chem. Phys.* **15**, 18336–18348, 2013.

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[6] S. M. Parker and F. Furche: Response Theory and Molecular Properties, in B. Kirtman, H. Nakatsuji, Y. Osaki, and M. Wójcik, editors, Frontiers of Quantum Chemistry, pp. 69–86, Springer, Tokyo, 2018.

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Abdelkader Kara

Interface characteristics of organic molecules on metal surfaces

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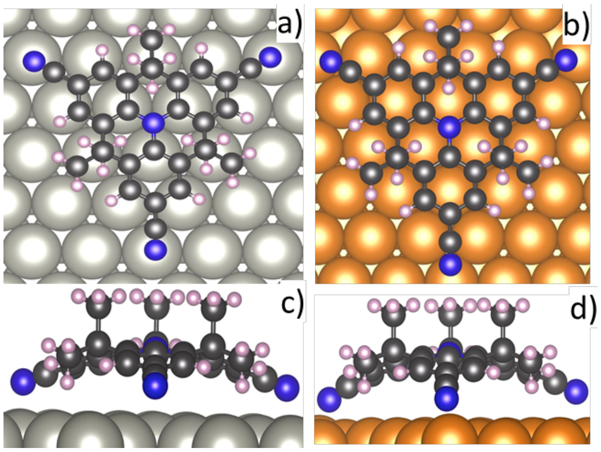
Abstract

We have investigated extensively the role of van der Waals (vdWs) interactions, when incorporated self-consistently into density functional theory (DFT). Our previous investigations followed two avenues: 1) 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. For example, we have showed that the inclusion of vdWs interactions, the nature of bonding of an olympicene molecule on Cu(111) changes from being week physisorption to strong chemisorption, upon self-consistent inclusion of the vdWs interactions. This was later proven to be true for other experimentally investigated large molecules.

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

1) Cyano-Functionalized Triarylamines on Coinage Metal Surfaces



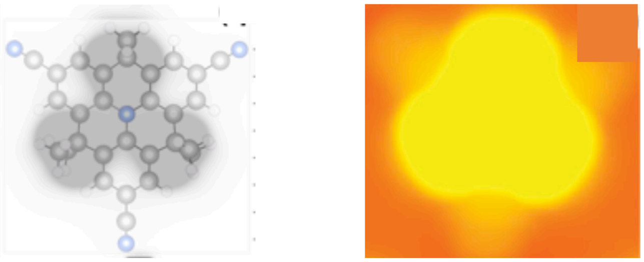


Fig. 1 On the left side: most stable adsorption configurations on Ag(111) (a, c) and Cu(111) (b, d). The side views (c, d) show the strong arching of **1**. Colour code: light grey: Ag, orange: Cu, blue: N, dark grey: C, white: H. On the right side: calculated and observed STM images.

The self-assembly of a cyano-functionalized triarylamine on Cu(111), Ag(111) and Au(111) was studied by means of scanning tunnelling microscopy, low-energy electron diffraction, x-ray photoelectron spectroscopy and density functional theory calculations, including non-local effects. Different bonding motifs like antiparallel dipolar coupling, hydrogen bonding and metal-coordination were observed. In contrast to Ag(111) and Au(111) where huge islands are formed, only small patches of a hexagonally close-packed network stabilized by metal coordination and a disordered arrangement are present on Cu(111). The remarkable differences can be explained by the subtle interplay between intermolecular and molecule-substrate interactions as well as by the different molecular mobility on the coinage metal surfaces. We found that inclusion of van der Waals interactions changed the nature of bonding from week physisorption to chemisorption. Not only the binding energy increased by an order of magnitude, but the overall shape of the adsorbed molecule changed substantially from the otherwise flat molecule, as can be seen in Fig.1.

2) Growth of dihydrotetraazapentacene on Cu(110)

The growth of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) deposited on Cu(110) has been investigated at different temperatures by the means of scanning tunneling microscopy (STM), low-energy diffraction (LEED) and DFT calculations using van der Waals interactions. We find three different ordered structures, which commensurate with the substrate corresponding to supercells in the matrix notation of (6 -1 | 1 2), (7 0 | 1 2), and (6 0 | 1 2), respectively. Simulations of the LEED patterns observed and density functional theory (DFT) calculations confirm the assigned of the observed structures (see Fig.2). Moreover, we conclude that DHTAP molecules are chemisorbed on the surface via Cu-N bonds. The three configurations correspond to three different coverages. As the coverage increases, the shape of the molecule changes.

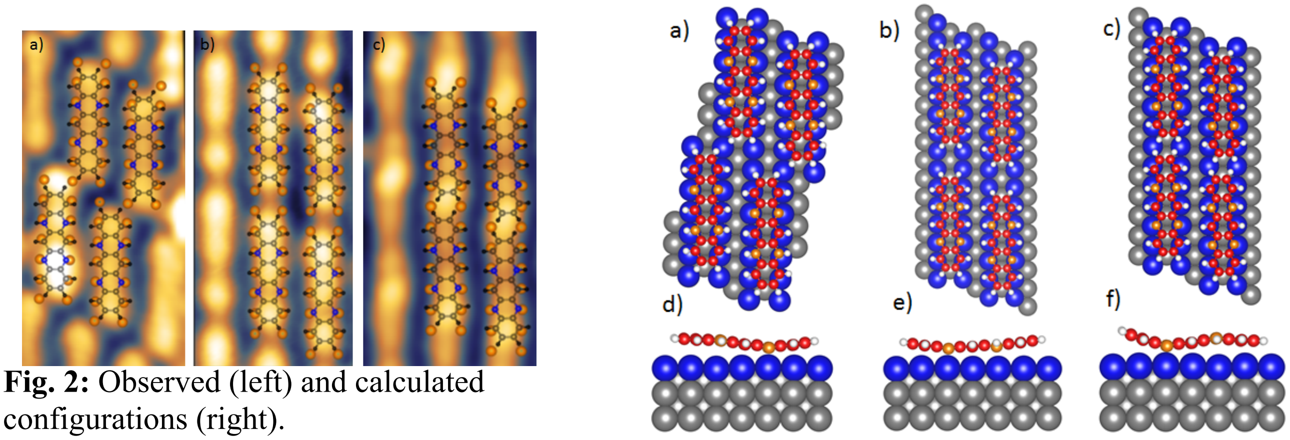


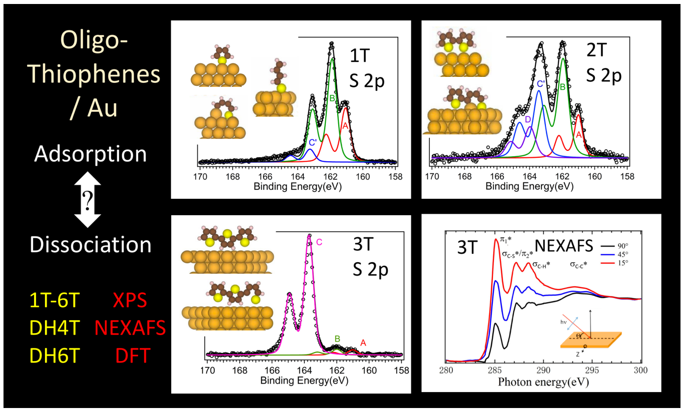
Fig. 2: Observed (left) and calculated configurations (right).

The above examples show that the inclusion of van der Waals effects brings the molecule closer to the surface resulting in a strong binding, which in turn induces strong distortions.

The excellent agreement between calculations and experiments is not always quantitative, especially when comparisons involve synchrotron measurements. The next example shows a qualitative agreement between the experimental data and the calculations, in the sense that the simulations “point” in the same directions as the experiment, but no quantitative agreement was possible. Here the measured quantity is the core level binding energy (X-ray Photo-electron Spectroscopy), for which large discrepancies are found when comparing absolute values of measured and calculated energies. This is an area that will need more improvement in the computational approach.

3) Thiophene Derivatives on Gold and Molecular Dissociation Processes

Adsorption of thiophene derivatives on gold surfaces is studied both experimentally and computationally. These molecules are of interest in molecular electronics, but some experiments indicated S-C bond scission in contact with metals.



We explored this dissociation aspect by photoemission for the case of monocrystalline Au(111) surfaces for a series of polythiophenes molecules (nT, n=1-4, 6). The S2p X ray photoelectron spectroscopy (XPS) peaks are found to have complex line shapes corresponding to S atoms with different core level binding energies (CLBE). Density functional theory calculations of adsorption energies and CLBEs were performed for various adsorption configurations of thiophene on a perfect Au(111) plane and for comparison, calculations were also performed for bithiophene, terthiophene, alkenethiol, alkenethiol chain and a broken thiophene related metallocycle, incorporating an Au adatom and an S atom. Based on these results we relate the different contributions to the S2p peak to intact molecules on different adsorption sites and broken molecules. Calculations in particular show that the CLBE's for intact thiophene (1T) can be the same as for the alkene and alkane thiol cases as opposed to usual assumption in the literature.

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. Preliminary results show that for the molecule HOMO-LUMO gap show that the SCAN approach brings a substantial improvement over GGA (PBE), which is in accord with previous accounts of the meta-GGA. We anticipate that the meta-GGA will bring improvements for the over-all electronic characteristics of the interface between organic molecules and metal surfaces. Of special interest is the charge transfer as it involves the un-occupied state or the LUMO of the molecule. An improved determination of these quantities will results in a better account of the charge transfer.

Our preliminary results show that the relaxed adsorption geometries resulting from SCAN and SCAN+rVV10 are very close to those resulting from the optB88 calculations. However, the overall cost of performing calculations at the SCAN level can be between 2 to 8 times more expensive than those of optB88. First, a single electronic loop can be 2 to 4 times more expensive for SCAN than optB88 (this depends on the system at hand). In addition, the ratio of the number of ionic loops (SCAN/optB88) can vary from 1 to 3 (or more is some cases). Since we have found, for the so far studied systems, that SCAN and optB88 yield similar relaxed atomic configurations, we have explored the idea of starting SCAN calculations using the relaxed optB88 configurations. The gain in the calculation time is substantial for all the systems studied. Details about differences between SCAN and optB88 in the electronic structure for several systems will be presented.

Grant Numbers and Grant Titles

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

Postdoc(s): Handan Yildirim, Karima Lasri

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

10 Recent Publications acknowledging DE-FG02-11ER16243:

1. W. Malone, J. Matos and **A. Kara**, Adsorption of thiophene on transition metal surfaces with the inclusion of van der Waals effects, Surf. Sci. **669**, 121 **(2018)** 10.1016/j.susc.2017.11.013
2. T. Jiang, W. Malone, Y. Tong, D. Dragoe, A. Bendounan, **A. Kara**, V.A. Esaulov, Thiophene Derivatives on Gold and Molecular Dissociation Processes, J. Phys. Chem. C **121**, 27923 **(2017)** 10.1021/acs.jpcc.7b08006
3. W. Malone, H. Yildirim, J. Matos and **A. Kara**, A van der Waals Inclusive Density Functional Theory Study of the Nature of Bonding for Thiophene Adsorption on Ni(100) and Cu(100) Surfaces, J. Phys. Chem. C, **121**, 6090 **(2017)** 10.1021/acs.jpcc.6b12064
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5. K. Müller, J.C. Moreno-López, S. Gottardi, U. Meinhardt,H. Yildirim, **A. Kara**, M. Kivala, M. Stöhr: Cyano-Functionalized Triarylamines on Coinage Metal Surfaces: Interplay of Intermolecular and Molecule–Substrate Interactions, Chemistry–A European Journal **22**, 581 **(2016).** 10.1002/chem.201503205
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Arun Yethiraj

Polymers in deep eutectic solvents

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University of Wisconsin-Madison

Abstract

Deep eutectic solvents (mixture of choline chloride and urea) have emerged as an exciting class of green solvents. They are obtained from natural sources, are inexpensive, and their properties are highly tunable. Incorporating these solvents into a polymer matrix via phase separation (followed by crosslinking the polymer) would allow for the creation of materials with the desired solvent properties. The goal of the project is to obtain the phase behavior of polymers in deep eutectic solvents.

We have developed a new method for determining, from computer simulations, the phase behavior of mixtures of complex fluids. Estimation of the phase behavior is difficult because the chemical potentials of the components in the different phases have to be equal. Since the chemical potential is the work done to insert a molecule, this requires insertions and deletions of molecules, which is difficult for large molecules such as polymers. One could simulate a large box with the coexisting phases and an interface, but the interface moves around during the simulation making it impossible to obtain the coexistence concentrations. In our method we use a concentration correlation function to align the interface from different snapshots, this obtaining the coexisting concentrations and the phase diagram. The method is shown in the figure where the top panel shows the two phases and the moving interface (the y-axis is time). The aligned profiles in the bottom panel allows the calculation of the coexistence concentrations and phase envelope. The method is easily implemented and applicable to any complex fluid mixtures.

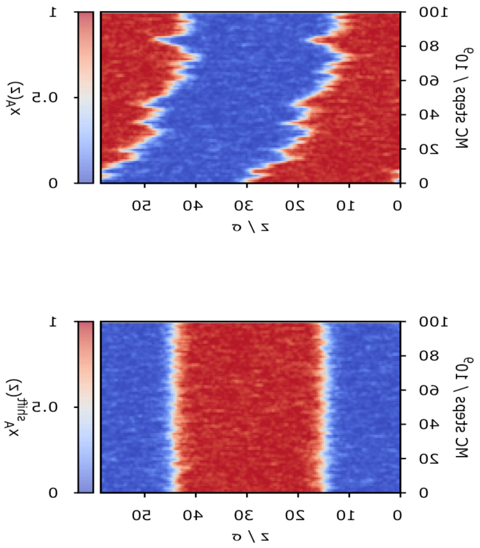

Figure 1: Time evolution of the concentration profile (top) with the two phases in red and blue (the ordinate is “time” in Monte Carlo steps). Aligned concentration profiles (bottom) that allow for a determination of the coexistence concentrations.

The presentation will present results for polymers in a related system, room temperatures ionic liquids, and describe and evaluate our simulation method for the phase diagram.

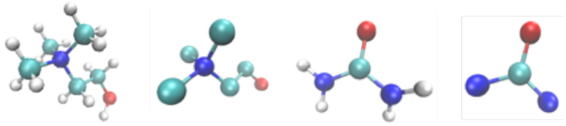

Figure 2: Atomistic and coarse-grained models for Choline (left) and Urea (right)

The proposed research has three goals. The first goal is to obtain fully atomistic polarizable force fields for choline chloride and urea (from first principles calculations), and coarse-grain these to obtain united atom force fields. The second goal is to obtain a force field for poly (ethylene oxide) (PEO) in this solvent. The third goal is to combine these to obtain the phase behavior of PEO in deep eutectic solvents, for a range of solvent compositions. The fourth goal is to study ion and charge transport in the solutions and thin films.

DE-SC0017877

Polymers in deep-eutectic solvents

Student(s): Hyun-Tae Jung and Kyeong-Jun Jeong

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

1. H.T. Jung and A. Yethiraj, "A simulation method for the phase diagram of complex fluid mixtures", J. Chem. Phys. (submitted).

Molecular Theory and Modeling

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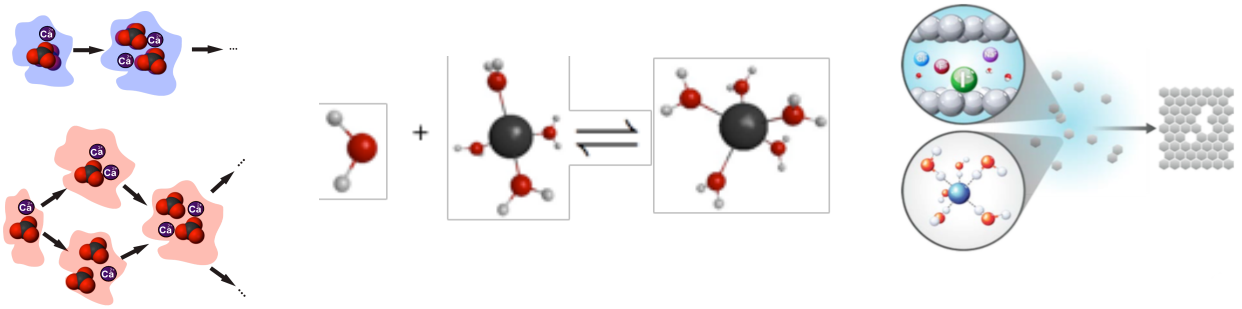
Abstract

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



Nucleation pathways and ion coordination by water control complex collective phenomena.

In current efforts, we focus on the water exchange process about ions, comparing the dependence on the descriptions of molecular interaction. In studying these exchange processes, it is necessary to find the proper balance between the ion-water and water-water interaction. In our studies, we search for the appropriate amount of explicit treatment of electronic structure that allows for efficient sampling of a statistical mechanical ensemble of a system of interest. [2,5,6,7,8] We also have been exploring more effective descriptors for collective phenomena, [1,4,9] formally establishing the role of coordination number in transition state theory descriptions of kinetics. [10] This has allowed us to extend powerful concepts contained in Marcus theory to the phenomena of water exchange. [1,4]

In a multidisciplinary effort involving computational statistical mechanics, material scientists, x-ray experimentalists [J. Fulton of CPIMS], state of the art calculations of x-ray spectroscopy [NEXAFS, N. Govind of CTC], and advanced Monte Carlo techniques [AVBMC, J. Siepmann of CTC], we were able to characterize the initial stages of calcium carbonate nucleation and confirm that a classical mechanism is relevant. [3] This required the construction of an effective reduced model for interaction that took advantage of electronic structure descriptions of molecular interaction coupled to statistical mechanical sampling to recover the proper balance between the details of short-range interaction and long-range electrostatics. Furthermore, advanced Monte Carlo techniques were required to evaluate free-energy differences between cluster populations. This required the development of a solution theory that was consistent with the thermodynamics of cluster formation. Such characterization of large cluster populations is not possible through direct statistical mechanical sampling.

Molecular Theory and Modeling FWP 16249

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

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

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8 Timothy T. Duignan, Marcel D. Baer, Gregory K. Schenter, and Christopher J. Mundy, "Electrostatic solvation free energies of charged hard spheres using molecular dynamics with density functional theory interactions," Journal of Chemical Physics **147** (16) (2017).

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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 of simulation approaches for modeling the nucleation of low-solubility crystals; and (ii) development of MOF intra-molecular force fields that capture the correct relative stability of various crystalline/amorphous phases; and (iii) application of these new methodologies to the simulation of MOF interfaces and to the nucleation of other low solubility "weak electrolytes".

Nucleation of weak electrolytes. Predictive modeling of the nucleation of weak electrolytes presents fundamental challenges of widespread relevance in many domains (e.g. $CaCO_3$/biomineralization, oxalates/kidney stones, MOF growth). Nonetheless, conventional "brute force" simulation approaches are unable to calculate the rigorous thermodynamics governing nucleation of such materials at relevant supersaturation due to a confluence of several challenges: intrinsically dilute saturated solutions, presenting high transport barriers and associated large system sizes; and substantial kinetic barriers to nucleation. We recently developed a rigorous Grand Canonical Monte Carlo (GCMC)-based methodology that allows us to model the nucleation of low-solubility crystals in explicit solvent. Our approach allows us to calculate the thermodynamic barriers governing the growth of small nucleates in solution, without relying on ad hoc "grafting" methods.

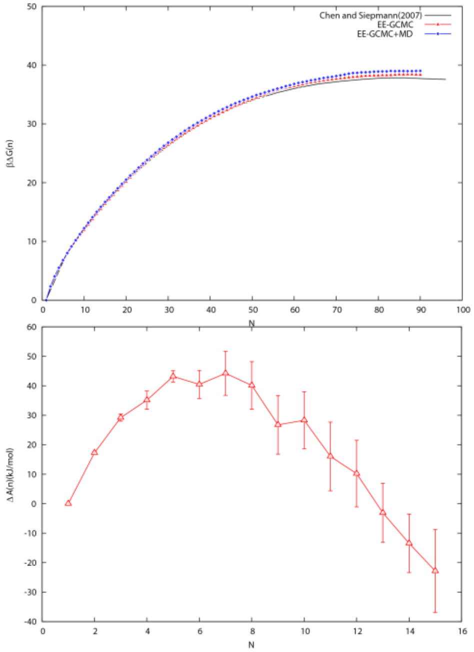

Figure 1. (Top) Method validation for nucleation of Ar from vapor; new EE-GCMC+MD calculated nucleation free energies as compared to benchmark data by Chen et al; (Bottom) EE-GCMC+MD calculated nucleation barrier for LiF(aq)

We recently overcome two significant challenges that now allow us to apply this methodology to non-trivial solutes. We demonstrated how GCMC can be coupled with constant temperature expanded ensemble molecular dynamics (MD) to facilitate application to cases involving solutes in explicit solvent. As far as we are aware, this represents the first application of such a GCMC-based cluster growth method in explicit solvent. Furthermore, we demonstrated that efficient sampling of various cluster sizes can be achieved via a Wang-Landau approach, even in the presence of extremely large nucleation barriers. We have validated the approach in the case of nucleation of Ar from vapor, where high-accuracy benchmark values are available; comparison between our GCMC-based particle growth methods and the benchmark values are shown in Figure 1a. A more realistic and challenging demonstration of the promise of the methodology is shown in Figure 1b, which presents results for the nucleation of crystalline LiF from a slightly supersaturated solution.

Structure of ZIF-solution interfaces and ZIF growth. Zeolitic imidazolate frameworks (ZIFs) represent a particularly interesting case study in MOF nucleation and growth, since ZIFs can be synthesized into a variety of topologies (for a single chemical composition). As a prelude to studies of ZIF nucleation and growth, we initially focused on the development of accurate classical force fields that can accurately capture the relative stability of various possible crystalline / amorphous topologies ("strain energy").We have utilized ab initio methods to develop first-principles *intra*-molecular force fields (i.e. bonded + non-bonded terms) that accurately reproduce the strain energy and structures (lattice constants and atom positions) for a wide variety of ZIFs. Results for these force fields are shown in Figure 2, which show tremendous improvements over traditional empirical force fields often used for ZIFs.

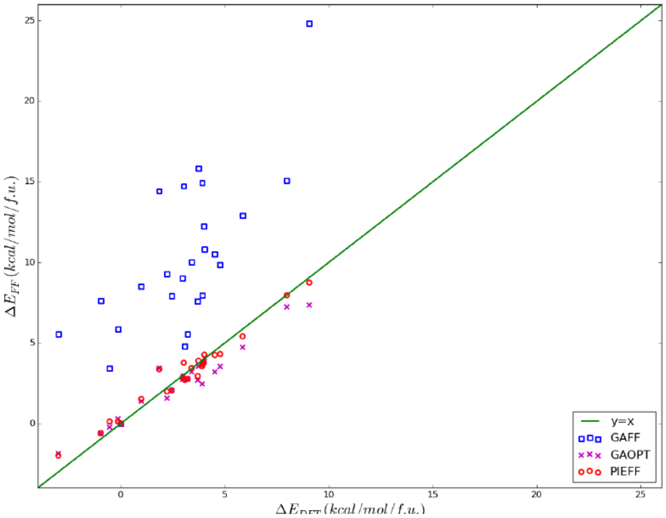

Figure 2. Comparison of force field and DFT-calculated strain energies for various ZIF topologies; original, unoptimized GAFF (blue); present work (red).

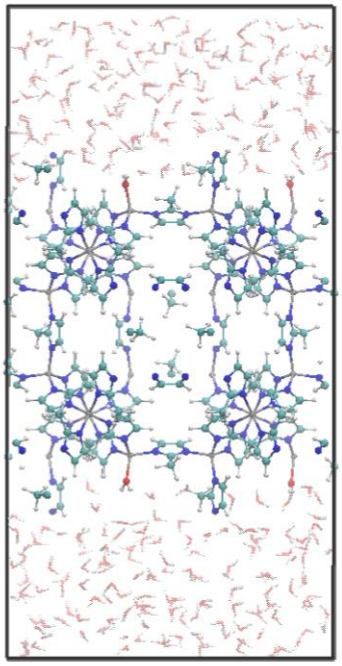

Figure 3. Snapshot from ongoing simulations of ZIF-solution interfaces.

More recently, we have validated these force fields for a wide variety of additional ZIF properties, including phonon frequencies, interfacial stability, as well as evaluated their transferability to unrelated ZIFs. Based upon the success of these studies, we are presently pursing studies of ZIF / solvent interfaces under synthetically-relevant conditions (see Figure 3). A key question of interest is the surface termination and surface structure of ZIFs under such conditions (e.g. termination of Zn groups, etc.) These ongoing simulations will provide highly complementary atomistic data that will be used in conjunction with experimental liquid cell AFM to provide a detailed picture of the ZIF surface in exposure to solvent and/or excess organic linking groups.

Integration of computational and time-resolved experimental data on MOF nucleation and growth. Extremely recent experimental time resolved and/or in situ experimental studies provide unique insights into the nucleation and growth of MOFs and key benchmarks for ongoing computational studies. To this end, we recently published a comprehensive *Chemical Review* article that summarize the state-of-the-art with regard to such experimental studies. Our review focuses specially on time resolved and/or in situ methods, since such methods can provide *direct* methods into the early stages of MOF nucleation. Crucially, the review highlights not only "ripe" opportunities for both future experimental and computational studies, but also several important general conclusions that can be extracted from the totality of the associated literature.

Grant Numbers and Grant Titles

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

Student(s):

- Mary Van Vleet (Partial support: NSF Graduate Fellowship)
- Tingting Weng
- Xinyi Li
- Kai Cui

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Projection-based quantum embedding for large and periodic systems

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Abstract

Quantum embedding methods are ideal for describing adsorption and reaction of chemical species within a large system where the reactive site is well localized, such as reactions that occur at metal nodes in a metal organic frameworks (MOFs). We have been developing a quantum embedding method in which a highly accurate wave function (WF) theory (such as CCSD(T), CASSCF, etc) is used to describe an active site, and the quantum mechanical interactions with the electrons in the surrounding environment is accounted for using a more computationally tractable level of theory—in this case density functional theory (DFT). This projection-based quantum embedding approach is numerically exact for the embedding of molecular and periodic systems, accurately calculates localized excited states, and precisely and efficiently reproduces the reaction energies from canonical WF methods.

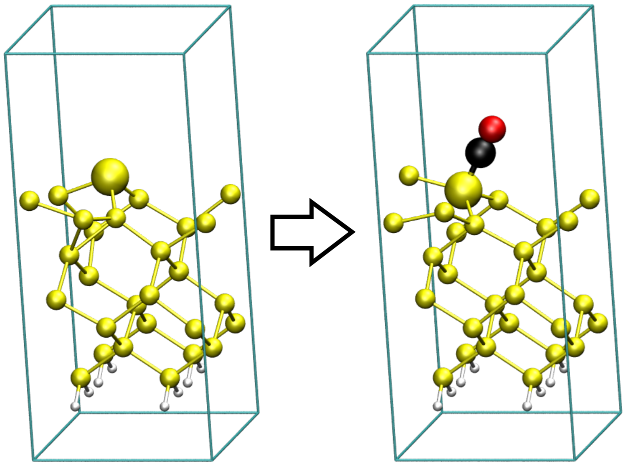

Figure: Unit cells used in examining the WF-in-periodic DFT binding of CO on to a Si(100)-2×1 surface. The larger atoms represent the WF subsystem.

With projection-based embedding, we have shown that the use of the Huzinaga[1,2] projection operator allows each subsystem to be expanded only in the atom-centered basis functions associated with that subsystem. This allows for substantial computational cost savings due to the small basis in which the WF calculations are preformed. This also removes the need for additional orbital localization techniques required of previous projection-based techniques. Furthermore, we have shown that for molecular systems this scheme, applied to WF-in-DFT embedding, reproduced canonical WF reaction energies to within 1 kcal/mol.[3] Therefore, these combinations of techniques, we have found, are *significantly cheaper* and *highly accurate*, and are more broadly applicable than previous WF-in-DFT methods.

Recently, we have been applying this projection-based technique to systems with periodic boundary conditions.[4] Our results show that we can obtain the exact total system energies and densities using periodic embedding. We demonstrated that our embedding protocol can accurately calculate chemical properties on surfaces and MOFs. The **Table** shows the adsorption energy for a CO molecule to Si(100)-2×1 measured from experiment compared to DFT and periodic embedding. DFT using the PBE and LDA function leads to significant errors of 9.1 and 20.5 kcal/mol, respectively. However, CCSD(T)-in-Periodic DFT embedding has only a slightly larger than 1 kcal/mol error regardless of whether PBE or LDA is used.

Table: Absorption Energy of CO on Si(100)-2×1 (in kcal/mol) from Canonical KS-DFT and CCSD(T)-in-Periodic DFT Embedding

Method	Energy	(Error)
Experiment[5]	11.6	
LDA	32.1	(20.5)
PBE	20.7	(9.1)
CCSD(T)-in-LDA	13.0	(1.4)
CCSD(T)-in-PBE	10.3	(1.3)

Additionally, the high-level region in these calculations is shown in the **Figure**, where the larger atoms are treated at the CCSD(T) level. Therefore, this significant increase in accuracy is found with one CCSD(T) calculation containing a single atom and one CCSD(T) calculation involving only 3 atoms. As CCSD(T) calculations on 3 atoms are extremely computationally efficient, highly accurate adsorption energies can thus be obtained with *essentially periodic DFT cost*. Therefore, this method is a powerful approach to accurately describe chemistry at interfaces, chemistry within MOFs and zeolites, and chemistry in the condensed phase.

We are currently working on using this periodic DFT embedding method for small molecule adsorption in MOFs. Specifically, we have been studying H_2 adsorption in MOF-5 and MOF-74. Additionally, we have started to study magnetic MOFs including Fe(1,2,3-triazolate)$_2$(BF$_4$). Magnetic MOFs are exceptionally challenging as we have found most DFT methodology inadequate to accurately predict magnetic ordering temperatures. However, with our periodic DFT embedding we can go beyond traditional DFT to study this challenging problem.

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Grant Information

DE-FG02-17ER16362 Predictive Hierarchical Modeling of Chemical Separations and Transformations in Functional Nanoporous Materials: Synergy of Electronic Structure Theory, Molecular Simulation, Machine Learning, and Experiment

Postdoc(s): Dhabih V. Chulhai
Student(s): Daniel Graham, Brianna Collins

Publications

D. V. Chulhai and J. D. Goodpaster, “Project-Based Correlated Wave Function in Density Functional Theory for Periodic Systems,” *J. Chem. Theory Comput.*, **2018**, 14, 1928. (10.1021/acs.jctc.7b01154)

Speaker: David R. Yarkony

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Grant Number: DE- SC0015997 **and Grant Title:** Nonadiabatic Photochemistry
Grant Period covered in this report: April 15, 2016–March 31, 2018

Program Scope

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

Accomplishments

Hua Guo

Effect of Geometric Phase(GP) in Nonadiabatic Tunneling. We have been investigating the impact of the geometric phase (GP or Berry's phase) on nonadiabatic tunneling in adiabatic dissociation near a conical intersection (CI). Despite the much lower energy than the CI, the dissociation dynamics can be significantly influenced by the GP around the CI. One such example is the tunneling facilitated dissociation of phenol:

$$C_6H_5OH(X^1A)+h\nu \rightarrow C_6H_5OH(2,3^1A) \rightarrow C_6H_5O\ (1,2^2A)+H \qquad (1)$$

The availability of accurate full-dimensional coupled quasi-diabatic potential energy surfaces (PESs) developed by Truhlar and by Yarkony has motivated several dynamical studies. The initial three-dimensional quantum dynamical study of the photodissociation revealed that the single-state adiabatic model predicted a significantly faster dissociation rate than a two-state diabatic model. A detailed analysis based on the vector potential approach of Mead and Truhlar suggested that the difference is due to the neglect of the GP and the diagonal Born-Oppenheimer correction (DBOC) in the single-state adiabatic model. The inclusion of the GP and DBOC largely recovers the correct tunneling lifetime. Mechanistically, the GP gives rise to the destructive interference between trajectories passing around the two sides of the CI on, thus retarding the tunneling rate. Interestingly, it was further demonstrated that the destructive interference can be converted to a constructive one if the initial vibrational state contains an odd number of nodes in the coupling coordinate. In addition, the interference depends sensitively on the anisotropy of the PES. These results suggest that the single-state adiabatic approximation is inadequate in describing tunneling in the presence of a CI even when the energy of the tunneling resonance is substantially lower than that of the CI.

The inclusion of the GP effect in real systems requires the accurate determination of the vector potential. This is not trivial because it is known that in most systems the derivative coupling cannot be completely removed by the adiabatic-to-diabatic state transformation. As a result, the phase associated with encircling the CI might not be exactly π. To avoid this difficulty, Yarkony proposed an effective approach in which the diabatization is approximately fit to ab initio data assuming only two states are involved. Numerical tests demonstrated that the resulting phase is exactly π, thus can be used as the vector potential in adiabatic dynamics calculations. This new approach has been implemented in a three-dimensional model based solely on ab initio data, which is the first time for non-symmetric systems with more than two active modes.

Nonadiabatic Photodissociation Dynamics. We have investigated the photodissociation of hydroxymethyl radical using a reduced-dimensional model based on accurate coupled diabatic PESs developed by Yarkony's group. Four active modes have been included in the model and the results were in excellent agreement with the experimental work of Reisler and coworkers.

Donald G. Truhlar

The photodissociation of thioanisole, as well as that of similar molecules such as phenol and thiophenol, is a prototype of photo-induced hydrogen/methyl detachment and proton transfer reactions mediated by conical intersections between a bound $^1\pi\pi^*$ state and a repulsive $^1\pi\sigma^*$ or $^1n\sigma^*$ state. Analytic diabatic potential energy matrices (PEMs) coupling the ground and two lowest singlet excited states of thioanisole ($C_6H_5SCH_3$) were constructed based on electronic structure calculations including dynamic correlation. The matrix elements are functions of all 42 internal degrees of freedom for a wide range of geometries including the Franck-Condon region and the reaction valley along the breaking S–CH_3 bond with full ranges of the torsion angles. The parameters in the PEMs were fitted to the results of smooth diabatic electronic structure calculations including dynamic electron correlation by the XMC-QDPT method for the adiabatic state energies followed by diabatization by the fourfold way. The fit was accomplished by the anchor points reactive potential method with two reactive coordinates and 40 nonreactive coordinates. The anchor-point force fields are obtained with a locally modified version of the *QuickFF* package. The PEMs and couplings were used for coherent-switches-with-decay-of-mixing (CSDM) dynamics calculations of the photodissociation process. The translational energy distribution was in good agreement with experiment, but the lifetime was too short and the experimentally observed mode selectivity was not observed. We made modified potential surfaces in which the S_1-S_2 conical intersection was moved farther out and higher up. CSDM simulations using these modified PEMs yielded photodissociation lifetimes much closer to the experimental values than had been calculated with the original PEM. This is because shifting the energy level of the S_2-S_1 MECI upwards means that the trajectories take more time to reach the strong interaction region. By shifting the energy level of S_2-S_1 MECI by about 0.3 eV, the lifetime of the photodissociation process increased by a factor of 69. This shows the importance of employing accurate electronic structure theory to obtain potential energy surfaces for dynamics simulations. In addition, we did find a little mode specificity for the S-1.8 PEM; by exciting the S-CH_3 stretching mode, the D_0/D_1 product branching ratio changes from 0.39 to 0.43, although this is still not as strong an effect as in the experimental results. We have also analyzed the total translational energy change when we shift the S_2-S_1 MECI energy level. The peak of the total translational energy shifts to a larger value when we shift the S_2-S_1 MECI energy level up.

Butadiene is the simplest polyene and has long served as a model system for many chemical and spectroscopic properties. However, this small molecule has presented significant challenges to theoretical chemistry. The 2^1A_g state, which is dark but photochemically important, is a prime source of this difficulty. Previous studies attributed the notorious difficulty in treating this state to strong double-excitation character of the 2^1A_g state, which prevents the application of linear response (LR) methods. Therefore one would require methods with much higher computational cost, especially for the analogs of this state in longer polyenes, and consequently studies of longer polyenes are very limited. We showed, however, that the difficulty stems more significantly from the inherently multi-configurational character of the ground state. In addition, we validated the possibility of employing LR time-dependent density functional theory to investigate such a state with reasonable accuracy.

We developed the dual-functional Tamm-Dancoff approximation (DF-TDA) method. DF-TDA is an alternative to linear-response time-dependent density functional theory (LR-TDDFT) with the advantage of providing a correct double cone topology of S_1/S_0 conical intersections. In the DF-TDA method, we employ different functionals, which are denoted G and F, for orbital optimization and Hamiltonian construction. We use the notation DF-TDA/G:F. We have also proposed that G be the same as F except for having 100% Hartree-Fock exchange. We use the notation DF100 to denote using the theory this way. A motivation for this is that functionals with 100% Hartree-Fock exchange are one-electron self-interaction-free. We validated the use of DF100 method based on the M06 density functional to compute vertical excitation energies and the global potential energy surface of ammonia near a conical intersection. We have made the method available to the community in the GAMESS+DF program available on our website.

David R. Yarkony

Nonadiabatic processes, like the conical intersections that drive them, are ubiquitous in nature, being germane to such essential processes as vision, photosynthesis, upper atmospheric and interstellar chemistry and solar energy conversion. The computational description of nonadiabatic processes requires a combination of nuclear dynamics (preferably full quantum dynamics although quasi-classical methods play an invaluable roll in larger systems) and electronic structure data, energies, energy gradients and derivative couplings – or the equivalent diabatic state parameters (preferably determined at a level that includes both static – to treat electronic near degeneracies, and dynamic correlation). The electronic structure aspects of nonadiabatic processes are computationally challenging. In the method espoused in this part of the research program, the electronic structure data is provided by coupled diabatic state Hamiltonians, denoted $\mathbf{H}^d$, fit to accurate ab initio adiabatic electronic structure data, determined at the multireference configuration interaction single and double excitation level. All internal coordinates are treated equivalently. This 'precomputed' electronic structure data, which is essential for full quantum nonadiabatic dynamics is the most reliable currently available for nonadiabatic dynamics although its determination offers challenges of its own. The related work of Truhlar also exploits precomputed coupled diabatic state Hamiltonians which are obtained using alternative electronic structure techniques.

The funding of this tripartite research effort has sustained a uniquely synergistic collaboration between Yarkony (electronic structure) and Guo (full quantum dynamics) and added the insights of Truhlar's combined electronic structure and quasi-classical dynamics work. In this portion of the report the focus is on the unique achievements that are obtained from a combination of accurate $\mathbf{H}^d$ and (reduced dimensionality) fully quantum mechanical dynamics. Two achievements are noteworthy: (i) an early work which resolved the controversy over the mode specific population of $NH_2(\tilde{A})$ in NH_3 photodissociation, (a J. Chem. Phys. communication) and (ii) the (DoE funded) discovery of a large (factor of ~100) discrepancy in the single Born-Oppenheimer state tunneling rate from the $\tilde{A}$ state of phenol when proper care is not taken of the GP effect described above by Guo. (This appeared as a JACS communication). The first of these communications was important from a didactic prospective and served to establish the value of the constructed $\mathbf{H}^d$. In DoE funded research we constructed the $\mathbf{H}^d$ used to describe the multistate photodissocation of phenol in its full 33 dimensional internal coordinates and two $\mathbf{H}^d$ for hydroxymethyl, one for the three state reaction

$$CH_2OH(X^2A) + h\nu \rightarrow CH_2OH(3^2A) \rightarrow H+CH_2O,\ H+cis\text{-}HCOH,\ H+trans\text{-}HCOH \qquad (1a)$$

and one for the two state reaction[5]

$$CH_2OH(X^2A) + h\nu \rightarrow CH_2OH(2^2A) \rightarrow H+CH_2O \qquad (1b)$$

in the full 9-dimensional space. The two state $\mathbf{H}^d$ was then used to determine the experimentally determined KER spectrum. Agreement between the measured and predicted spectra were found to be excellent. The peaks in KER were assigned to the vibrationally excited CO stretch in the H_2CO product which was previously not possible. Again these results strongly support the accuracy of the $\mathbf{H}^d$. Thus the $\mathbf{H}^d$ provide a key tool in the determination of *accurate* nonadiabatic dynamics, a key goal of our research effort.

The phenol communication is of fundamental concern since in it the direct correspondence between the topography of a transition state barrier (its height and curvature) and the tunneling rate is eliminated while raising the long dormant issue of the applicability of standard single surface dynamics when energetically *inaccessible* conical intersections are present. The challenge in treating the effects of energetically inaccessible conical intersections is the need to construct a single electronic state Hamiltonian that accurately incorporates the geometric phase. We have, as part of other funded research shown how a 2x2 $\mathbf{H}^d$ can be used to accomplish this. Thus our ability to construct $\mathbf{H}^d$ that accurately reproduce adiabatic data, energies, energy gradients and especially the derivative couplings provide a unique capability to study, with unprecedented accuracy, multistate nonadiabatic processes, based on fully quantum mechanical dynamics as well as nonadiabatic single potential energy surface dynamics (not an oxymoron) where the existence of energetically inaccessible conical intersections necessitates inclusion of the GP effect.

These observations have motivated us to extend our ongoing studies of multistate nonadiabatic dynamics to included systems for which previous high quality first principles studies have been carried out using the *standard* Born-Oppenheimer approximation which eschews the inclusion of the GP.

Future Work

Hua Guo

We plan to expand the nonadiabatic tunneling study to systems involving the ground electronic state. Although the conventional treatment of unimolecular dissociation reactions has been based on a single-state adiabatic model, many systems are affected by conical intersections. As we have demonstrated earlier, the presence of the conical intersection could have a strong influence on the adiabatic dissociation dynamics. An example is the high overtone dissociation of hydroxymethyl, extensively study by Reisler and coworkers. Our initial study of this process, which utilized Yarkony's two state H^d method and established the importance of including the GP in the adiabatic simulation, recently appeared as an editor's choice JACS comunciation.

Another project is to identify the active mode(s) in photodissociation dynamics in multidimensional systems. This is important because it is still difficult to perform full-dimensional quantum dynamical studies beyond four-atom systems. Thus, how to capture the correct dynamics with reduced dimensional models becomes important.

Finally, we are working on a six-dimensional quantum dynamical code for studying the $OH(A\ ^2\Sigma^+) + H_2 \rightarrow H_2O + H$ reaction, using the PESs produced by Truhlar and by Yarkony.

Donald G. Truhlar

We have made progress on calculating and fitting externally correlated coupled potential energy surfaces and surface couplings for the electronically inelastic reaction $OH^* + H_2 \rightarrow H_2O + H$, where * denotes electronic excitation ($A\ ^2\Sigma^+$), and for the photodissociation of methylamine and thiophenol. For $OH^* + H_2 \rightarrow H_2O + H$ and thiophenol, we are using the orbital-based fourfold way for diabatization and for methylamine we are using orbital-free DQ diabatization. We will complete the fitting of the surfaces and couplings for these three systems, and we will perform semiclassical dynamics simulations of the electronically nonadiabatic processes by the CSDM method. These calculations will include electronically adiabatic and electronically nonadiabatic tunneling by our recently developed army ants tunneling approximation. We will also provide these surfaces and couplings to Hua Guo for quantum mechanical wave packet calculations.

We will also compare coupled surfaces and couplings to the work of David Yarkony, and we will compare semiclassical dynamics calculations to the quantum wave packet calculations of Hua Guo.

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

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

David R. Yarkony

With the growing importance of diabatic representations in nonadiabatic dynamics, and as we have noted in ostensibly adiabatic dynamics, it is important to juxtapose distinct approaches to constructing diabatic representations. Our tripartite collaboration provides just that opportunity for the archetypical HO_3 system, a system which has frustrated previous attempts at computational description. For $OH(A\ ^2\Sigma^+) + H_2 \rightarrow H_2O + H$ reactive quenching we are well along in the process of determining the $\mathbf{H}^d$ for this three electronic state quenching process. The current $\mathbf{H}^d$ represents data at ~15000 nuclear configurations of which 5000 are symmetry unique in the complete nuclear permutation inversion group. The 3:1 ratio reflects our use of the abelian subgroup G_4. In the absence of this symmetry 30,000 nonunique data points (with a corresponding increase in the number fitting parameters) would be required.

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RECENT PUBLICATIONS ACKNOWLEDGING DOE SUPPORT BY THIS GRANT

Hua Guo

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Multiple Coupled Potential Energy Surfaces with Application to Combustion

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Program Scope: Hydrocarbon combustion involves the dynamics of numerous small radicals such as HO_2, HCO, and HOCO. HOCO is an intermediate in the HO + CO → H + CO_2 reaction which is the last and heat releasing step in hydrocarbon combustion and the subject of many ongoing studies. Accurate calculations of their potential energy surfaces (PESs) are possible using traditional quantum chemistry methods such as MRCI. However, multistate and non-adiabatic processes can be important, and tunneling effects may supersede the more common kinetic or thermodynamic control of rates and branching ratios. Significant fractions of molecular products can also result from radicals roaming far from conventional minimum energy paths and tight transition states. Dynamical calculations for these relatively simple systems are very sensitive to the detailed topography of their global potential energy surfaces (PESs).

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

Recent Progress: This section describes recent progress achieved along various directions of the project occurring over the past 12 months since the last report from April 2017. The initial start date of this project was 07-15-2013.

Three review articles were published recently on the methods developed in relation to this project. The first was a *Molecular Physics* review of methods for *Automated Construction of Potential Energy Surfaces*.[1] The second, for *International Reviews of Physical Chemistry*, describes *Single- and multireference electronic structure calculations for constructing potential energy surfaces*.[2] A third, in collaboration with Hua Guo, is a JPC A review on fitted PESs and the quantum dynamics of X + H_2O (X = F, Cl and O) reactions.[3] This year significant effort went into writing a book chapter (104 pages) to appear in *Reviews in Computational Chemistry* (ed. Lipkowitz, 2018). The book chapter provides extensive background and a pedagogical presentation of these topics aimed at a beginning graduate student audience. It also describes our latest developed methods and codes.

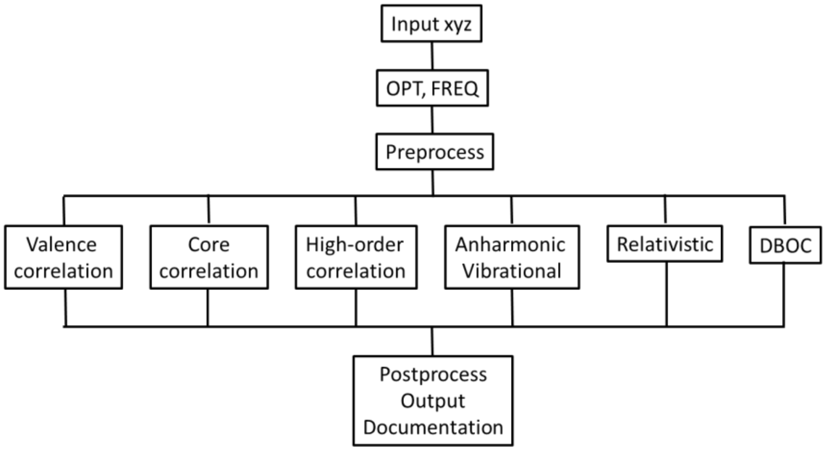
QMC. We have been developing scripts and testing methods to use multi-configurational trial wavefunctions in VMC/DMC calculations of PECs for small molecules using a code called CASINO. A tutorial is available on our website, http://web.mst.edu/~dawesr/educational.html. Graduate student Andrew Powell published two benchmark studies, the first on N_2 and CO,[4] and the second on ozone.[5] For the DMC calculations, we have found the QMCPACK code (Paul Kent, Oak Ridge) to be advantageous for multiconfigurational trial wavefunctions (due to the Table method algorithm). Our recent study of ozone also explored the FCIQMC method of Alavi[6] and compared internally contracted *ic*MRCI with uncontracted MRCI at the complete basis limit for this challenging highly multiconfigurational reaction path. Important insights were obtained into all of these methods.

Student Andrew Powell graduated with his Ph.D. in June 2017. His expertise in QMC methods gained through this project led to his current postdoc position with Geert-Jan Kroes (Leiden) applying QMC methods to studies of materials. Ph.D. Candidate Bradley Welch is now supported by this project.

Bradley Welch recently published a paper on photo-initiated reactions in vdWs complexes,[7] but his main thrust is computational thermochemistry including collaboration with Branko Ruscic at ANL. He was recently awarded an SCGSR fellowship by the DOE to support a 2018 visit to ANL to work with Branko as his co-mentor. Branko is known for his decades of work developing the Active Thermochemical Tables (ATcT) which are based upon statistically analyzing and self-consistently solving thermochemical networks.[8,9] The ATcT thermochemical network incorporates a variety of thermochemical determinations, connecting large families of species via interwoven webs of reaction mechanisms. These determinations come from various experimental and theoretical sources. Remarkably, the accuracy of quantities derived from the network approach typically exceeds that of any one particular measurement or calculation (both sources of data being seamlessly included). Sufficiently reliable theoretical approaches or protocols allow for rapid generation of thermochemical data that can be included in the ATcT and used to reanalyze the thermochemical network.

We have developed a highly specialized *framework* to automate the computational workflow. After a few initial steps and analysis, all of the necessary quantities can be computed independently using different amounts of resources (and even different resources altogether). Different codes can be used for the various contributions (our current protocol employs four). A master Python script controls each of the code and resource specifications.
Shown in *flowchart 1*, the procedure begins with a rough input structure (*xyz*). Next, a geometry optimization and harmonic frequency calculation is performed, followed by processing to automatically report any imaginary frequencies and the number of low frequency (potentially floppy large amplitude) modes that might raise concern for the anharmonic vibrational analysis to follow. If the calculation passes that stage, then six independent contributions are computed simultaneously with resource allocations designed to balance the costs and efficiency of parallelization etc. The default protocol is very high-level, employing energy extrapolations that include up to five-zeta basis sets with explicitly-correlated coupled-cluster theory. The known

cost scalings of each contribution with respect to *N*-nuclei and *n*-electrons allows us to tailor the procedure to balance cost and accuracy. The cost of each contribution is also considered relative to its overall importance and individual as well as global error bars are assessed. The default protocol is most applicable to families of species with up to 50 electrons and up to 12 nuclei. In post-processing, each contribution is tested to see if it falls within its expected range. Indications of multireference character are reported such as T_1 and D_1 diagnostics, the contribution of triples (T) to the total atomization energy, and unusual progression in the high-order correlation. Finally, any unusual vibrational frequencies create warnings. When all goes well, all of the computed quantities are reported in a formatted output file suitable for integration into the ATcT network. The complete set of generated files is retained as documentation. A paper is in prep,[10] and several more are anticipated to come from Bradley's visit to ANL. The tentative initial goal is to confirm the consistency of the data generated by the protocol by recomputing 50 species already in the network (which may also improve some of those values), before expanding the network from its current ~1200 species by at least 20%.



Flowchart 1: Illustration of the automated process to generate highly accurate thermochemical data using parallel computation on distributed resources.

MCTDH: **Rovibrationally and electronically inelastic scattering.** Previously, a time-dependent quantum dynamics method known as MCTDH was applied to studying inelastic scattering at high collision energies where more typical time-independent calculations (Molscat) become prohibitively expensive.[11] We are including the effects of multiple coupled electronic states on scattering dynamics. A paper describing spectroscopically accurate coupled PESs for the important combustion radical HCO was published recently.[12] The new coupled PESs have been used to study photodissociation and scattering dynamics and multiple publications are in preparation.

In a combined theory/experiment study including theory collaborator Hua Guo and experimental collaborator Jingsong Zhang, oscillations in the rotational distribution of the CO product following photoexcitation are now closely matched by simulations using the PESs. The oscillations can be understood as an interference effect due to multiple paths leading to the same product states.[13]

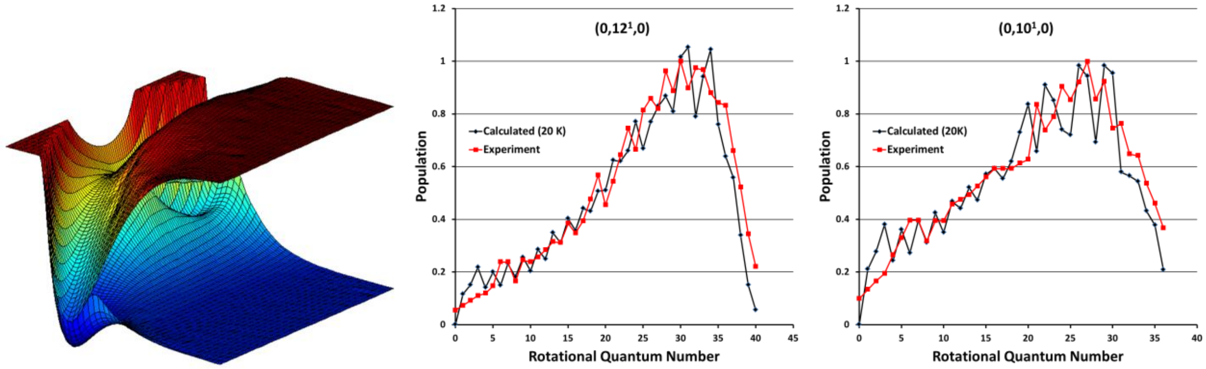


Figure 1: (left) Surface plot of the fitted adiabatic X and A state PESs for HCO in Jacobi coordinates as a function of $R_{\text{H—CO}}$ and theta. (middle) Calculated and recorded rotational distributions of CO product, with thermal averaging over initial rotational states based on the estimated 20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

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Electron-Ion Dynamics with Time-Dependent Density Functional Theory

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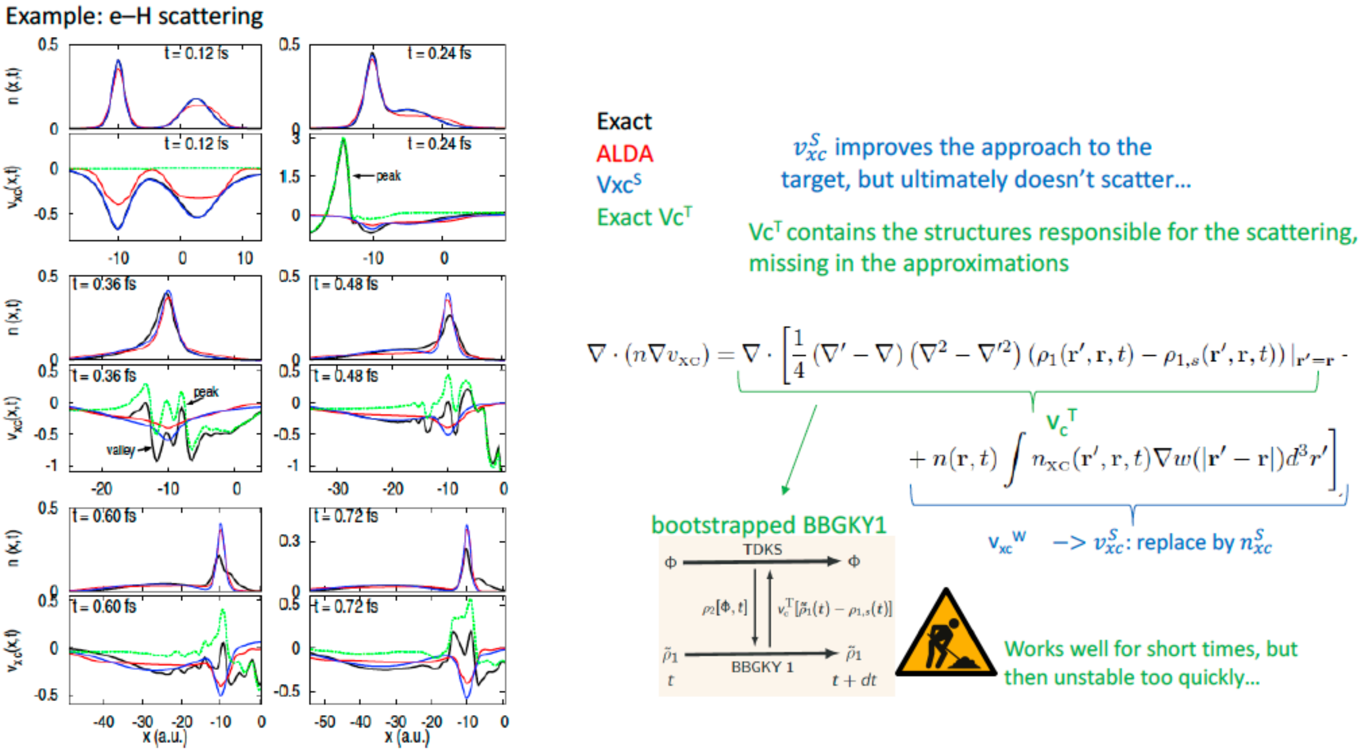
Abstract

To improve the reliability of time-dependent density functional theory (TDDFT) simulations of electron-ion dynamics, especially when systems are driven far from the ground-state, as in photovoltaics, we have been working in two directions: (i) developing a new direction for building time-dependent exchange-correlation functional approximations, that go beyond the adiabatic approximation, and (ii) investigating mixed quantum-classical algorithms based on the exact factorization approach. The overall goal is to derive more reliable methods based on these investigations that predict photo-induced dynamics in materials more accurately.

The new direction for the development of non-adiabatic time-dependent exchange-correlation functionals stems from a decomposition of the exact exchange-correlation potential into kinetic and interaction components, which are approximated in a self-consistent way. The exact interaction component involves the exact exchange-correlation hole, which, in the approximation, we replace with the time-evolving Kohn-Sham exchange correlation hole. This approximation, we call $v_{xc}{}^{S}$, is a very good approximation for this term, regardless of the initial configuration (i.e. beyond Slater determinants). In electron-atom scattering, for example, it almost perfectly describes the approach of the electron to the target, when the initial Kohn-Sham state was chosen judiciously, far better than adiabatic exact-exchange or ALDA (see Figure). The exact kinetic component involves the difference between the exact and Kohn-Sham one-body reduced density matrices (1RDM), and we have explored various "frozen" approximations to this as well as a dynamic approximation based on co-evolving an equation for the 1RDM in which the two-body term involves the time-evolving Kohn-Sham density matrix ("bootstrapped BBGKY1"). The latter is very promising at short times but has numerical instabilities that we are currently working on to tame. The general approach results in practical, self-consistent, orbital-dependent approximations that have initial-state dependence and history-dependence, and improve upon the standard non-adiabatic approximations in tests on model systems.

In developing the exact factorization approach to coupled electron-ion dynamics, we had found using simple model systems that the exact potentials that drive the electronic and nuclear subsystems differ significantly from those used in traditional approximations. The difference between the traditional and exact potentials accounts for dynamical electron-nuclear correlation, including effects like wavepacket branching and decoherence. The relative nuclear velocity is critical in determining the size of these dynamical correlation terms. We are investigating mixed quantum-classical (MQC) schemes based on these equations, and so far have deconstructed how the recently proposed CT-MQC of Min, Agostini, and co-workers operates, its relation to traditional MQC approaches, and its limitations. We are also currently studying numerical convergence and stability aspects of the exact coupled electronic and nuclear equations

as these have a very different form than the usual Schrödinger equation, which implies that in making approximations special considerations need to be given to Hermiticity and well-posedness; the numerical stability of the exact electronic equation in particular is important to understand for future approximations and for density-functionalizations of the exact-factorization approach.



v_{xc}^S improves the approach to the target, but ultimately doesn't scatter...

Vc^T contains the structures responsible for the scattering, missing in the approximations

$$\nabla \cdot (n \nabla v_{\rm XC}) = \nabla \cdot \Big[\underbrace{\frac{1}{4} (\nabla' - \nabla) (\nabla^2 - \nabla'^2) (\rho_1(\mathbf{r}', \mathbf{r}, t) - \rho_{1,s}(\mathbf{r}', \mathbf{r}, t)) |_{\mathbf{r}'=\mathbf{r}}}_{v_c^T} \underbrace{+ n(\mathbf{r}, t) \int n_{\rm XC}(\mathbf{r}', \mathbf{r}, t) \nabla w(|\mathbf{r}' - \mathbf{r}|) d^3 r'}_{v_{xc}^W} \Big]$$

v_{xc}^W –> v_{xc}^S: replace by n_{xc}^S

Works well for short times, but then unstable too quickly...

Future research will continue the development of memory-dependent functionals along the lines described above, first taming the numerical instability, testing on a range of model systems, and eventually developing these in a code for dynamics in real molecules. For the coupling to ions, we will use the knowledge gained from deconstructing the CT-MQC method to develop a more general mixed quantum-classical method that does not rely on an expansion in Born-Oppenheimer states, while gaining some insight into what makes a stable consistent approximation for the electronic equation in methods derived from the exact factorization scheme.

Grant Numbers and Grant Titles

DE-SC0008623 and DE-SC0015344, Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

Postdoc(s): Lionel Lacombe, Johanna I. Fuks, Ali Abedi, Elham Khosravi

Student(s): none funded by this grant

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

(1) *Exact time-dependent exchange-correlation potential in electron-scattering processes*, Y. Suzuki, L. Lacombe, K. Watanabe, and N. T. Maitra, Phys. Rev. Lett. **119**, 263401 (2017).

(2) *Charge-Transfer in Time-Dependent Density Functional Theory*, N. T. Maitra, Topical Review in J. Phys. Condens. Matt. **29**, 423001 (2017).

(3) *Electronic Non-Adiabatic Dynamics in Enhanced Ionization of Isotopologues of* H_2^+ *from the Exact Factorization Perspective,* E. Khosravi, A. Abedi, A. Rubio, and N. T. Maitra, Phys. Chem. Chem. Phys. **19**, 8269 (2017).

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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.

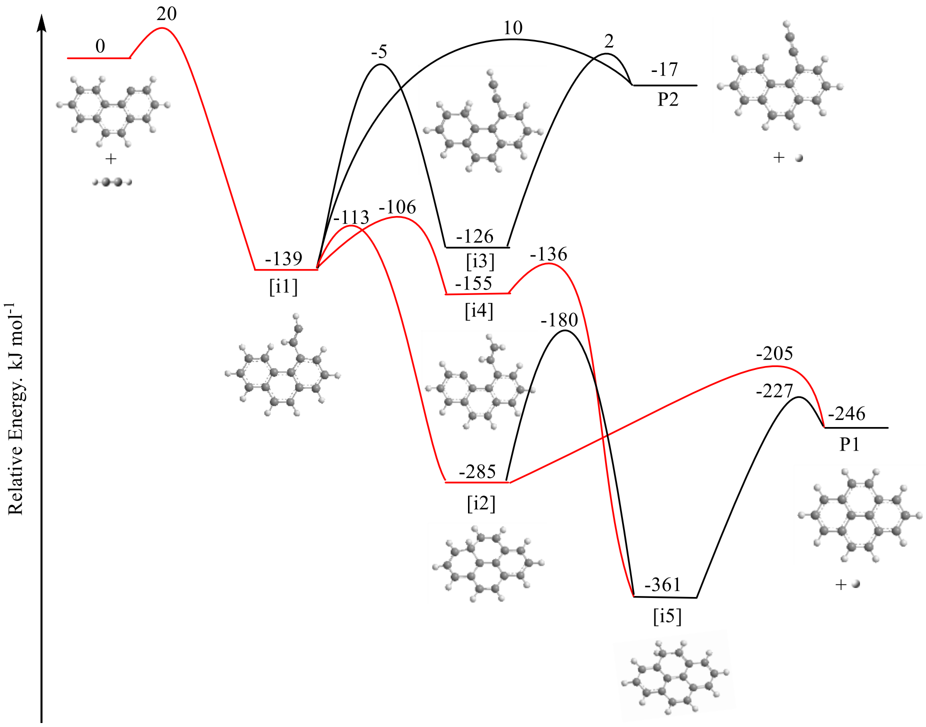
Recent Progress

Oxidation of the cyclopentadienyl radical with O, OH, and O_2. We carried out a detailed theoretical investigation of the oxidation mechanism of the cyclopentadienyl radical with the main oxidants present in combustion flames, including O, OH, and O_2. Ab initio calculations of potential energy surfaces in conjunction with the RRKM-Master Equation theoretical approach have been employed to evaluate temperature- and pressure-dependent total and product specific rate constants and product branching ratios for these and related reactions. The formation of the cyclobutadiene + CO products via a ring contraction/CO elimination mechanism is shown to be the prevailing channel for the unimolecular thermal decomposition of 2,4-cyclopentadienone C_5H_4O but the reaction is found to be relatively slow. Decomposition of cyclopentadienone can be greatly facilitated through bimolecular encounters with H atoms. The C_5H_4O + H reaction is predicted to be fast, with rate constants ranging from 4.6×10^{-12} to 1.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at $T = 500$-2500 K and finite pressures. Cyclic C_5H_5O intermediates formed after the initial H addition undergo ring openings by β-scissions and then decompose to either butadienyl C_4H_5 + CO or 1-oxoprop-2-enyl H_2CCHCO + C_2H_2, which are respectively predicted as the major and the minor reaction products. The calculations predict that thermal decomposition of the *ortho* and *meta* C_5H_5O radicals as well as pyranyl nearly exclusively forms the C_4H_5 + CO products, whereas decomposition of hydroxycyclopentadienyl C_5H_4OH predominantly produces cyclopentadienone + H. The C_5H_5 + O reaction is shown to proceed by barrierless oxygen addition to the ring followed by fast H migration, ring opening, and dissociation to C_4H_5 + CO. The C_5H_5 + O rate constant is calculated to be close to 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and to be pressure-independent and nearly independent of temperature. PESs for the C_5H_5 + OH and $C_{15}H_9$ + OH reactions allowed us to unravel the mechanism of oxidation of the cyclopentadienyl radical and five-member-ring radicals embedded in a sheet of six-member rings with OH and to quantify relative yields of various products. The C_5H_5 + OH reaction is shown to proceed either by well-skipping pathways without stabilization of C_5H_6O intermediates leading to the bimolecular products *ortho*-C_5H_5O + H, C_5H_4OH (hydroxycyclopentadienyl) + H, and C_4H_6 (1,3-butadiene) + CO, or via stabilization of the C_5H_6O intermediates, which then undergo unimolecular thermal decomposition to *ortho*-C_5H_5O + H and C_4H_6 + CO. The well-skipping and stabilization/dissociation pathways compete depending on the reaction conditions; higher pressures favor the stabilization/dissociation and higher temperature favor the well-skipping channels. For the $C_{15}H_9$ + OH reactions, the results demonstrate that embedding decreases the oxidation rate constants and hinder the decarbonylation process; the removal of CO grows less likely as the number of common edges of the five-member ring with the surrounding six-member rings increases. For the C_5H_5 + O_2 reaction, the results show that at low temperatures from 500 to 800-1250 K (depending on pressure), the reaction predominantly forms a collisionally-stabilized C_5H_5-OO complex and then, the thermalized complex rapidly decomposes back to the reactants establishing a C_5H_5 + O_2/C_5H_5-OO equilibrium. At higher temperatures, typically above 1000 K, the mechanism is different and the C_5H_5 + O_2 reaction proceeds to form various bimolecular products. Cyclopentadienone C_5H_4O + OH are predicted to be the predominant product (63.5-83.3%). Relatively minor products include $H_2CCHCHC(H)O$ + CO (20-3%), vinylketene + HCO (12-2%), and highly endothermic C_5H_5O + O (up to 6.5% at 2500 K) produced directly by the O-O bond cleavage in the initial complex. The CO_2 loss channel leading to the formation of 1,3-butadien-1-yl C_4H_5 is shown to be negligible. The total reaction rate constants at all considered pressures from 0.03 to 100 atm merge at 1375 K and show no pressure dependence at higher temperatures, as only the bimolecular products are formed. Overall, the rate constant of the C_5H_5 + O_2 reaction at combustion-relevant temperatures is predicted to be very slow, 10^{-16}-10^{-15} cm^3 $molecule^{-1}$ s^{-1}, that is typically ~5 orders of magnitude lower than those for the oxidation reactions of cyclopentadienyl with OH and $O(^3P)$.

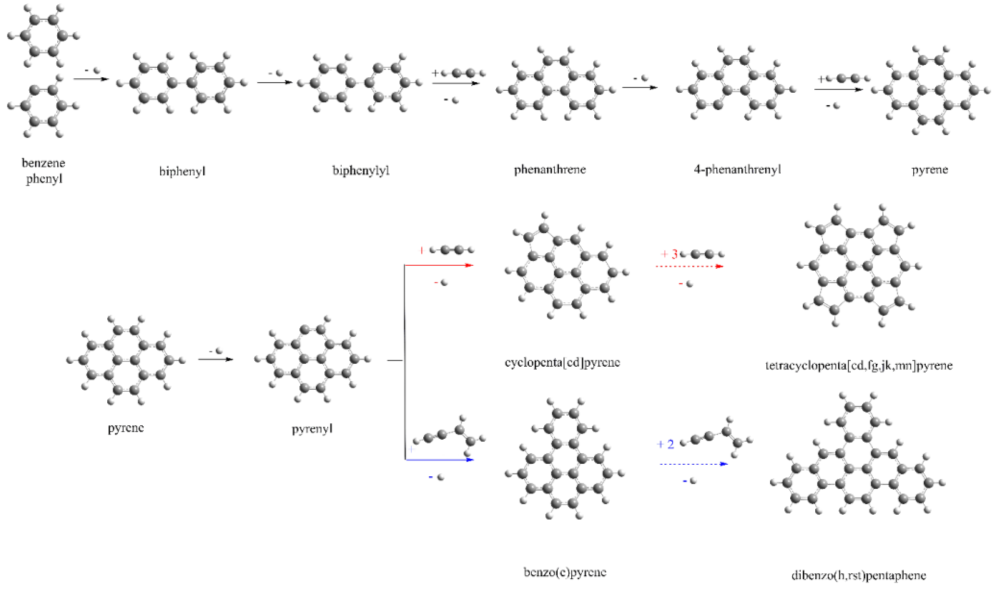
Combined experimental and theoretical studies of the formation of phenanthrene and pyrene by HACA. In collaboration with R. Kaiser's and M. Ahmed's groups, who performed experiments in a pyrolytic chemical reactor with product detection by photoionization spectroscopy with the Advanced Light Source (ALS) at LBNL, we uncovered the mechanisms for the formation of the three- and four-ring PAHs phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$) via the Hydrogen Abstraction aCetylene Addition (HACA) routes closing the 'bay' on the armchair edges of the smaller PAH molecules, biphenyl and phenanthrene, respectively. In particular, by exploring the reactions of the *ortho*-biphenylyl radical ($C_{12}H_9$) and the 4-phenanthrenyl radical ($C_{14}H_9$) with acetylene (C_2H_2) under conditions prevalent in carbon-rich circumstellar environments, we demonstrated a facile, isomer-selective formation of phenanthrene and pyrene. Along with the Hydrogen Abstraction – Vinylacetylene Addition (HAVA) mechanism, molecular mass growth processes from pyrene may lead through systematic ring expansions not only to more complex PAHs, but ultimately to two-dimensional graphene-type structures. These fundamental reaction mechanisms are of crucial significance to facilitate an understanding of the origin and evolution of the molecular universe and in particular of carbon in our galaxy.

Future Plans

We will continue detailed studies of the mechanism and temperature- and pressure-dependent rate constants of the variety of prototypical reactions of PAH growth, such as C_5H_5 + C_5H_6, C_7H_7 + C_3H_3, and C_6H_5 + C_3H_5, which potentially form naphthalene and indene. The focus



Potential energy diagram for pyrene formation via C_2H_2 addition to the 4-phenanthrenyl radical



Molecular mass growth processes to PAHs involving HACA and HAVA

will be put on Variable Reaction Coordinate – Transition State Theory (VRC-TST) calculations of rate constants for barrierless entrance reaction steps, which require sophisticated theoretical treatment using multireference methods of the *ab initio* theory. The VRC-TST rate constants will be combined with RRKM rate constants for the other reaction steps in RRKM-Master Equation calculations aimed to generate reliable phenomenological rate constants for the PAH growth. Together with the experimental work by R. Kaiser and M. Ahmed's groups we will continue investigating the HAVA mechanism producing PAH molecules with multiple rings through the calculations of PESs and rate constants for the reactions of naphthyl radicals with vinylacetylene (C_4H_4) forming phenanthrene and anthracene and the reactions of phenanthrenyl radicals with C_4H_4 leading to triphenylene and [4]helicene. The work on oxidation of PAH radicals will be continued in collaboration with M. Frenklach. Here, we will study a cooperative oxidation mechanism where the O_2 molecule attacks a hydroxylated six-member ring on a PAH/soot edge. Calculated rate constants for the cooperative oxidation mechanism will be included in the latest kinetic models for soot oxidation to try to reconcile the disagreement of these models with the experimental data on low-temperature soot oxidation.

Grant Number and Grant Title

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

Postdoc: Alexander N. Morozov

Students: Daniel Belisario-Lara, Juan Alarcon

DOE/BES sponsored publications (2016-2018)

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SPEC: Scalable Predictive methods for Excitations and Correlated phenomena

High-level formulations of the Green's function formalism

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Abstract

This effort is part of the Center for Scalable, Predictive methods for Excitation and Correlated phenomena (SPEC), which is a partnership between the Pacific Northwest National Laboratory (lead institution), the University of Washington, Lawrence Berkeley National Laboratory, the University of Illinois at Urbana-Champaign and the University of Michigan. SPEC will enable scientists to simulate excited states and excited state processes with unprecedented predictive power and orders-of-magnitude greater computational performance than current methods. This will remove a major barrier to realizing discoveries from next-generation experiments at BES light sources and accelerate progress on Grand Challenges in fields such as solar energy capture, catalysis, and energy storage. SPEC's multidisciplinary team consisting of researchers with expertise in domain science, computer science and applied mathematics will couple new theoretical and computational advances to deliver scalable, open-source software libraries suitable for simulating realistic systems on extreme-scale leadership computing facilities.

Our work concentrates on the development of Green's function approaches that employ a hierarchical structure of many-body correlation effects. The main focus of the present effort is on perturbative Many-Body Green's Function (MBGF) and Coupled-Cluster Green's Function (GFCC) methodologies. While the MBGF approach is deeply rooted in the perturbative expansion for the self-energy operator, the GFCC formalism utilizes the exponential Ansatz for a N-electron system to provide the desired level of accuracy. Several numerical examples will be discussed to illustrate the performance of the proposed schemes. In particular, we will discuss the accuracy of recent implementations of the GFCC formalism in describing the spectral functions for a wide energy range including the inner- and outer-valence regions as well as the core-level states for several benchmark systems (see Fig. 1).

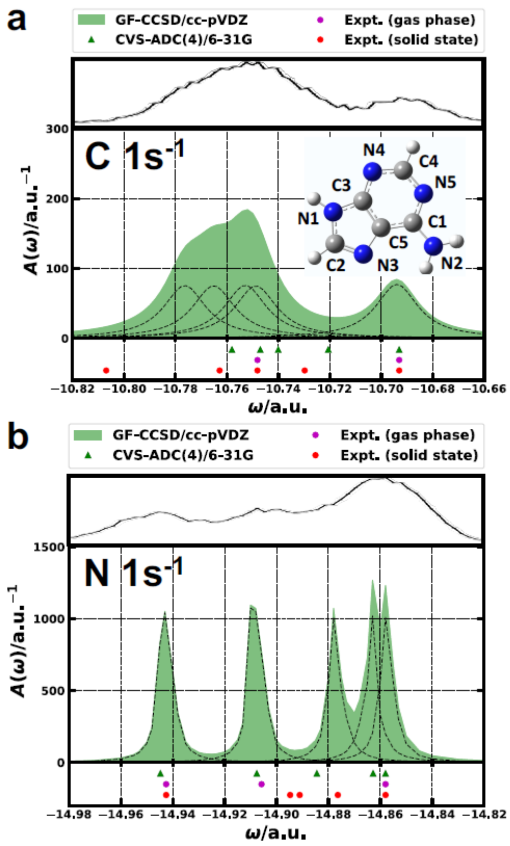

Figure 1. Spectral functions of adenine in the X-ray energy regime corresponding to core ionizations computed by GFCCSD and comparison with experiment.

The efficiency of the GFCC approach across these broad energy ranges will play a crucial role in interpreting the experiments carried out at the BES-supported light sources. The accurate Green's function formulations are also inextricable elements of the self-energy embedding theory, which is also an integral part of the Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC) project.

We will furthermore discuss strategies for the inclusion of higher-order many-body effects, that are necessary for obtaining a qualitative and accurate description of satellite states. These strategies are based on (1) the inclusion of higher order terms in the perturbative expansion and (2) applying higher order excitations in the so-called inner part of the coupled-cluster Green's function. In particular, a new "(n+1) rule" for forming CC Green's function has been formulated to increase the accuracy needed for proper locations of poles without increasing the excitation level in the ground-state CC Ansatz. Finally, we will outline active-space strategies to improve the quality of Green's function in pre-defined energy windows as well as novel numerical strategies to represent CC Green's function on the entire complex plane. The main numerical challenge in the GFCC calculation is related to the need of solving a large number of linear equations that describe the properties of the Green's function approach associated with the connected nature of the corresponding diagrammatic expansion. On the other hand, the linear character of the underlying equations is an ideal target for highly efficient parallel implementation.

Grant Numbers and Grant Titles

This work was supported as part of the Computational Chemical Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division in the Center for Scalable and Predictive methods for Excitations and Correlated phenomena (SPEC) at Pacific Northwest National Laboratory.

Postdoc(s):

Dr. Bo Peng (PNNL Linus Pauling post-doctoral fellow)
Dr. Nicholas Bauman (joining on May 21, 2018)

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

1. Bo Peng, Karol Kowalski, "Green's function coupled-cluster approach: simulating spectral functions for molecular systems," *J. Chem. Theory Comput.* (submitted, 2018)
2. Karol Kowalski, "Properties of coupled-cluster equations originating in excitation sub-algebras," *J. Chem. Phys.* **148**, 094104 (2018).

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

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I. Program Scope

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

II. Recent Progress (2015 – 2017 and January 1 – April 15, 2018)

Our research in the reporting period has consisted of two distinct and yet closely related parts, namely, **(1)** development of new generations of *ab initio* electronic structure approaches exploiting the exponential CC ansatz, which has been accompanied by substantial programming work and benchmark calculations, and **(2)** applications of new and existing quantum chemistry approaches to ground and excited-state molecular potential energy surfaces, followed by time-dependent dynamics simulations, singlet-triplet and singlet-singlet gaps in biradical and prototype magnetic species, photoelectron spectra of transition metal nanoparticles, and structural and electronic properties of metal clusters.

In the area of new *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 in Refs. [1,2,6,7,10], by focusing on the CC(P;Q) formalism. The CC(P;Q) theory and the generalized moment expansions that define it, which were originally proposed 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)], enable one to contemplate a wide variety of 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 biradical systems that agree with the parent full CCSDT data to within small fractions of a millihartree at a tiny fraction of the computational cost, to the CC(t,q;3), CC(t,q;3,4), and CC(q;4) models including connected quadruple excitations [6,10]. By examining the double dissociation of water, insertion of Be into H_2, and singlet–triplet gap in $(HFH)^-$, we demonstrated that the CC(t,q;3) and CC(t,q;3,4) approaches, especially the latter one, reproduce the exact, full CI, or virtually exact, CCSDTQ, total and relative energies to within small fractions of a millihartree at tiny fractions of the computational effort involved in the parent CCSDTQ calculations, even when electronic quasi-degeneracies are substantial. Paper [10] extended these studies by examining the performance of CCSD, CCSD(T), CCSD(2)$_T$, CR-CC(2,3), CCSDt, CC(t;3), CCSDT, CCSD(TQ), CR-CC(2,4), CCSDtq, CC(t,q;3), CC(t,q;3,4), CCSDTq, CC(q;4), and CCSDTQ in describing the challenging potential energy curve and vibrational term values of the beryllium dimer. 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(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 results, outperform the analogous approaches correcting CCSD in faithfully reproducing the results obtained with their respective CCSDT and CCSDTQ parents. For example, it is hard to distinguish between the CC(q;4) and CCSDTQ potential energy curves and vibrational term values. We also 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 of Be_2, including states near the dissociation threshold, to within ~1 cm^{-1} (5 cm^{-1} at worst). Other examples of a successful exploitation of the CC(*P*;*Q*) methodology can be found in Refs. [2,7,9]. In particular, Ref. [7] takes advantage of our CC(t;3) and CCSDT codes to examine the performance of a novel geminal-based approach, abbreviated as EERPA-GVB, in calculations of intermolecular potentials involving monomers with stretched intramonomer covalent bonds, where one has to capture weak long-range and strong non-dynamic correlations at the same time, as in the challenging $NH_3 \ldots F_2$ complex, where we dissociated the F–F bond in F_2, and the strongly correlated $H_{12} \ldots H_{12}$ dimer, in which we stretched all H–H bonds in the linear H_{12} chains (as in models of metal-insulator transitions). Another work, where we benefitted from the CC(t;3) methodology, was a collaboration with Professor Donald Truhlar, where we computed the equilibrium geometries, binding energies, adiabatic ionization potentials, and adiabatic electron affinities for $Mg_n^{0,\pm1}$ clusters with $n = 1 - 7$ using 39 exchange-correlation functionals in Kohn-Sham density functional theory (DFT) and several CC methods with singles, doubles, and triples, including CCSD(T) for all species, CCSD(2)$_T$ and CR-CC(2,3) for species with n = 1–3, and CCSDt, CC(t;3), and CCSDT for species with n = 1 and 2 [2]. We demonstrated that the geometry and binding energy of the weakly bound Mg_2 dimer requires a robust treatment of connected triple excitations, represented by CR-CC(2,3), CC(t;3), and CCSDT, which are more accurate than the popular CCSD(T) approach, although CCSD(T) is sufficiently accurate for larger Mg clusters. We also showed that hybrid functionals, especially PW6B95, SOGGA11-X, M11, and PWB6K, are more accurate than the local ones.

Progress in the development of the CC(*P*;*Q*) methodology reported in Refs. [6,10] is undoubtedly substantial, but our utilization of the CC(*P*;*Q*) framework in proposing a radically new way of obtaining accurate energetics equivalent to high-level CC (CCSDT, CCSDTQ, etc.) calculations by merging the CC(*P*;*Q*) formalism with the stochastic configuration interaction (CI) Quantum Monte Carlo (QMC) and CC Monte Carlo (MC) ideas, described in Ref. [9], represents a much larger breakthrough. According to one of the reviewers of Ref. [9], 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 typically ends up with highly complex systems of algebraic equations, whose solution requires enormous computer power, or turn to stochastic wave function sampling using, as in QMC. In Ref. [9], we propose a third-way, namely, use the stochastic methods, based on propagating the wave function in the many-fermion Hilbert space, to identify the leading wave function components and the deterministic CC computations, combined with CC(*P*;*Q*) corrections, to provide the rest of the information. As shown in Ref. [9] and a longer paper presently in preparation, independent of the type of the Monte Carlo sampling, the convergence toward target CC energetics (so far, we have tried full CCSDT and CCSDTQ) is rapid, already in the early stages of the Monte Carlo wave function propagations, even when higher-order correlation effects and electronic quasi-degeneracies become substantial, accelerating high-level CC calculations by one or more orders of magnitude and freeing us from relying on user and system dependent concepts, such as active orbitals.

Other significant advances in the area of new CC and EOMCC methods were reported in Refs. [5,8], where we continued our work on extending the active-space EOMCC theories to the doubly electron-attached (DEA) formalism applicable to open-shell species with two electrons outside the closed-shell cores, especially the electronic spectra of biradicals and single bond breaking, without invoking complicated steps of multi-reference CC theories. In particular, following our 2013 and 2014 studies [J. Shen and P. Piecuch, *J. Chem. Phys.* **138**, 194102 (2013); *Mol. Phys.* **112**, 868 (2014)], we demonstrated that the nearly exact DEA-EOMCC approach with up to 4-particle–2-hole (4*p*-2*h*) excitations can be extended to a much less expensive model, in which both 3*p*-1*h* and 4*p*-2*h* terms, not just the latter ones, are selected using active orbitals [5]. By examining the low-lying singlet and triplet states of the methylene, $(HFH)^-$, trimethylenemethane, cyclobutadiene, and cyclopentadienyl cation biradicals and bond breaking in F_2, we showed that the DEA-EOMCC methods with an active-space treatment of 3*p*-1*h* or 3*p*-1*h* and 4*p*-2*h* excitations reproduce the results of the analogous parent calculations, in which these excitations are treated fully, at the small fractions of the computational effort and with virtually no loss in accuracy. We also demonstrated that the DEA-EOMCC methods with the active-space treatment of 3*p*-1*h* and 4*p*-2*h* or 4*p*-2*h* excitations considerably improve the DEA-EOMCC theories truncated at 3*p*-1*h* excitations, while making the results almost insensitive to the type of molecular orbitals (MOs) used in the calculations [5]. The latter observation should be contrasted with the DEA/DIP-EOMCC methods truncated at 3*p*-1*h*/3*h*-1*p* excitations, which can be quite sensitive to the choice of MO basis. We also published a paper in collaboration with Professors Laura Gagliardi and Donald Truhlar, in which our converged DEA-EOMCC values of the singlet–triplet gaps in a series of antiaromatic molecules, including cyclobutadiene and its derivatives and cyclopentadienyl cation, provided definitive information for benchmarking CASPT2 and RASPT2, allowing us to develop compact active spaces that can be extended to larger biradicals [8].

We also continued working on the previously developed ionized (IP) EOMCC methodologies. For example, we used the scalar relativistic IP-EOMCC approaches to provide an accurate and complete assignment of peaks and other key features in the experimental photoelectron spectra of Ag_3^- nanoparticle, including electron binding energies as high as about 6.5 eV, for the first time [3]. In analogy to our earlier study of the photoelectron spectrum of Au_3^- [N.P. Bauman, J.A. Hansen, M. Ehara, and P. Piecuch, *J. Chem. Phys*. **141**, 101102 (2014)], we demonstrated that one has to correlate semi-core electrons, in addition to the valence ones, use larger basis sets, and include the high-order 3*h*-2*p* effects to obtain meaningful results. We also showed that geometry relaxation during electron ejection from Ag_3^- contributes to the peak widths, in addition to multiple electronic states behind a given spectral feature.

We continued developing, testing, and applying the older CR-CCSD(T) and CR-EOMCCSD(T) and the more recent CR-CC(2,3) and CR-EOMCC(2,3) approaches. In particular, we examined vertical excitation energies for a comprehensive test set of about 150 singlet excited states of 28 medium-size organic molecules to benchmark two variants of the approximately size-intensive δ-CR-EOMCCSD(T) method and the analogous two variants of the newer, rigorously size-intensive, δ-CR-EOMCC(2,3) approach based on the biorthogonal moment expansions against the previously published CASPT2, CC3, and EOMCCSDT-3 results and the so-called theoretical best estimate (TBE) values [P. Piecuch, J.A. Hansen, and A.O. Ajala, *Mol. Phys.* **113**, 3085 (2015)]. We demonstrated that the non-iterative triples corrections to the EOMCCSD excitation energies defining the relatively inexpensive, single-reference, black-box δ-CR-EOMCC approaches provide significant improvements in the EOMCCSD data, while closely matching the results of the iterative and considerably more expensive CC3 and EOMCCSDT-3 calculations and their CASPT2 and TBE counterparts, proving the utility of the cost effective δ-CR-EOMCC methods in applications involving molecular electronic spectra. Our δ-CR-EOMCC approaches were also used to characterize about 50 additional excited states, including several states having substantial two-electron excitation components, which have not been found in the earlier studies. We uncovered a relationship between the reduced excitation level diagnostic obtained with EOMCCSD, introduced by our group in 2005, and the magnitude of the δ-CR-EOMCC triples corrections to the EOMCCSD excitation energies, allowing us to estimate the effect of triples on the EOMCCSD results solely on the basis of EOMCCSD calculations. We are preparing a paper, which shows that further improvements in the CR-EOMCC(2,3) excited-state data can be made if we replace the CR-EOMCC corrections by their CC(t;3) counterparts. We performed the unprecedented CR-CC(2,3), active-space CCSDt, EOMCCSD, and multireference CI computations for the low-lying singlet and triplet states of the challenging organic biradical, 1,2,3,4-cyclobutanetetraone, which present major problems to the existing single- and multi-reference wave function and DFT approaches [1]. In collaboration with Professor Weston Thatcher Borden, we provided a definitive state ordering, showing that the ground state is a triplet, and obtained a very good agreement with the negative ion photoelectron spectroscopy measurements of the tiny singlet-triplet gap.

Finally, in collaboration with Professor Marcos Dantus, we revisited the classic problem of the femtosecond transition-state spectroscopy of sodium iodide, taking advantage of modern lasers and pulse-shaping to better map the low-lying electronic states, some forming predissociative wells through curve crossings. Our contribution to the project, reported in Ref. [4], was to carry out high-level *ab initio* multi-reference CI calculations including spin-orbit coupling terms and using very large correlation-consistent basis sets to arrive at very accurate ground- and excited-state potential energy curves of NaI. We then used the density matrix calculations employing vibrational wave functions determined from our *ab initio* X 0^+ and A 0^+ potentials to simulate time-dependent wave packet dynamics of NaI pumped to the A 0^+ state, obtaining perfect agreement with the experimental data obtained by Professor Dantus' group [4].

III. Future Plans

Our future method development will focus on **(i)** continuation of our work on the CC(P;Q) formalism, with emphasis on combining the deterministic CC(P;Q) and stochastic CIQMC and CCMC ideas, **(ii)** extension of approximate coupled-pair theories for strongly correlated systems to higher-order dynamical correlations, **(iii)** extension of the active-space variants of the EA/IP and DEA/DIP EOMCC methodologies to the triply electron-attached (TEA) and triply ionized (TIP) cases, and **(iv)** highly parallel, linear scaling, local correlation CC codes exploiting the previously developed cluster-in-molecule (CIM) ideas and their multi-level extensions. As in the past, all of the proposed methodological advances will be accompanied by code distribution through GAMESS as well as benchmark and realistic computations, especially those that can be tied to the ongoing experimental work in small molecule spectroscopy and dynamics, elementary chemical reactions, catalysis, photoelectron spectroscopy, and photochemistry.

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

[1] J.A. Hansen, N.P. Bauman, J. Shen, W.T. Borden, P. Piecuch, "*Ab Initio* Coupled-Cluster and Multi-Reference Configuration Interaction Studies of the Low-Lying Electronic States of 1,2,3,4-Cyclobutanetetraone," *Mol. Phys.* **114**, 695-708 (2016).

[2] K. Duanmu, O. Roberto-Neto, F.B.C. Machado, J.A. Hansen, J. Shen, P. Piecuch, D.G. Truhlar, "Geometries, Binding Energies, Ionization Potentials, and Electron Affinities of Metal Clusters: $\mathrm{Mg}_n^{0,\pm1}$, $n = 1 - 7$," *J. Phys. Chem. C* **120**, 13275-13286 (2016).

[3] N.P. Bauman, J.A. Hansen, P. Piecuch, "Coupled-Cluster Interpretation of the Photoelectron Spectrum of Ag_3^-," *J. Chem. Phys.* **145**, 084306-1 – 084306-9 (2016).

[4] G. Rasskazov, M. Nairat, I. Magoulas, V.V. Lozovoy, P. Piecuch, M. Dantus, "Femtosecond Real-Time Probing of Reactions MMXVII: The Predissociation of Sodium Iodide in the A 0^+ State," *Chem. Phys. Lett.* **683**, 121-127 (2017).

[5] A.O. Ajala, J. Shen, P. Piecuch, "Economical Doubly Electron-Attached Equation-of-Motion Coupled-Cluster Methods with an Active-Space Treatment of Three-Particle–One-Hole and Four-Particle–Two-Hole Excitations," *J. Phys. Chem. A* **121**, 3469-3485 (2017).

[6] N.P. Bauman, J. Shen, P. Piecuch, "Combining Active-Space Coupled-Cluster Approaches with Moment Energy Corrections via the CC(P;Q) Methodology: Connected Quadruple Excitations," *Mol. Phys.* **115**, 2860-2891 (2017).

[7] E. Pastorczak, J. Shen, M. Hapka, P. Piecuch, K. Pernal, "Intricacies of van der Waals Interactions in Systems with Elongated Bonds Revealed by Electron-Groups Embedding and High-Level Coupled-Cluster Approaches," *J. Chem. Theory Comput.* **13**, 5404-5419 (2017).

[8] S.J. Stoneburner, J. Shen, A.O. Ajala, P. Piecuch, D.G. Truhlar, L. Gagliardi, "Systematic Design of Active Spaces for Multi-Reference Calculations of Singlet–Triplet Gaps of Organic Diradicals, with Benchmarks against Doubly Electron-Attached Coupled-Cluster Data," *J. Chem. Phys.* **147**, 164120-1 – 164120-12 (2017).

[9] J.E. Deustua, J. Shen, P. Piecuch, "Converging High-Level Coupled-Cluster Energetics by Monte Carlo Sampling and Moment Expansions," *Phys. Rev. Lett.* **119**, 223003-1 – 223003-5 (2017).

[10] I. Magoulas, N.P. Bauman, J. Shen, P. Piecuch, "Application of the CC(P;Q) Hierarchy of Coupled-Cluster Methods to the Beryllium Dimer," *J. Phys. Chem. A* **122**, 1350-1368 (2018).

Maria Victoria Fernandez-Serra

More Efficient & Accurate DFT-based Dynamics via Machine Learning

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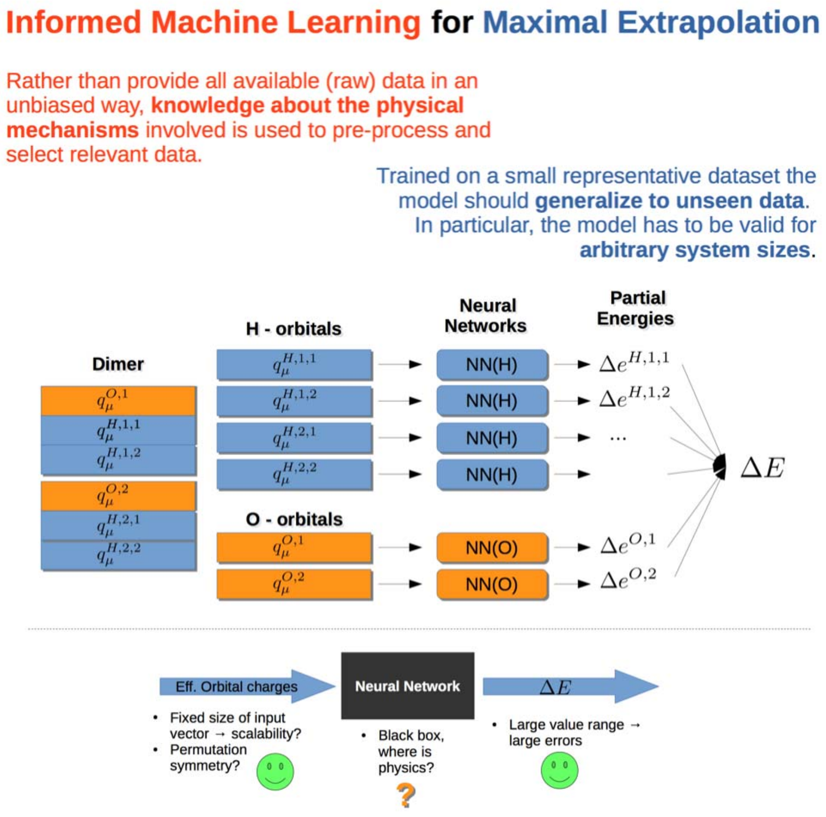
Abstract

In recent years a lot of progress has been made in the study of water and its different phases. Empirical methods are progressing to the point of being better than first principle methods, thanks to the unlimited degrees of freedom allowed in more and more complex force fields and the availability of better accurate data. These methods are however limited in their scope, and completely incapable of being generalized or of treating reactive environments. At the ab-initio level, to reach chemical accuracy, one often has to rely on hybrid functionals, thereby limiting the size of systems for which simulations are feasible. Several attempts have been made in the past to solve this problem. Most approaches try to re-parametrize the exchange part of the generalized gradient approximation (GGA) functional. However, it turns out that one of the main deficiencies of GGA, namely its self-interaction error, places an upper bound on the accuracy of these techniques.



Informed Machine Learning for Maximal Extrapolation

Rather than provide all available (raw) data in an unbiased way, **knowledge about the physical mechanisms** involved is used to pre-process and select relevant data.

Trained on a small representative dataset the model should **generalize to unseen data**. In particular, the model has to be valid for **arbitrary system sizes**.

We propose a new method that uses artificial neural networks (ANN) to improve DFT calculations of water. Given our model's flexibility, we are able to correct the self-interaction error made by GGA functionals and accurately reproduce total energies for a variety of systems. We show that the ANN can be trained both using the density matrix and the real space density, and that it can work both for total energy and forces. As our ANN only relies on the local charge density around a single molecule, the model scales to arbitrary system sizes, in spite of being trained only on small systems of up to three molecules. The methodology using the real space density is basis set independent and can be easily ported between different electronic

structure codes. We further show that our model does not only improve pair correlation functions for liquid water but that it can also be potentially used in situations which empirical force fields fail to describe correctly, such as heterogeneous systems or reactive environments.

Extending on the idea of using an ANN to correct for DFT errors, we also show that it can be used to correct less converged calculations (smaller basis sets). This allows us to transform perform "quick and dirty" calculations with the accuracy of well converged simulations. We explore this in situations where sampling in time and size is critical such as the electrochemical interface.

Award Number: DE-SC0001137
Title: Development and Application of Methods for understanding Interfacial Charge Transfer in Photocatalytic Water Splitting Materials**Postdoc(s):** First M. Last

Student(s): Sebastian Dick, Vidushi Sharma.

Scope and Future progress: The project aims to study water/solid functional interfaces (photocatalytic materials and metallic electrodes for electrochemistry) using state of the art density functional thery-based methods. Among the current directions being pursued by the PI's research group we highlight charge transfer reactions at water/oxide interfaces modeled suing non adiabatic ab initio molecular dynamics within the time dependent DFT formalism and Ehrenfest dynamics.

We are also working on making ab initio molecular dynamics simulations of these interfaces more efficient without losing accuracy. Our goal is to be able to perform simulations at the quantum mechanic atomistic level for large systems using a global interface that does not rely on either coarse graining or changing between different codes using workflows. The study aims to go from proof of concept simulations to actual scientific results. For this we have chosen the water/Au interface as our model system.

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

- **Bias-dependent local structure of water molecules at a metallic interface,** Luana S. Pedroza, Pedro Brandimarte, Alexandre Reily Rocha, Marivi Fernandez-Serra, Chem. Sci., 2018, Advance Article
- **Insights into the Structure of Liquid Water from Nuclear Quantum Effects on the Density and Compressibility of Ice Polymorphs,** Betül Pamuk , P. B. Allen, and M.-V. Fernández-Serra, The Journal of Physical Chemistry B Article ASAP DOI: 10.1021/acs.jpcb.8b00110
- **Unveiling two types of local order in liquid water using machine learning,** Adrian Soto, Deyu Lu, Shinjae Yoo,and Marivi Fernandez-Serra, submitted (2017)
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Open Chemistry: Interactive Data Analytics Platform for Simulations and Experiment

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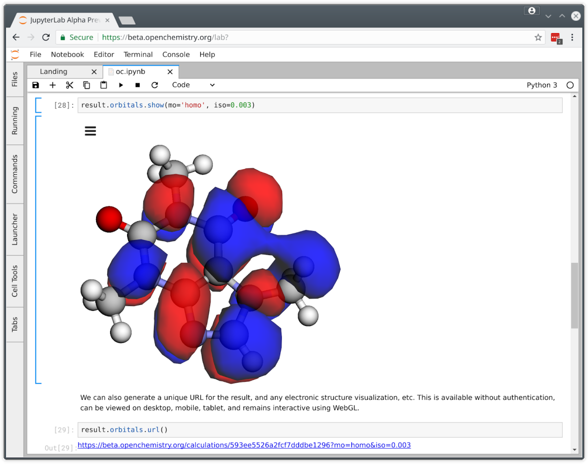
Abstract

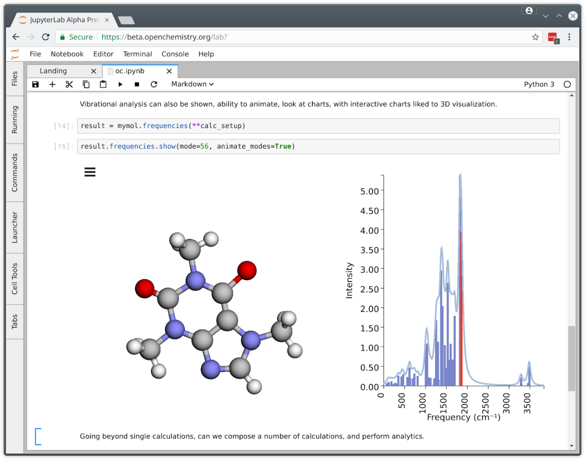
The development of open, interactive interfaces employing data-centric workflows have been developed, reusing best-of-breed open source software in order to deliver an integrated platform for knowledge discovery. The Jupyter project offers a powerful electronic notebook interface, with server-side software kernels executing Python code. The JupyterLab web frontend provides a web-based interface with interactive cells where code can be edited, and panels where data can be visualized in various ways. Coupling these interfaces with a powerful data server, capable of triggering simulations, analyses, and other workflows offers a powerful capability to seamlessly execute codes from a pre-configured environment.



```
[28]: result.orbitals.show(mo='homo', iso=0.003)
```

We can also generate a unique URL for the result, and any electronic structure visualization, etc. This is available without authentication, can be viewed on desktop, mobile, tablet, and remains interactive using WebGL.

```
[29]: result.orbitals.url()
Out[29]: https://beta.openchemistry.org/calculations/593ee5526a2fcf7dddbe1296?mo=homo&iso=0.003
```



Vibrational analysis can also be shown, ability to animate, look at charts, with interactive charts liked to 3D visualization.

```
[14]: result = mymol.frequencies(**calc_setup)
[15]: result.frequencies.show(mode=56, animate_modes=True)
```

Going beyond single calculations, can we compose a number of calculations, and perform analytics.

Extension of the Python software kernels and web interface with chemistry specific capabilities results in a software environment as shown above. The Phase I project resulted in a deployed demonstration capability on a commercial cloud provider and at NERSC using Cori. The NWChem code has been integrated, and can be used to trigger computational jobs, which are run interactively or can be found at a later time from identifiers embedded in the notebooks. The data server has a second single-page interface offering a unique web link for a given record/visualization that reuses the same web components displayed in the JupyterLab cells.

As the project moves into Phase II a powerful software platform will be developed focusing on five major areas: data/metadata, server platform, Jupyter integration, web application, and extending desktop/command-line tools to interact with the server. In collaboration with MolSSI a JSON specification is being developed for quantum chemistry data, with plans to offer a binary representation and mapping to semantic representations. Support for a greater range of codes will be added, with increasingly advanced workflows supporting coupled with analytics and machine learning in the browser.

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

Grant number: DE-SC0017193

Molecular absorption properties with DFT and beyond

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Abstract

The properties of molecular systems calculated within density functional theory vary substantially depending on the choice of the exchange-correlation functional. We have been working on implementation of some of the recent developments in functionals as well as methods with applications toward photo driven processes. The goal is to examine the light harvesting and spin state properties of molecular systems. We have been working on the implementation and applications of the Fermi-Lowdin orbital method for self-interaction correction. The self-interaction correction is done on a orbital by orbital basis following the Perdew-Zunger approach. Moreover, the local orbitals used for the construction of the self-interaction correction potential depend on a set of descriptor positions which need to be varied to find the energy variationally. As a result this approach requires significantly larger computational resources and time compared to pure DFT applications.

The chromophores used in organic light harvesting systems typically are conjugated molecules. The polarizability of the conjugated molecules is generally not well-described using DFT. The reasons are delocalization errors that occur in DFT. We have carried out calculations on the polarizabilities of the first and second row atoms and a few molecules with conjugated bonds. These calculations are done by applying an electric field which leads to changes in the dipole of the system and the polarizabilties are derived from the finite difference derivatives of the dipole moments. The atomic calculations in DFT are generally done approximating the atom to have a spherical electron cloud. However within the Fermi-Lowdin scheme this approximation cannot be applied. Therefore, for the nonspherical atoms and the molecules the electric field is applied from different directions to capture the response of the non-spherical electron density. We have also noticed that the convergence of the SCF cycle for calculations with SIC can be hard to achieve for some directions of the electric field. We have decent agreement with experimental values of polarizabilities for the first and second row atoms. Similar calculations are also carried out for a set of polycyclic aromatic chromophores starting from benzene to pentacene. The polarizability values calculated within the local density approximation with SIC show similar deviation from experiment as the PBE results. This result has prompted us to look at the delocalization errors in these systems within the self-interaction scheme. The delocalization error leads to smaller ionization potential of molecular systems. We have calculated the ionization potential of the polyacenes with different approximations as well as including the self-interaction correction. The results show an interesting trend with the Fermi-Lowdin orbital based SIC scheme. The ionization potentials calculated from the eigenvalues of the HOMO showed higher values compared to that obtained from the delta-SCF of cation and the neutral. The standard PBE-GGA ionization energies show delocalization errors with increasing deviation with respect to experimental numbers. On the other hand, the use of self-

interaction corrected density with LDA functional produced high quality results indicating that the errors in these systems are due to the errors in the self-consistent density produced by the LDA functional.

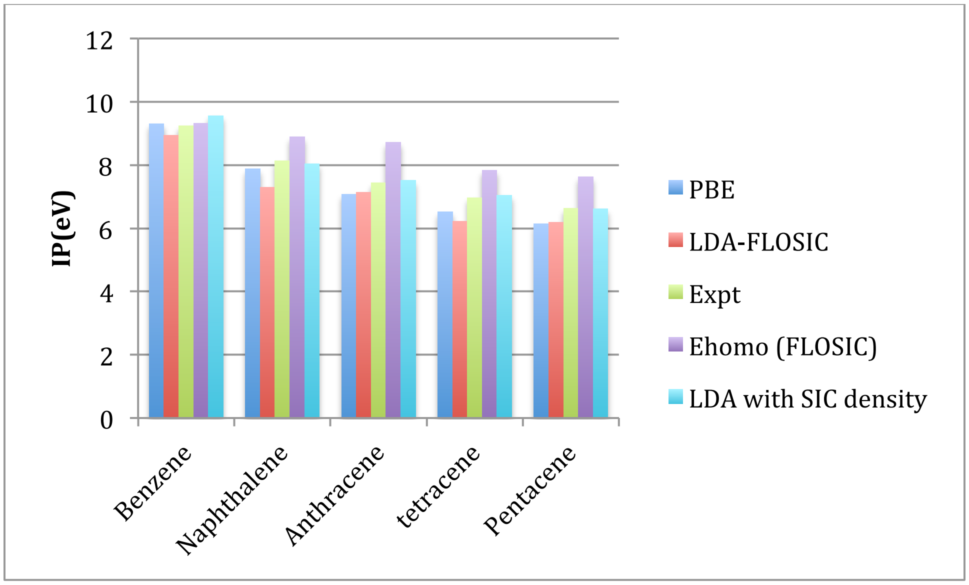

Fig.1 : The ionization potential of polyacenes in eV.

DE-SC0002168: DFT based methods for light harvesting molecules

Postdoc(s): Yoh Yamamoto

Student(s): Sharmin Akter

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Quantum Mechanical Evaluation of Alternative Photovoltaic Materials

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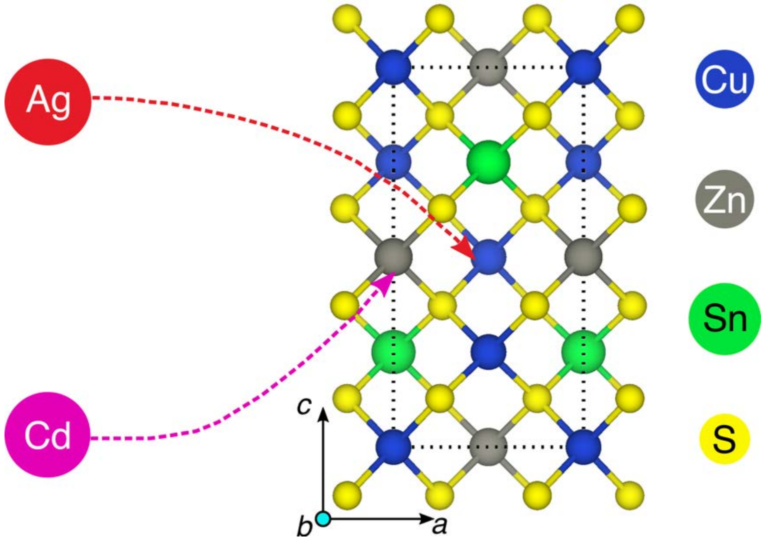
Abstract

Although silicon solar cells currently claim dominant market share for sunlight-to-electricity conversion devices, it is incumbent on the materials chemistry community to explore other materials and device configurations that could be less expensive and less environmentally harmful to produce, as well as potentially more efficient at energy conversion. This poster will present recent theoretical work aimed at accurate evaluation of key materials properties associated with optimizing alternative photovoltaic materials components, with specific focus on Cu_2ZnSnS_4 (CZTS)-based solar cells, which constitute an inexpensive, beyond-Si photovoltaic (PV) technology. CZTS cells often suffer from low open-circuit voltage and efficiency, attributed to disorder in the Cu and Zn sub-lattices, caused by anti-site defects, of the kesterite structure. One strategy hypothesized to reduce disorder within CZTS is to employ isovalent dopants, such as Cd^{2+} and Ag^{+} for Zn^{2+} and Cu^{+}, respectively, given that experiments (*ACS Energy Lett.* 2016, **1**, 1256 and *Chem. Mater*. 2016, **28**, 5821) have shown improved open-circuit voltage and efficiency in Cd- or Ag-doped cells. Nevertheless, the fundamental driving force for performance improvements in doped CZTS cells remains unclear. Using calculations based on density functional theory (DFT) thermodynamics to study bulk stability, defect, and surface energetics, as well as the electronic structure of Cd and Ag-doped CZTS, we find that Cd and Ag increase efficiency via contrasting mechanisms, depending on the dopant concentration and Cu-content used during synthesis. For example, Cd (Ag) stabilizes the lower (higher) band gap stannite (kesterite) structure at high concentrations. Low Ag (Cd) doping inhibits the formation of detrimental anti-site defects under high (all) Cu concentrations used during synthesis. Finally, we suggest the exploration of alternate abundant, non-toxic, isovalent dopants to improve the performance of CZTS.



The rest of this abstract provides further details regarding the work above, as well as recent theoretical advances in embedding methods published this past year that will enable future treatment of, e.g., excited states in semiconductors.

Quantum embedding theory provides an efficient means to obtain accurate electronic energies for systems too large for full-scale, high-level quantum calculations (for a recent review of our methods, see doi: 10.1002/9781119129271.ch2). It adopts a hierarchical approach that divides the total system into a small embedded region and a larger environment, using different levels of theory to describe each part. Previously, we developed a density-based quantum embedding theory called density functional embedding theory (DFET), which achieved considerable success for metals and semiconductors. More recently, we extended DFET into a density-matrix–based nonlocal form, enabling DFET to study the stronger quantum couplings between covalently bonded subsystems. We denote this theory density-matrix functional embedding theory (DMFET), and we demonstrated its performance in test examples that resemble various real applications in both chemistry and biochemistry. DMFET yields excellent results in all cases tested thus far, including for isomerization energies, proton transfer energies, and highest occupied molecular orbital–lowest unoccupied molecular orbital gaps for local chromophores (*Proc. Natl. Acad. Sci. USA.* 2017, **114**, E10861).

Apart from DFET, our potential functional embedding theory (PFET) also can be used to perform embedding calculations. While DFET provides a fast but non-self-consistent density-based embedding scheme, PFET offers a more rigorous theoretical framework to perform fully self-consistent, variational correlated wave function (CW)/DFT calculations. When originally presented, PFET was only tested at the DFT/DFT level of theory as a proof of principle within a planewave (PW) basis. In a two-part series (*J. Chem. Theor. Comp.* 2017, **13**, 1067 and *J. Chem. Theor. Comp.* 2017, **13**, 1081), we demonstrated that PFET can be made to work well with mixed Gaussian type orbital (GTO)/PW bases and then we performed calculations at the CW/DFT level, comparing them to DFET and full CW benchmarks. We tested the performance of PFET at the CW/DFT level for a variety of types of interactions (hydrogen bonding, metallic, and ionic). By introducing an intermediate CW/DFT embedding scheme denoted DFET/PFET, we showed how PFET remedies different types of errors in DFET, serving as a more robust type of embedding theory. We now turn to updates on our efforts characterizing and optimizing the low-cost solar cell material, CZTS; this work has been submitted for publication.

To understand the origins of efficiency improvements in Ag- and Cd-doped CZTS cells, we calculated the bulk, defect, and surface energetics of Cu_2ZnSnS_4 using DFT. Specifically, we began by using the strongly constrained and appropriately normed (SCAN) functional for describing the electronic exchange-correlation (XC) for all bulk and defect calculations, since SCAN satisfies all 17 known constraints for the behavior of an XC functional (*Phys. Rev. Lett.* 2015, **115**, 36402), unlike the generalized gradient approximation (GGA). We also benchmarked the SCAN-predicted formation enthalpies of binary Cu-, Zn-, Sn-, Cd-, and Ag-sulfides and the lattice parameters of layered-SnS_2 and kesterite-Cu_2ZnSnS_4 against experimental values and found fair agreement between SCAN-predicted and experimental quantities.

Notably, our benchmarking indicates that SCAN does not predict band gaps of semiconductors accurately, with a calculated eigenvalue gap of ~0.13 eV and ~0.05 eV for kesterite and stannite Cu_2ZnSnS_4, respectively. These values are significantly lower than those reported experimentally (~ 1.4 – 1.6 eV) and theoretical values employing advanced many-body methods (1.64 – 1.33 eV). Indeed, the performance of SCAN is of similar quality to GGA, which is well known for underestimating band gaps of semiconductors for the case of kesterite and stannite Cu_2ZnSnS_4. Therefore, we used GGA+*U* calculations to perform qualitative comparisons of band gaps in the kesterite and stannite structures with Cd- and Ag-doping. We use *U*-values derived from embedded Hartree-Fock calculations, namely 3.6 eV for Cu, 4.5 eV for Zn, and 4.8 eV for Sn (*J. Chem. Phys.* 2014, **140**, 121105). In the case of Ag- and Cd-doping, we used the *U* values derived for Cu and Zn, respectively, to be consistent in describing the electronic structure of Cu/Ag and Zn/Cd pairs. Also, we calculated surface energies in pure, Cd-doped and Ag-doped Cu_2ZnSnS_4 by using GGA+*U* instead of SCAN in order to directly compare with previous calculations that have used GGA+*U* to estimate cleavage energies in the Cu_2ZnSnS_4 system (*Chem. Mater.* 2015, **27**, 2920).

For evaluating defect formation energies, we considered three scenarios that constrain the chemical potentials involved. (*i*) Cu-rich: Cu_2ZnSnS_4 is in equilibrium with metallic Cu. Since Zn-rich and Sn-rich conditions during Cu_2ZnSnS_4 are preferred during synthesis, we constrain the Zn and Sn chemical potentials to be in equilibrium with ZnS (Zn-rich) and SnS (Sn-rich) phases, respectively. (*ii*) Constrained Cu-poor: the lowest Cu-chemical potential that Cu_2ZnSnS_4 can attain while ensuring equilibrium with both ZnS and SnS). The Zn and Sn chemical potentials therefore are constrained in this scenario. (*iii*) Cu-poor: the most negative Cu-chemical potential of Cu_2ZnSnS_4 without any constraints being placed on the chemical potentials of the other species (Zn, Sn, S, and Cd/Ag). In the case of Cd- and Ag-doping, we consider the Cd- and Ag-containing phases exhibiting the highest possible Cd and Ag chemical potentials, respectively, while in equilibrium with Cu_2ZnSnS_4 for each of the aforementioned conditions.

In the case of Cd-doping, Cd clearly prefers the occupation of Zn- over Cu-sites in the kesterite structure, as indicated by the lower formation energy for Cd_{Zn} anti-sites (~ 0.12 eV) rather than for Cd_{Cu} anti-sites (~ 1.21 – 1.4 eV). Importantly, Cd inhibits disorder only at low doping concentrations, as indicated by the higher energy to form disordering anti-sites (~ 0.32 – 0.62 eV) rather than undoped Cu_2ZnSnS_4 (~ 0.22 – 0.25 eV). At higher Cd-content, the stannite structure becomes increasingly stable alongside an increasing tendency of the kesterite to disorder. Additionally, Cd-doping is expected to decrease the overall band gap of both the kesterite and stannite polymorphs. Thus, the contrasting behavior of Cd at low- and high-doping levels indicates that there will be a specific, low Cd-concentration at which Cu_2ZnSnS_4 will achieve peak efficiency and V_{oc}, in agreement with experimental observations of maximum efficiency at ~ 5% Cd-doping (*Chem. Mater.* 2016, **28**, 5821).

In Ag-doped Cu_2ZnSnS_4, the site preference of Ag is sensitive to the chemical potential of Cu within the kesterite structure. For example, under Cu-poor conditions, Ag^+ can be doped either on Cu^+ (isovalent anti-site) or on Zn^{2+} (*p*-type) sites, as indicated by comparable Ag_{Cu} (~ 0.14 eV) and Ag_{Zn} (~ 0.03 eV) formation energies. Doping of Ag within Cu_2ZnSnS_4 therefore is highly sensitive to Cu-conditions during synthesis. Additionally, at low Ag-doping levels and especially under Cu-poor conditions, Ag does not suppress cation disorder within the kesterite structure, as indicated by the low formation energy of disorder-inducing anti-sites (~ 0.14 eV) compared to undoped Cu_2ZnSnS_4 (~ 0.22 – 0.25 eV). Note that low Ag-doping can suppress disorder at higher Cu chemical potentials (higher formation energies of ~ 0.34 – 0.78 eV from constrained Cu-poor to Cu-rich conditions). Thus, low levels of Ag-doping may not be an effective strategy to improve the performance of Cu_2ZnSnS_4 cells since Ag requires Cu-rich conditions to suppress disorder, which disfavors the formation of Vac_{Cu} and the retention of *p*-type behavior in Cu_2ZnSnS_4. Notably, Ag-substitution in Cu_2ZnSnS_4 stabilizes the kesterite structure, in addition to increasing the band gap of both the kesterite and stannite polymorphs. Altogether, increased disorder at low Ag-concentrations versus increased band gap in kesterite may be the origin of the peak efficiency and V_{oc} typically observed in low Ag-doped samples (*ACS Appl. Mater. Interfaces* 2017, **9**, 21243). Interestingly, Ag is more effective at reducing disorder in the kesterite at higher Ag-concentrations within the structure, as indicated by higher formation energies of disorder inducing anti-sites (~ 0.30 – 0.45 eV), across Cu chemical potentials. Hence, the effectiveness of Ag in improving the efficiency of a Cu_2ZnSnS_4-based solar cell will be highly dependent on the synthesis conditions, specifically on the concentration of Ag being doped and the Cu-content used during synthesis.

Coincidentally, at low levels of doping, both Cd and Ag inhibit lattice disorder within kesterite under constrained Cu-poor conditions. This is in qualitative agreement with experimental observations of maximum efficiency resulting from using Cu-poor, Zn-rich, and Sn-rich conditions during Cu_2ZnSnS_4 synthesis. Interestingly, Cd and Ag stabilize different polymorphs despite both ions being isovalent dopants (for Zn and Cu, respectively) and being significantly larger than the ions they replace, which may be attributed to a combination of electrostatic and steric effects. Notably, we did not consider the effect of selenization in combination with Ag- or Cd-doping in Cu_2ZnSnS_4. Previous experimental studies have shown that conditions employed during the selenization process (~500 ^{o}C) can result in particle coarsening of the as-synthesized Cu_2ZnSnS_4. Since we do not observe notable changes (0.1% – 2%) in the energies of the (110) and (112) surfaces of the kesterite with Cd-doping while finding a significant decrease (31% – 48%) in the (110) and (112) surfaces with Ag-doping, we speculate that the particle coarsening reported in both Cd- and Ag-doped is due to the annealing conditions during the selenization process rather than any effect due to the dopants themselves on surface energies.

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Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications

Postdocs: Gopalakrishnan Sai Gautam, Kuang Yu, and Thomas P. Senftle

Graduate Student: Nima Alidoust

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Jeffrey P. Greeley

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

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Abstract

Program scope and definition

We are exploring the fundamental principles of electrocatalysis and electrocatalytic reaction mechanisms at electrified solid/liquid interfaces using periodic Density Functional Theory methodologies. This continuing 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.

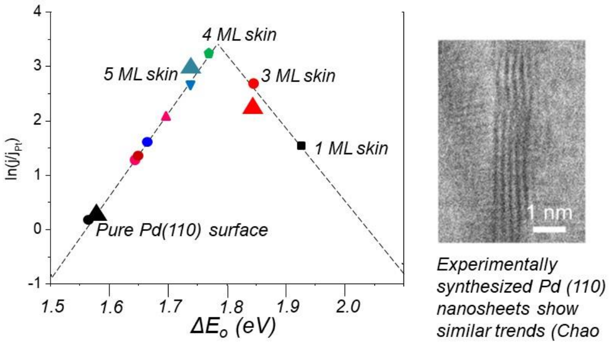
Recent Progress

In the past project year, we have focused on three primary topic areas related to thermodynamic and mechanistic analyses of electrochemical phenomena (we have also been investigating several side projects that are maturing into longer-term research directions, but those are not described here). The first major area comprises a continuing investigation of complex elementary reaction networks on platinum group transition metal surfaces. In the past project year, we developed a comprehensive description of the electrokinetics for nitrate reduction, a model reaction that is of interest for remediation of nitrates in groundwater streams. This approach employed a combination of DFT-based calculations of activation barriers and energy changes of elementary reactions, together with kinetic Monte Carlo analyses of reaction rates, to predict reaction mechanisms for this chemistry on pure platinum surfaces. We have now extended this analysis to platinum-containing alloys, beginning with Pt_3Sn, to identify catalysts that will produce more valuable/environmentally benign products than does Pt itself. To efficiently treat the structural complexity of the alloy surfaces, we have developed a method, based on geometric characterization and machine learning, to rapidly enumerate all plausible configurations for adsorbed reaction intermediates at different surface coverages. The approach demonstrates that surface coverage effects, and associated direct interactions between adsorbates, is the dominant factor in tuning the reaction selectivity to desired products such as dinitrogen and hydroxylamine. We are currently extending this work to other alloy surfaces.

The second major area of interest relates to the development of simplified descriptions of charge transfer barriers for proton-coupled electron transfer (PCET) across electrochemical double layers to transition metal surfaces. These descriptions form an essential component of our continuing efforts to increase the accuracy of our electrokinetic reaction models while preserving the efficiency of the simplified mechanistic analyses described above. We have, in particular, considered three primary elementary reactions related to our nitrogen-cycle electrochemistry work, including $N^* + H^+ + e^- \rightarrow NH^*$, $NO^* + H^+ + e^- \rightarrow NOH^*$, and $NOH^* + H^+ + e^- \rightarrow NO^* +$

water, where a “*” indicates a species adsorbed on a transition metal surface. In a recently submitted paper, we have used a plate capacitor model, combined with saddle point search algorithms, to estimate charge transfer barriers for these reactions at a constant surface voltage (electron chemical potential). The work has demonstrated that a universal linear free energy relationship, relating charge transfer barriers to thermodynamics, exists for these reactions on at least eight transition metal surfaces at a wide range of electrode potentials, a result that has been widely assumed but never rigorously verified on metal surfaces. Further, we have very recently demonstrated that the slopes of these linear correlations, which correspond to elementary symmetry factors in classical electrochemical reaction kinetics, can be directly related to the structure of the calculated transition states, and this relationship can be further quantified using a Marcus Theory formalism. We are currently seeking to extend this formalism to elementary charge transfer reactions that are relevant to other important electrocatalytic processes, and we expect that the results will enable significantly more accurate, yet also computationally efficient, analysis of electrocatalytic reaction networks than has previously proved possible.

An additional strategy that we are pursuing to enhance the accuracy of our electrocatalytic predictions at liquid/solid interfaces is to develop schemes to evaluate solvation energies for species on metal surfaces. We are in the early stages of using extended ab-initio molecular dynamics (AIMD) simulations to estimate such quantities. A promising technique employs a combination of energy histogram analysis, to determine average potential energies and standard deviations, with computation of quasi-harmonic vibrational densities of states to estimate entropies of solvated adsorbates. When applied to bulk water, the later approach yields entropies within ~10% of experiment, and it exhibits a similar level of accuracy when used to estimate the loss of entropy associated with idealized water bilayer formation on close-packed Pt(111) surfaces.



Experimentally synthesized Pd (110) nanosheets show similar trends (Chao

Figure. Comparison of predicted (circles) and measured (triangles) electrokinetic currents for oxygen reduction (ORR) on palladium nanosheets.

To further illustrate the applications of these physico-chemical modeling strategies to electrocatalytic reactions for energy applications, we have recently developed a novel strategy to manipulate the surface reactivity of heterogeneous electrocatalysts via introduction of controlled levels of strain. Motivated by the structural analysis of quasi-two dimensional materials that we have carried out in previous project years, we performed a careful study of the predicted oxygen reduction reaction (ORR) rates on palladium nanosheets with thicknesses of 1-8 ML. We have used a combination of ab-initio-based solvation energies and electrochemical charge transfer analysis, described above, to predict ORR reaction rates on these novel nanostructures. We have found that the intrinsic surface stress of the nanosheets leads to significant compressive strain in the Pd surfaces, which in turn modifies the catalytic activity in a manner that is highly sensitive to the Pd thickness. As shown in the Figure, the combination of the strain analysis, reactivity theory, and solvation techniques previously developed yield predictions of ORR rates that are ~20 times those of bulk Pd surfaces. Motivated by these predictions, our collaborator, Chao Wang at Johns Hopkins University, has synthesized Pd nanosheets with thicknesses of 3 and 5 ML, and the results show a remarkable correspondence with the theoretical predictions. We are in the process of evaluating the extent to which these self-induced strains can be used to tune the activity of other fundamental electrocatalytic reactions.

Future Plans

In addition to future work mentioned in the body of the abstract, we are continuing to apply our ultrathin film/three-phase boundary analyses to other electrocatalytic reactions, including CO electrooxidation and oxygen reduction, and we are exploring to what extent the resulting reactivity trends depend upon the particular structure of the metal surface (open, close-packed, or defected) that supports the films. We are additionally extending our analysis of NO electroreduction to other transition metal alloys to probe the influence of alloy structure and composition on the product selectivity. Further, we will continue to refine our electrochemical double layer models to improve estimates of entropies and free energies of solvation, and we will begin to generate more complex double layer models that incorporate solvated ions other than protons. Finally, we intend to explore the use of advanced statistical techniques, including variations on umbrella sampling, to more accurately evaluate the entropic contributions to such charge transfer barriers, in collaboration with other CTC PI'

Grant Numbers and Grant Titles

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

Postdoc(s): Zhenhua Zeng

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

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

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Molecular level characterization of quantum design principles for efficient and robust exciton and charge migration

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Abstract

This research project has the following two primary objectives: (1) To extract and verify a clear set of molecular level design principles for efficient and robust exciton dynamics within and across light harvesting complexes of purple photosynthetic bacteria; (2) To conduct computational modeling of conjugated oligomers and polymers so as to gain better understanding of exciton and charge carrier processes in organic molecular environments. Major outcome of the project during the past year are (i) comprehensive computer simulations and quantum calculations of both light harvesting 2 (LH2) and light harvesting 3 (LH3) complexes of purple bacteria [7], and (ii) a comprehensive review on delocalized excitons in natural light harvesting complexes [8], which offers clarification of important molecular features contributing to the efficient functionality of natural light harvesting complexes. Significant progress has also been made in computational study of exciton dynamics in aggregates of LH2 complexes, computational modeling of electronic transitions in oligothiophenes (OTs), and simulation of charge migration dynamics in disordered quantum environments.

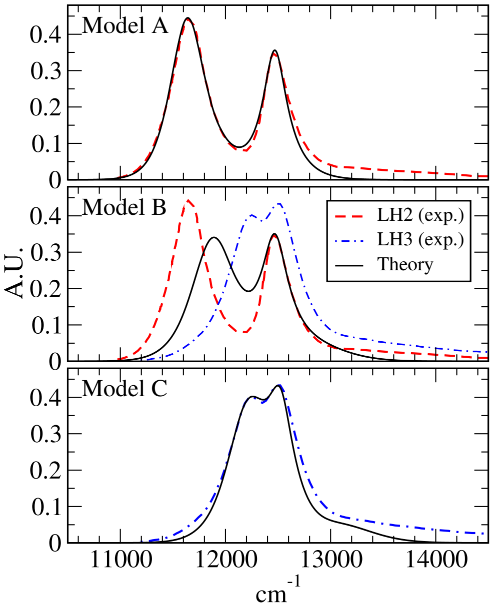

Figure 1. Comparison of theoretical and experimental absorption lineshapes for LH2 and LH3 complexes. Model A represents LH2 complex, Model B represents LH3 including the effects of hydrogen bonding, and Model C represents LH3 with additional shifts in the excitation energies of BChls by 320 cm^{-1}.

LH2 is a cylindrically shaped complex of bacteriochlorophylls (BChls) and protein scaffolds, and serves as the primary exciton-harvesting complex in the photosynthetic unit (PSU) of purple bacteria. Aggregates of LH2 complexes constitute the majority of the PSU and also provide major pathways for exciton migration. LH3 complex is a natural variant of the LH2 complex formed under low light condition. Its pigment molecules are the same as those of LH2, and its proteins have tertiary structures that are very similar to those of LH2. However, spectral features of LH3 are distinctively different from those of LH2. The major difference is that the B850 nm absorption band of LH2 shifts to near 820 nm region in LH3. Most recently, we conducted a comprehensive simulation and calculation of LH2 and LH3 complexes [7]. This was to clarify molecular level features determining their spectra and to establish exciton-bath models that can be used for large scale simulations. Through analyses of configurations sampled from molecular dynamics simulations of both LH2 and LH3 complexes and calculation of excitation energies using time dependent density functional theory (TD-DFT) method, we confirmed that different hydrogen bonding patterns are responsible for only about half of the spectral shift. However, the difference in the torsional angle of the BChl, which was often suggested as possible cause of the shift, turned out not to make significant contribution to the spectral difference between LH2 and LH3. Instead, through comprehensive spectroscopic modeling, we were able to demonstrate that shift of the excitation energies of BChls by about 320 cm^{-1} due to nonspecific change in BChl-protein interactions can explain the spectroscopic features reasonably well [7]. Figure 1 shows comparison of theoretical lineshapes with experimental ones supporting this conclusion.

Light harvesting complexes in natural photosynthetic organisms capture photons in the form of Frenkel-type excitons that are typically delocalized over a few pigment molecules. Such excitons remain well protected despite the disorder and fluctuations that are prominent in the natural protein environments. A large body of information offering insights into how nature executes efficient light harvesting has been amassed through decades of research. However, these have not yet led to clear understanding of major factors enabling their light harvesting functionality. We have conducted survey and analysis of major theoretical and experimental works on three major types of light harvesting complexes, Fenna-Matthews-Olson complex of green sulfur bacteria, light harvesting 2 complex of purple bacteria, and phycobiliproteins of cryptophyte algae [8]. This review [8] provides a comprehensive account of major theoretical, computational, and spectroscopic advances that have contributed to our current understanding, and clarifies the issues that need to be addressed concerning the role of delocalized excitons in achieving efficient energy transport mechanisms.

We have made significant progress in the computational study of electronic excitations of OTs and their charged species. Comparison of our computational results with experimental data confirm excellent performance of the TD-DFT method with M06-2X functional in calculating electronic absorption and emission energies of neutral OTs. On the other hand, it is shown to overestimate the excitation energies of OT cations and anions by about 0.4-0.5 eV. If these systematic errors are corrected, the results of the M06-2X functional once again can be viewed as more reliable compared to others. For all the cases, we have found that the distance dependences of excitation energies can be fitted well by both Frenkel-exciton model and particle in a box with sinusoidal modulation of potential energy. However, the asymptotic values of energies based on the former are about 0.3 eV larger than those based on the latter.

We have extended our previous work on charge transport along one dimensional chain in quantum environments to the cases with external potential gradients and two dimensional cases. Both direct calculation of Pauli master equation by Runge-Kutta algorithm and kinetic Monte Carlo simulation were used, the results of which were shown to agree well. We continue pursuing these simulation studies in order to understand the effects of disorder and quantum environments on charge hoping dynamics in general environments.

Overall, during the past year, we have clarified important molecular level details contributing to the spectroscopic difference between the LH2 and LH3 complexes [7], completed a comprehensive review on theoretical and experimental works on major light harvesting complexes and analysis of their implications [8], made significant progress in computational modeling of OTs, and simulation of charge transport dynamics in disordered quantum environments. Future effort will be dedicated to completion of these two latter ongoing projects as well as the project on the simulation of exciton dynamics in the aggregates of LH3 complexes. We will also seek for integration of lessons learned from both natural and synthetic systems for the identification and validation of molecular level design principles for efficient migration of delocalized excitons.

Grant Numbers and Grant Titles

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

Postdoc(s): Marta Kowalczyk (part time)

Student(s): Ning Chen and Taner Ture

Publications Acknowledging this Grant in the last 3-4 years

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Modeling $L_{2,3}$-edge XAS with Exact Two-Component Relativistic Time-dependent Density Functional Theory

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Abstract

X-ray absorption spectroscopy is a powerful technique to probe local electronic and nuclear structure. There has been extensive theoretical work modeling K-edge spectra from first principles. However, modeling L-edge spectra directly with density functional theory poses a unique challenge requiring further study. Spin-orbit coupling must be included in the model and a non-collinear density functional theory is required. Using the exact two-component method we are able to variationally include one-electron spin-orbit coupling terms when calculating the absorption spectrum.

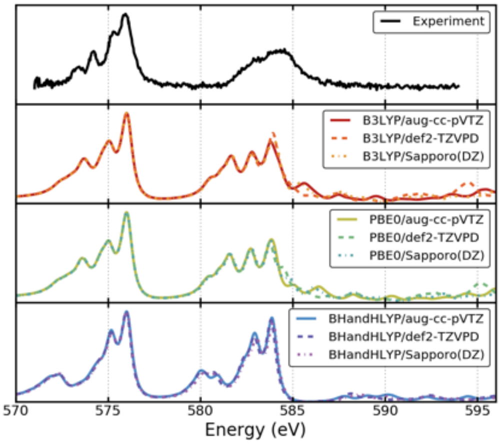

Figure 1. Experimental and modeled $L_{2,3}$ absorption edges for CrO_2Cl_2.

In this work we have demonstrated calculations of $L_{2,3}$-edge absorption spectra using the two-component X2C-TDDFT method. The method is general for both closed- and open-shell systems and allows the entire absorption spectrum to be computed at once. One-electron spin-orbit coupling is variationally included in the Hamiltonian along with a correction term to account for the neglect of two-electron spin-orbit terms. This leads to ~6% error in the splitting of the $2p_{1/2}$ and $2p_{3/2}$ orbitals and an error in the spacing between the L_2 and L_3 edges. Core excitation spectra are typically shifted to match with the experimental spectrum and an additional shift can be applied to account for the error arising from the empirical Boettger's treatment of one-electron spin-orbit coupling. Spectra modeled with B3LYP and PBE0 agree well with experiment, but spectra from BHandHLYP tend to overestimate d-orbital splitting. This is due to the comparable amounts of HF exchange in B3LYP and PBE0 and the large amount in BHandHLYP.

Results from a particular functional are relatively insensitive to the choice of basis set, except in the quasi-continuum regime, although we note that smaller basis sets such as def2-TZVPD may not be sufficient. Using the time-dependent molecular orbital pair contributions to the density, an analysis of the molecular orbitals involved in the transitions can also be obtained, yielding valuable theoretical information that can be used to connect the local electronic structure with the experimental observables.

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: A core goal of this project is to develop the theoretical capacity for generating methodologies to unravel the importance of two-electron spin couplings in chemical processes. The research, driven by fundamental science, holds the potential to design new materials with unprecedented properties and functionality based on the selective introduction and control of multiple spin centers for sensing, energy, and spintronic applications. The product of the proposed research includes: a first-principles spin dynamic method that accounts fully for all spin couplings in the relativistic two-component TDDFT framework, a variationally optimized numerical integration engine that supports efficient integral evaluation for relativistic two-component TDDFT in the atomic orbital basis, and a computational spectroscopic method that can accurately predict static and time-resolved L-edge X-ray spectroscopy using first-principles spin dynamics.

Recent Progress: Since the last report, we have published >10 papers. Highlights of our recent progress include: (1) a variational relativistic TDDFT method that satisfies the zero-torque theorem for generalized gradient functionals (2) a variational relativistic TDDFT method to compute $L_{2,3}$-edge X-ray absorption spectrum, and (3) a well-tempered eigensolver to obtain high-energy excited states in a dense manifold of spectral region.

Future Plans: In the next report period, we plan to (1) develop two-electron spin-couplings, including two-electron spin-orbit and spin-spin interactions, in relativistic TDDFT theory, and (2) investigate the importance of various relativistic spin-couplings on the $L_{2,3}$-edge spectroscopic characteristics.

Postdoc(s): Andrew Jenkins, David Lingerfelt

Student(s): Andrew Wildman

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

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DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION: ON THE EXACT CARTESIAN MAPPING OF FERMIONS FOR INVESTIGATING ELECTRODE PROCESSES

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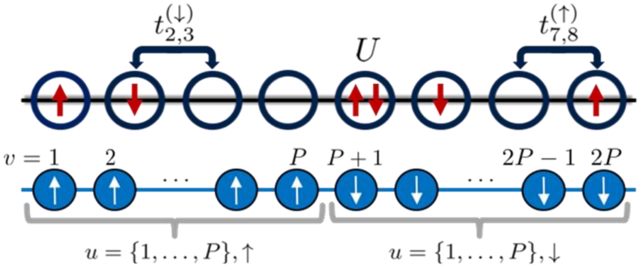
Abstract

The development of next generation energy conversion and catalytic systems requires fundamental understanding of the interplay between photo-excitation and the resulting proton and electron transfer processes that occur in solution. To address these challenges requires accurate and efficient methods to compute ground and excited states, as well as the ability to treat the dynamics of energy transfer in the presence of solvent fluctuations. Our team is developing accurate and efficient theoretical models for solution phase reactions. These developments provide an improved understanding of photo-initiated excitations, electron transfer, and proton coupled electron transfer processes.

The exact treatment of real time nonadiabatic quantum dynamics in condensed phase chemical systems remains a significant challenge that spurs the ongoing development of approximate methods that are accurate, efficient, and can treat large systems with a wide range of different forms of interactions. Quantum-classical (semiclassical) trajectory-based methods provide some of the most appealing solutions to this problem that offer a hierarchy of approaches with different balances between accuracy and computational cost. However, since moving up this hierarchy typically requires orders of magnitude more computational effort, only the lowest tiers are likely to be practical, both now and in the foreseeable future, for nonadiabatic problems containing large quantum subsystems. As part of this project we have shown how quantum-classical approaches can be made both more accurate and efficient by combining them with the formally exact quantum master equation framework [4, 9]. This combination of quantum-classical theory and master equation techniques makes it possible to obtain the accuracy of much more computationally expensive approaches at a cost an order of magnitude lower than even the most efficient trajectory-based approaches, providing the ability to treat the quantum dynamics of atomistic condensed phase systems for long times.

Our most recent work has focused on extending the developments of quantum-classical GQME-based dynamics to many-fermion problems where the discrete energy levels are so numerous as to create continua, as is the case for processes near metallic and semiconducting interfaces. To achieve the accuracy benefits from the GQME approach one must have a prescription to generate the initial conditions exactly. In cases where one can write the Hamiltonian in terms of Cartesian positions and momenta, this can usually be achieved straightforwardly using path integral approaches. For Hamiltonians containing discrete states, the Meyer-Miller-Stock-Thoss (MMST) protocol can be used, however, for those that include fermionic creation and annihilation operators an exact Cartesian mapping has remained elusive. In our recent work, we have therefore derived a rigorous, quantum mechanical map of fermionic creation and annihilation operators to continuous Cartesian variables that exactly reproduces the matrix structure of the many-fermion problem. We have shown how our scheme can be used to map a general many-fermion Hamiltonian and then consider two specific models that encode the fundamental physics of many fermionic systems, the Anderson impurity

and Hubbard models. We have then used these models to demonstrate how efficient mappings of these Hamiltonians can be constructed using a judicious choice of index ordering of the fermions. For example, the figure shows how the 1D Hubbard Hamiltonian can be exactly mapped from its usual form in terms of fermionic creation and annihilation operators to an isomorphic form in terms of Cartesian positions and momenta. Perhaps most remarkably in this case, by using an appropriate choice of index ordering, one can eliminate the need to treat the nonlocal operator that imposes the fermionic anticommutivity.



$$\hat{H} = \sum_u U_u \hat{n}_{\uparrow,u}\hat{n}_{\downarrow,u} + \sum_{u,\lambda} t^{(\lambda)}_{u,u+1}\left[\hat{c}^\dagger_{\lambda,u}\hat{c}_{\lambda,u+1} + \hat{c}^\dagger_{\lambda,u+1}\hat{c}_{\lambda,u}\right]$$

$$\text{“}\mapsto\text{”} \sum_u U_u \hat{\eta}_{\uparrow,u}\hat{\eta}_{\downarrow,u} + \frac{1}{2}\sum_{u,\lambda} t^{(\lambda)}_{u,u+1}\left[\hat{x}_{\lambda,u}\hat{x}_{\lambda,u+1} + \hat{y}_{\lambda,u}\hat{y}_{\lambda,u+1}\right]$$

Figure 1:Mapping and index ordering for the 1D Hubbard model using our Cartesian mapping approach.

This development thus provides an alternative exact route to calculate the static and dynamical properties of fermionic systems and sets the stage to exploit the quantum-classical and semiclassical hierarchies to systematically derive methods offering a range of accuracies, thus enabling the study of problems where the fermionic degrees of freedom are coupled to complex anharmonic nuclear motion and spins which lie beyond the reach of most currently available methods. These extensions should now allow us to simulate the GQME dynamics using memory kernels generated from a wide variety of quantum-classical approaches for large quantum subsystems coupled to fully atomistic environments. These developments are essential for treating problems such as proton coupled electron transfer in solution and at interfaces.

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

PI and co-PI(s): Christine Isborn (Merced, PI), Aurora Clark (WSU, co-PI), Thomas Markland (Stanford, co-PI)

Markland Group Postdoc(s): Andres Montoya-Castillo (current), Ondrej Marsalek (previous), Aaron Kelly (previous)

Up to Ten Publications Acknowledging this Grant, Markland Group

[1.] On the exact continuous mapping of fermions. *A. Montoya-Castillo, T. E. Markland. arXiv:1803.05561 and Submitted to J. Chem. Phys. (2018)*

[2.] Nuclear quantum effects enter the mainstream. *T. E. Markland and M. Ceriotti Nature Rev. Chem., 2, 0109 (2018)*

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Next generation extended Lagrangian first principles molecular dynamics

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Abstract

Quantum based molecular dynamics (QMD) simulations provide a highly powerful, but computationally expensive, multidisciplinary tool to predict, understand and design materials and processes directly from the first principles of quantum physics. Merging QMD with future extreme-scale computing holds the promise of a major paradigm shift in computer-driven science with applications in chemistry, molecular biology, and materials science, addressing multiple DOE/Office of Science/Basic Energy Sciences research objectives of relevance to our future energy and security needs. Unfortunately, this potentially revolutionary opportunity will never be fully realized without a radical re-design of established QMD simulation schemes to overcome a number of interconnected fundamental problems. Our overarching goal is to go beyond conventional QMD simulation tools and to create a framework for a next generation first principles QMD schemes that overcomes previous shortcomings and limitations. This will open the door to reliable and highly efficient atomistic simulations of large complex systems that radically extends current capabilities.

Some of our most recent developments include: i) a more rigorous theoretical formulation of a next generation extended Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD) with a comparative analysis to Car-Parrinello molecular dynamics [8]; ii) new kernel approximations for XL-BOMD that appears as a preconditioner in the extended electronic equations of motion, which provides exceptional stability even for reactive chemical systems without relying on any explicit iterative ground state optimization prior to the force evaluations (See Fig. 1) [8]; iii) a graph-based approach to linear scaling electronic structure theory suitable for hybrid architectures [4]; iv) extended Lagrangian excited state molecular dynamics allowing accelerated and stable simulations [9]; and v) applications of XL-BOMD for polarizable force fields, including the construction of higher-order shadow potentials [6,7,10].

These recent accomplishments have opened a number of new opportunities and challenges that we plan to address in the coming years: a) practical QMD simulations of reactive chemical systems with up to 100,000 atoms; b) extended Lagrangian formulations including spin-degrees of freedom; and c) applications and extensions using

machine learning technologies, using hierarchical deep neural networks and high-performance tensor core implementations. The outcome of our ongoing research is a rapidly emerging next generation QMD, enabling applications to an extended interdisciplinary range of energy related research problems far beyond what is possible to study with existing capabilities.

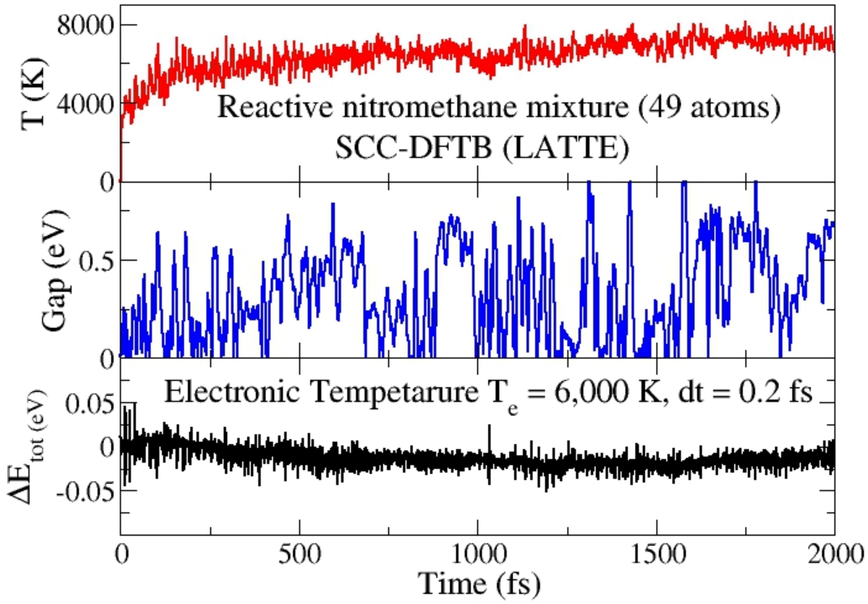

Figure 1 XL-BOMD simulation of a reactive chemical system without relying on any explicit, iterative electronic ground state optimization prior to the force evaluations. This is possible thanks to a new kernel approximation that appears as a pre-conditioner to the electronic equations of motion [8]. The total energy remains stable while the electronic HOMO-LUMO gap is opening and closing.

LANL2014E8AN, "Next generation first principles molecular dynamics"

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Enhancing Rare Events Sampling In Molecular Simulations

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

In our previous work, we developed software called SAFFIRE (previous called Scalable Forward Flux Sampling (ScaFFS)) to perform large scale forward flux sampling (FFS) calculations efficiently and effectively in high performance computing (HPC) infrastructure. In FFS, transitions from state A to state B are sampled through several intermediate transitions by dividing the phase space between A and B into sub-regions marked by interfaces. Several simulations are initiated at a given interface and configurations from those which reach the next interface are harvested. Then several simulations are initiated from the harvested configurations at the "new" interface to obtain configurations for the next interface. This process is continued until the final state is reached. While the process is straightforward, the application of the method to realistic systems can result in large number of simulation jobs and huge amount of data. To handle these large jobs and amounts of data effectively, we have developed SAFFIRE. SAFFIRE represents a collaboration of state-of-the-art techniques in molecular simulations with those from Big Data to enable rare event simulations at massive scales. SAFFIRE is designed to be adaptive, data-intensive, high-performance, elastic, and resilient. SAFFIRE uses Hadoop in a novel manner to handle the millions of simulations performed and files generated in FFS calculations. Through this approach we have been able to address several of the challenges related to implementing FFS.

Using SAFFIRE we have performed some of the largest scale FFS studied of ice and hydrate nucleation. We find that even with these extensive simulations, large number of successful transition pathways arise from a handful of configurations at the initial stages of the transition. This is further challenging because it cannot be predicted *a priori* whether the starting configurations will lead to successful transition pathways and therefore, it cannot be corrected for without performing the largescale simulations! This necessitates developing methods that overcome these challenges. In this project we use a multipronged approach to develop methods that address such challenges.

Program Scope and Definition: In our project, we combine state-of-the-art tools in molecular simulations, BigData and multitasking handling systems, and visualization techniques to develop a robust infrastructure for performing rare event simulations. We build FFS to develop multidimensional FFS methods (nDFFS) that will enable us to address the issue of finding appropriate order parameters for any given transition on-the-fly. This methodology has the potential of addressing the major knowledge gap – lack of an ability to find reaction coordinates on-the-fly – in simulations of rare events. We do so by simultaneously developing novel FFS based methods, integrating them with machine learning techniques and assimilating it into SAFFIRE to test our methods beyond test cases – on more realistic systems such as ice nucleation.

Recent Progress:

<u>2DFFS methods</u>: We have developed multiple approaches to perform nDFFS calculations and studied them using toy models. Our model test case systems include analytical two well potential energy surfaces as shown in Figure 1. Figure 1, left panel is a relatively simple two-well potential while right panel represents a more complicated potential energy surface. Our calculations illustrate that even for such a system it is possible to have "bias in the sampling" of the transition paths when using 1DFFS. We describe two methods we have developed towards performing nDFFS.

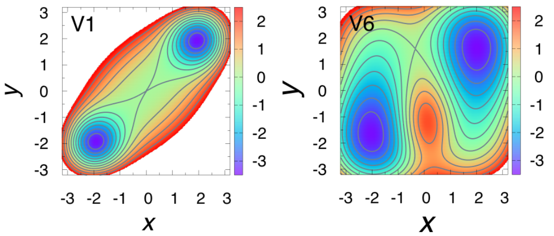

Figure 1: Examples of potential energy surfaces used to test the nDFFS methods developed. The color bar represents the energy scale where higher positive number means higher energy. The blue regions correspond to the stable states.

Set-based sampling method: In set-based sampling, we place the interfaces by following the trajectories in multiple directions (i.e. along multiple order parameters). In the set-based approach, the next interface is placed based on the order parameter sampling obtained from trajectories propagated at any given interface. This enables us to have any "shape" of the interface. An example of sampling from the set-based approach is shown in Figure. 2. As can be seen, we are able to outline the underlying potential energy surface for the non-simple toy models. However, we find that while we enhance sampling, set-based approach also leads to sampling several unproductive directions, which is undesirable. We are currently devising methods to address this.

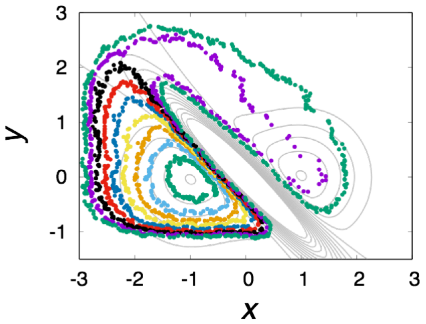

Figure 2: Results from set-based sampling approach applied to our toy model system. The points represent the interfaces selected based on the propagation of the system along the x- and y- direction. Different colors correspond to different interfaces.

2DFFS sampling: We have devised a method to propagate the system along two order parameters. We have performed detailed studies of the improvement in sampling achieved for six test toy models. The improvement is being assessed based on the sampling of the transition region as well as the computational resources required for achieving this sampling. We compare the results between 1DFFS with suboptimal order parameter, 1DFFS with optimal order parameter, 2DFFS and standard Langevin dynamics. We find that in most cases 2DFFS gives us improved sampling however, this is not always the case!! In some scenarios, the shortcomings in 1DFFS are in fact enhanced in 2DFFS. We are probing this further and will extend the test to more complex test cases.

LJ nucleation: We have performed largescale FFS simulations of Lennard Jones liquid-to-solid transition. These simulations represent some of the largest FFS simulations of LJ systems. We are currently developing machine learning methods to analyze the structures obtained during the nucleation process. This work is being done by an undergraduate student under the supervision of the graduate student.

Future Work:
In the next year, we will focus on the following aspects of the project:

- nDFFS methods: We will continue to develop methods for nDFFS. Based on our approaches so far, while we have developed novel methods we also have identified the pitfalls associated with them. Therefore, we are continuing to devise methods that help us address these pitfalls. In addition, we are working towards identifying appropriate test cases that are more challenging than the toy models used so far, but less challenging than the realistic systems we ultimately want to study.
- We are developing machine learning (ML) methods to identify and characterize the pathways obtained from our FFS studies of LJ systems. We will use the insights from the ML techniques to further develop our nDFFS methods.

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

Grant Number and Title:
DE-SC0015448 Enhancing Rare Events Sampling in Molecular Simulations of Complex Systems

Students: Ryan DeFever (PhD student)
Steven Hall (Undergraduate student)

A Unified Formulation of Tensor HyperContraction Coupled-Cluster Theory

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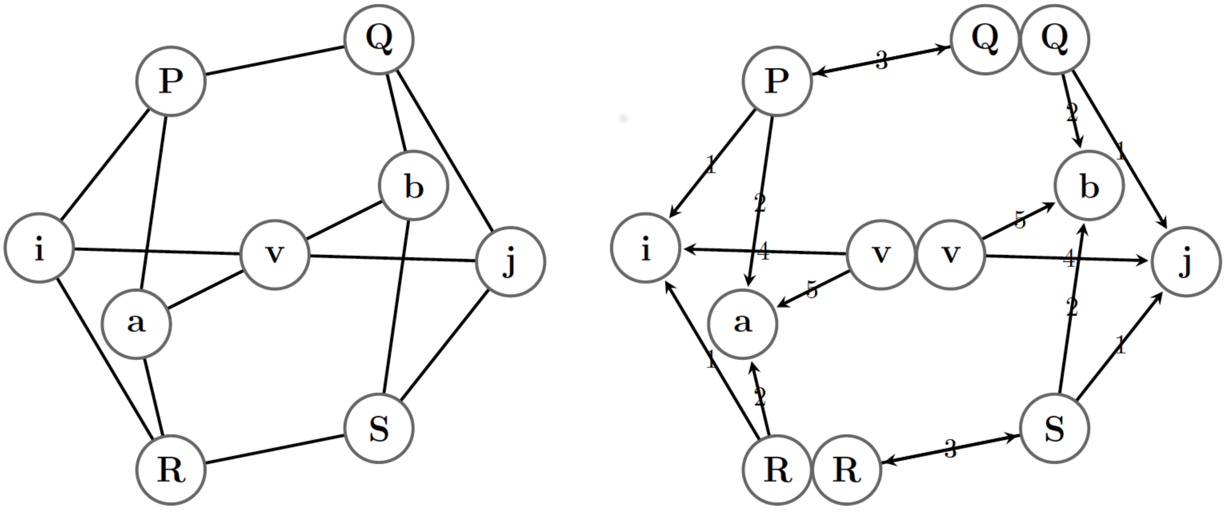
Abstract

First principles simulation of electronically nonadiabatic dynamics plays an increasingly important role in our understanding of excited-state processes. The applicability of these simulations is limited by both the scalability and accuracy of the underlying electronic structure methods. In recent years, simultaneous advances in computer architecture and sparsity-exploiting electronic structure algorithms have made nonadiabatic dynamics simulations routinely possible for molecular systems with up to ~100 atoms. Due to the significant approximations required in this context, extensive validation is required to ensure that the potential energy surfaces are physically reasonable. Some of the methods that are best suited for unbiased benchmarking of general excited-state potential surfaces are equation-of-motion coupled-cluster (EOM-CC) methods including singles and doubles with some approximate account of triple excitations. The accuracy and black-box nature of these approaches makes them ideally suited for unbiased validation of lower-cost methods. The principal limitation of EOM-CC methods is their computational complexity: triples corrected equation-of-motion coupled-cluster methods scale $O(N^7)$ with system size.

One approach to removing the scaling bottleneck from coupled-cluster theory is the use of low-rank factorization of the electron repulsion integrals and wavefunction coefficients within the framework of Tensor HyperContraction (THC). This technique allows most common correlated methods including single and double excitations to be evaluated with effort scaling as $O(N^4)$. We posit that, in the context of coupled-cluster theory, approximate triples corrections (both perturbative and iterative) can be formulated in a manner that will scale $O(N^5)$. Our previous efforts to develop reduced-scaling implementations of coupled-cluster methods have been limited to CC2 (where an exact factorization of doubles amplitudes is possible) and a proof-of-concept implementation of THC-CCSD. A more general approach to the factorization of the doubles amplitudes is CCSD is required if we are to extend these methods to EOM methods and response properties. We are in the process of developing a unified formulation of rank-reduced coupled-cluster singles and doubles methods from the EOM perspective that will allow us to target these molecular properties.



$$E_{\mathrm{MP2,J}} = \sum_{v}\sum_{ijab}\sum_{PQRS} X_i^P X_a^P Z^{PQ} X_j^Q X_b^Q X_i^R X_a^R Z^{RS} X_j^S X_b^S \tau_i^v \tau_j^v \tau_a^v \tau_b^v \qquad E_{\mathrm{MP2,J}} = \sum_{vQR}\left(\sum_{iaP} \tau_i^v \tau_a^v X_i^P X_a^P Z^{PQ} X_i^R X_a^R\right)\left(\sum_{jbS} \tau_j^v \tau_b^v X_j^Q X_b^Q Z^{RS} X_j^S X_b^S\right)$$

To expedite the development of these coupled-cluster methods, we are working to remove a bottleneck from the code development process: namely, the automatic factorization and code generation of THC contractions. By working with heavily factorized intermediates, a new bottleneck to code development was introduced. Consider the Coulomb term in the MP2 energy expression. When THC is applied, this term is expressed as a contraction of 14 matrices; there are now 13! possible ways to implement this term. In general, this search space is far too large to identify the optimal contraction path by brute force. We have developed a highly efficient graphical approach to identifying the least computationally demanding path and, subsequently, automatically generating a GPU-accelerated implementation of these contractions. This technique is enabling rapid development of new THC coupled-cluster algorithms.

This project is part of a larger SciDAC program that brings together a diverse group of researchers to the computational design of photocatalysts. Our work on reduced-scaling coupled-cluster methods will provide accurate energetics of the catalytic systems that will inform the computational design process. Over the next three years, we will be leveraging contributions from other members of our SciDAC team in applied mathematics as well as computer science into the development and implementation of these coupled-cluster methods.

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

Student(s): Yao Zhao

Dr. Scott W. Sides

RemoteSTREAMM: A Web Application for Running HPC Materials Simulations in the Cloud

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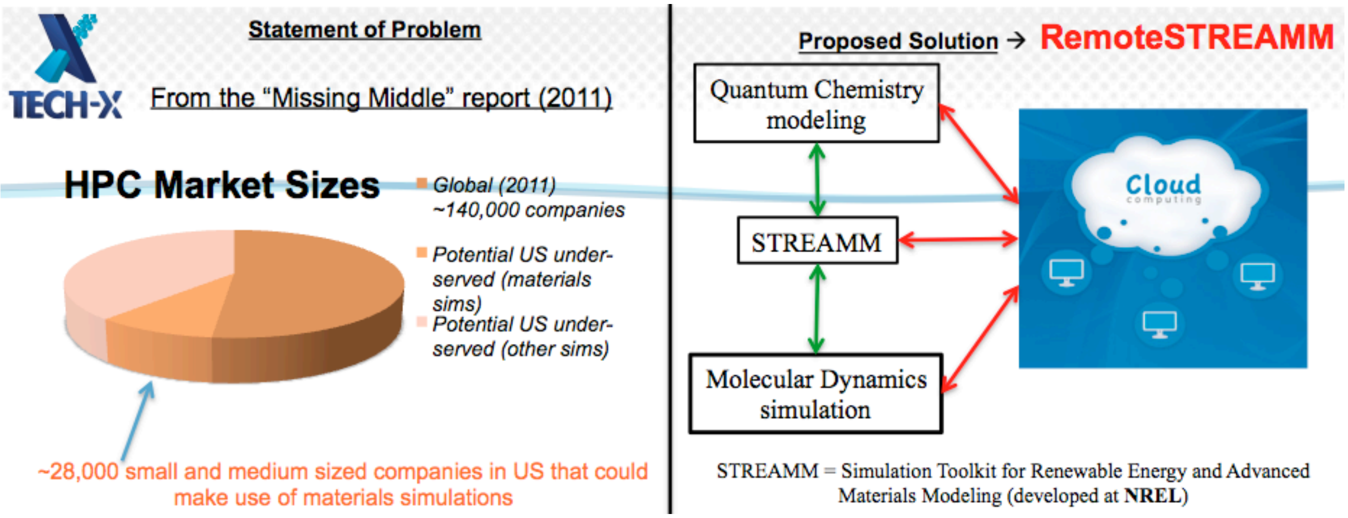
Abstract



Numerical studies relevant to fields such as solar cells, nanotechnology and pharmaceuticals need simulations of materials across a wide range of length scales and require workflows that include a variety of simulation algorithms. However, simulations such as these are under-utilized for small- and medium-sized businesses [1] in the commercial sector due to the high barriers required to develop complex simulation workflows and access HPC resources needed to address real-world design questions. According to a recent survey by the Council on Competitiveness [2], faster time to market, return on investment, and enabling work that could not be performed by any other means are cited as the most common justifications for HPC in industry. Unfortunately, one of the most striking features of the Council on Competitiveness survey, is the under-representation of the companies that would be most likely to take advantage of soft materials simulations. The biosciences sector accounted for only 5.9% and the chemical engineering sector accounted for only 4.0% of respondents on their use of HPC resources [2].

Initial Phase I work on the RemoteSTREAMM project aimed to address these challenges by integrating the STREAMM (Simulation Toolkit for Renewable Energy and Advanced Materials Modeling) framework for linking QM/MD codes together (initially developed at NREL) into lightweight, virtual machine containers that are able to run on a wide variety of Cloud Computing Services. With the help of our UberCloud partners, the molecular dynamics (MD) package LAMMPS, the electronic structure package NWChem, and the STREAMM framework were all ported to HPC cloud-ready containers. ***The HPC parallel performance of these cloud-ready Docker containers is shown to be excellent on multi-node cloud clusters, thereby providing the technical basis to proceed with Phase II work.***

The proposed Phase II work will build on the success of Phase I development by containerizing additional simulation codes in order to address a wider variety of advanced research workflows and fully implement these workflows in a user-friendly application RemoteSTREAMM. In addition to the advanced materials workflow of interest to NREL, two additional workflows will be implemented and will be described in the poster. The additional codes to be containerized and made HPC cloud-ready are specifically tied to small/medium industry collaborators in the local Colorado area in the advanced coatings and pharmaceutical fields. The workflow related to pharmaceutical research has been developed with input from Array BioPharma (Boulder, CO), and letters of support are included from NREL and ForgeNano (Louisville, CO) on the photovoltaic and atomic layer deposition workflows respectively. This progress will positively impact one of the goals of the Materials Genome initiative to enhance the rate of breakthroughs in complex materials chemistry and materials design. Enabling these smaller companies to leverage the cheap computing power becoming increasingly available in the cloud will enhance the overall efficiency of many of the small/medium companies in their respective fields. Leveraging these advances in computational chemistry and materials research will allow them to more effectively compete against larger companies that have more resources.

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Barry D. Dunietz

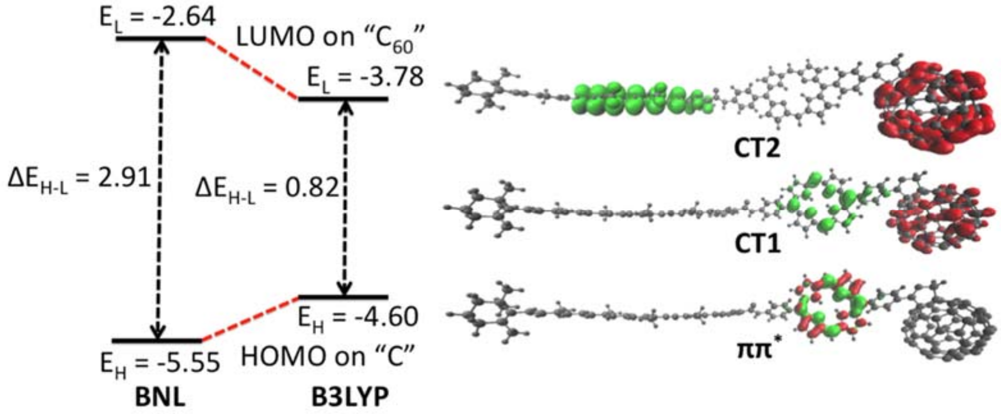
Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials

Margaret Cheung, Barry D. Dunietz, Eitan Geva
University of Houston, TX; Kent State University, OH; University of Michigan, MI

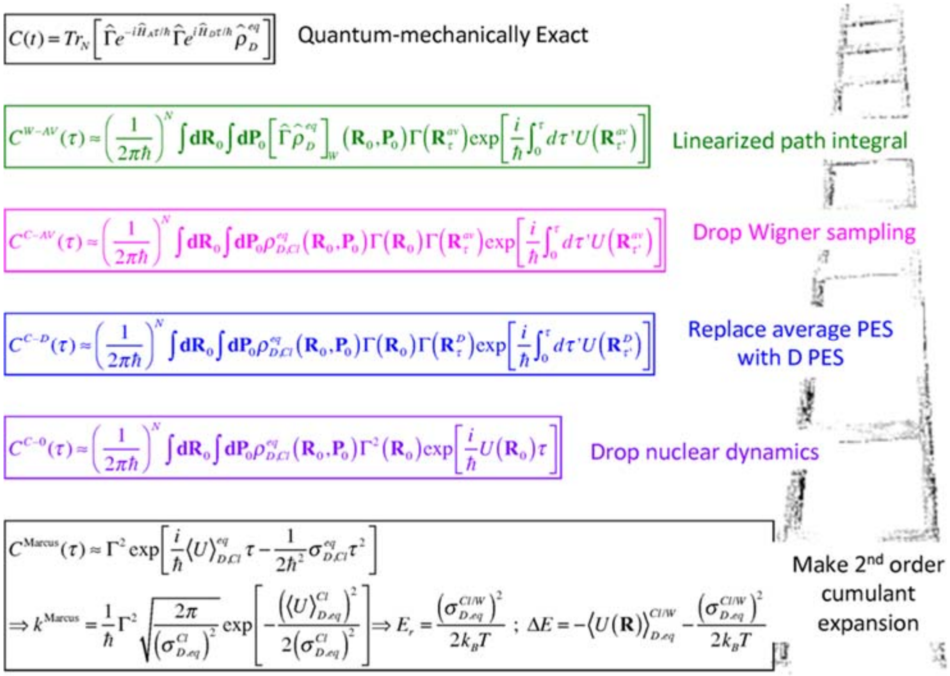
Abstract

The goal of the research program is to understand charge transfer (CT) processes, which is key to improve alternative energy applications. In particular we are concerned with CT across interfaces related to organic photqovoltaics systems. We develop a transformative computational scheme, where we do not resort to otherwise widely used simplifications. to achieve realistic descriptions of CT processes. We provide unique insight, where the molecular environment is properly addressed and that will benefit relevant experimental efforts.

Since the underlying challenges are substantial we pursue a comprehensive approach based on diverse expertise. Our collaboration brings together three principal investigators with expertise in molecular dynamics simulations (Cheung), electronic structure calculations (Dunietz), and quantum dynamics theories of the condensed phase (Geva).



The triad system is used to demonstrate our linearized semi-classical approach that open the door to develop a hierarchy of methodologies from a semi-classical (Marcus approach) to a Fermi-Golden rule level where molecular environment is represented using molecular dynamics simulations. Our approach combines all-atom molecular dynamics simulations with an 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 constants, is established by comparing the rate constants calculated with and without resorting to this approximation.



$$C(t)=Tr_N\left[\hat{\Gamma}e^{-i\hat{H}_A t/\hbar}\hat{\Gamma}e^{i\hat{H}_D t/\hbar}\hat{\rho}_D^{eq}\right]$$

$$C^{W-AV}(\tau)\approx\left(\frac{1}{2\pi\hbar}\right)^N\int d\mathbf{R}_0\int d\mathbf{P}_0\left[\hat{\Gamma}\hat{\rho}_D^{eq}\right]_W(\mathbf{R}_0,\mathbf{P}_0)\Gamma(\mathbf{R}_\tau^{av})\exp\left[\frac{i}{\hbar}\int_0^\tau d\tau' U(\mathbf{R}_{\tau'}^{av})\right]$$

$$C^{C-AV}(\tau)\approx\left(\frac{1}{2\pi\hbar}\right)^N\int d\mathbf{R}_0\int d\mathbf{P}_0\rho_{D,Cl}^{eq}(\mathbf{R}_0,\mathbf{P}_0)\Gamma(\mathbf{R}_0)\Gamma(\mathbf{R}_\tau^{av})\exp\left[\frac{i}{\hbar}\int_0^\tau d\tau' U(\mathbf{R}_{\tau'}^{av})\right]$$

$$C^{C-D}(\tau)\approx\left(\frac{1}{2\pi\hbar}\right)^N\int d\mathbf{R}_0\int d\mathbf{P}_0\rho_{D,Cl}^{eq}(\mathbf{R}_0,\mathbf{P}_0)\Gamma(\mathbf{R}_0)\Gamma(\mathbf{R}_\tau^{D})\exp\left[\frac{i}{\hbar}\int_0^\tau d\tau' U(\mathbf{R}_{\tau'}^{D})\right]$$

$$C^{C-0}(\tau)\approx\left(\frac{1}{2\pi\hbar}\right)^N\int d\mathbf{R}_0\int d\mathbf{P}_0\rho_{D,Cl}^{eq}(\mathbf{R}_0,\mathbf{P}_0)\Gamma^2(\mathbf{R}_0)\exp\left[\frac{i}{\hbar}U(\mathbf{R}_0)\tau\right]$$

$$C^{\mathrm{Marcus}}(\tau)\approx\Gamma^2\exp\left[\frac{i}{\hbar}\langle U\rangle_{D,Cl}^{eq}\tau-\frac{1}{2\hbar^2}\sigma_{D,Cl}^{eq}\tau^2\right]$$

$$\Rightarrow k^{\mathrm{Marcus}}=\frac{1}{\hbar}\Gamma^2\sqrt{\frac{2\pi}{\left(\sigma_{D,eq}^{Cl}\right)^2}}\exp\left[-\frac{\left(\langle U\rangle_{D,eq}^{Cl}\right)^2}{2\left(\sigma_{D,eq}^{Cl}\right)^2}\right]\Rightarrow E_r=\frac{\left(\sigma_{D,eq}^{Cl/W}\right)^2}{2k_BT}\ ;\ \Delta E=-\langle U(\mathbf{R})\rangle_{D,eq}^{Cl/W}-\frac{\left(\sigma_{D,eq}^{Cl/W}\right)^2}{2k_BT}$$

Figure: Hierracy of semi-classical approximations

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

Student(s): Srijana Bhandari

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

- A Computational Study of Charge Transfer Dynamics in The Carotenoid-Porphyrin-C60 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.* **Just Accepted** (2018).

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

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

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

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

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

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  Arun K. Manna, and Barry D. Dunietz *J. Chem. Phys. (comm.)* , **141** (2014) 121102

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  Zilong Zheng, Arun K. Manna, Heidi Phillips, Morgan Hammer, Chenchen Song, Eitan Geva and Barry D. Dunietz *J. Amer. Chem. Soc. (comm.)* , **136** (2014) 16954–16957

Activities, Solubilities, and Nucleation Rates in Aqueous Electrolyte Solutions

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Presentation Abstract

Interactions mediated by ions and charged groups play an important role in determining forces between surfaces in solution and in determining the structure and thermodynamic properties of aqueous electrolyte interfaces. Our work under in the past year focused on developing methods for determination of activity coefficients, salt solubilities, and nucleation rates in aqueous electrolyte solutions, using molecular models. The methods developed were able to address the major sampling challenges encountered for these strongly interacting systems. These properties had not been included in ion model development in the past, because of the computational challenges in obtaining them with sufficient accuracy. Our work identified significant deficiencies of current models for water and ions. In our presentation, we plan to discuss forward-flux sampling calculations of the homogeneous nucleation rate of the Joung-Cheatham NaCl force field combined with the SPC/E water model at 298 K and 1 bar. The results shown in Fig. 1 suggest that this model combination underestimates the nucleation rate at all relative supersaturations by several orders of magnitude (note the highly compressed logarithmic ordinate scale).

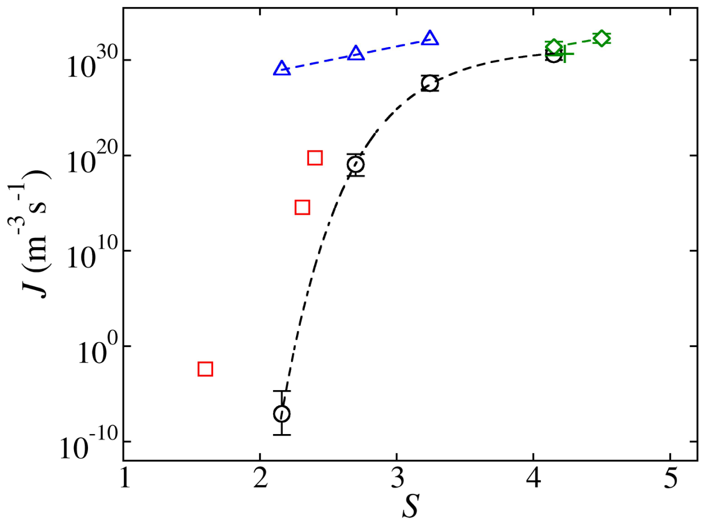

Fig. 1. Homogeneous nucleation rate J for aqueous NaCl as a function of the supersaturation ratio S, from [1]. Black open circles are from our forward-flux sampling simulations for the Joung-Cheatham NaCl + SPC/E water model combination, red squares are experimental data, and blue triangles are from simulations of Zimmerman *et al.* [2]. The green cross and diamonds are estimated from the induction time of spontaneous nucleation in unbiased molecular dynamics simulations of the same model and are consistent with the forward-flux-sampling simulations.

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

PI: Athanassios Z. Panagiotopoulos

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

PhD Students (past 3 years): Andrew Santos; Jeffrey Young; Shuwen Yue

1 PROGRAM SCOPE

This project aims to provide a better physical understanding and quantitative modeling tools for interactions and self-assembly in ionic systems, utilizing cutting-edge simulation algorithms. The focus is on free-energy calculation methods for activity coefficients and salt solubilities in aqueous electrolyte solutions using atomistic models. These properties have not been included in ion model development in the past because of the computational challenges in obtaining them with sufficient accuracy. Atomistic models that can be used in a fully predictive mode offer distinct advantages over previously available phenomenological and implicit-solvent models; their performance at elevated temperatures, which are important for separations and CO_2 geophysical sequestration applications, had not been previously determined. Work underway has identified significant deficiencies of current models for water and ions, which result in large errors in modeling activity coefficients and solubilities. In the area of surfactant self-assembly, we are investigating the relationship between grand canonical Monte Carlo methods for determining critical micellar concentrations and methods based on extrapolation with respect to total surfactant loading. The project takes advantage of powerful computational techniques and conceptual frameworks developed with prior DOE support, while striving to break new ground both in terms of both simulation methods and molecular model development.

2 RECENT PROGRESS

In the past year, a major area of work under the project has been the development of efficient methods for obtaining activity coefficients and solubilities of aqueous electrolytes [reference 5 in the publication list of section 4]. Using implicit-solvent calculations for which much lower statistical uncertainties are possible, we found that there are strong finite-size effects at low concentrations. Somewhat counterintuitively, we also found that lower systematic errors for the Henry’ s law reference chemical potential are obtained by using simulations at higher concentrations (for which system-size effects are much smaller) to obtain estimates for the reference chemical potential. This is the case even though at these higher concentrations deviations from the Debye-Hückel limiting law (or its empirical extensions) are greater than those at lower concentrations. We completed forward-flux sampling calculations of the homogeneous nucleation rate of the Joung-Cheatham NaCl force field combined with the SPC/E water model at 298 K and 1 bar [6]. We have also developed a new method for contact-angle measurements based on the “phantom-wall” concept [2] and reviewed recent work on molecular models of aqueous electrolytes, including polarizable model development and testing [1]. In the area of computational methodologies for the study of self-assembly, we investigated aggregation properties of systems with competing interactions [3], a simple model for charged colloidal dispersions, and also worked with an undergraduate student [4] to carefully compare surfactant self-assembly for different molecular architectures, but at conditions resulting to identical critical micelle concentrations.

Finally, the PI has been involved in a multi-author effort [7] that resulted in the resolution of a long-standing controversy on the properties of (metastable) liquid water at low temperatures and the possible existence of a liquid-liquid transition.

3 FUTURE PLANS

Our planned work involves extending the limits of applicability of the computational methods we have developed and on obtaining electrolyte models that can be used over broad ranges of temperatures, solvent environments, and inhomogeneities such as dielectric discontinuities present at interfaces. Of particular interest will be temperature-dependent properties and the behavior of multivalent ions. These are much harder systems relative to the room-temperature monovalent systems which were the focus of prior work. In addition to activity coefficients and solubilities, nucleation rates from supersaturated solutions, and transport properties such as viscosity and ion mobilities will be studied. A direct collaboration will be initiated with a Princeton-centric group focusing on *ab initio* simulations of water and aqueous solutions to guide the model development part of our work. In turn, our computational methodologies will likely be applicable not only in connection to conventional classical force fields, but also for emerging many-body, machine-learning based models that better represent the actual potential energy surface in aqueous solutions and that offer the possibility of accurate modeling of complex systems for which empirical potentials fail.

4 PUBLICATIONS FROM THIS PROJECT IN THE PAST YEAR (SINCE PRIOR PI MEETING)

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3. A. P. Santos, J. Pekalski and A. Z. Panagiotopoulos,” Thermodynamic signatures and cluster properties of self-assembly in systems with competing interactions,” *Soft Matter*, **13**: 8055-63, (2017). DOI: 10.1039/c7sm01721a
4. S. Jiao, A. P. Santos, and A. Z. Panagiotopoulos, “Differences in free surfactant concentration and aggregation properties for amphiphiles with the same critical micelle concentration,” *Fluid Phase Equil.*, (2018). DOI: 10.1016/j.fluid.2017.10.026
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Probing Large Complex Systems with DFTB: Parallelization Enhancements and Self-Interaction Corrections

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1. Abstract

This project is comprised of two complementary (but parallel) thrusts: (1) implementing massively-parallelized enhancements (with new computational hardware that may replace GPUs) for calculating the electron dynamics of large chemical systems, and (2) introducing self-interaction corrections for improving the accuracy of the density functional tight binding (DFTB) approach. While classical molecular dynamics can handle hundreds of thousands of atoms, it cannot provide a first-principles based description of mesoscale systems at the quantum level. At the other extreme, conventional Kohn-Sham DFT methods can probe the true quantum mechanical nature of chemical systems; however, these methods cannot tackle the large sizes relevant to mesoscale dynamics and length scales. The DFTB formalism utilized in this project provides a viable approach for probing these large systems at a quantum mechanical level of detail. However, to utilize the DFTB approach for accurate calculations of electronic properties, it is crucial to incorporate *quantum-based non-empirical corrections* in DFTB since exchange-correlation effects can still remain very strong in these large systems. At the same time, enhancing the computational efficiency of DFTB is also essential since optimal computational performance is required for addressing the large size scales associated with mesoscale systems. As such, the new non-empirical corrections and other hardware enhancements implemented in this project will enable accurate *and* computationally efficient approaches to directly probe quantum dynamics in these large, complex systems.

2. Recent Progress

The start date of this project was 08/15/2016, and during the middle of the second year in this project we have devoted most of our efforts to finalizing our development and implementation of self-interaction corrections (SICs) in an open-source, massively-parallelized, all-electron DFT code (NWChem). During our implementation phase, we actually uncovered a few interesting scientific and technical details on new convergence techniques for Fermi-Orbital SIC (FO-SIC) that have not been previously reported in the literature. A rapid communication on these recent findings has been submitted, and this paper (still under review) gives additional insight on alternative convergence techniques that should be avoided when solving the iterative FO-SIC equations. Niranjan Ilawe, a graduate student funded by this DOE project, is scheduled to graduate in June 2018, and a follow-up paper on real-time, TDDFTB plasmonics was submitted to *J. Mater. Chem. C*. At the time of this DOE abstract submission, this manuscript is undergoing a first revision, and this manuscript is Niranjan's final paper on this topic as he finishes his PhD thesis. A short summary of both of these efforts and our progress in each of these initiatives are described further below.

The FO-SIC formalism is a variant of SIC that utilizes unitarily-invariant self-interaction corrections with Fermi Orbitals (FOs) as described by Pederson and coworkers (Pederson, M.R.; Ruzsinszky, A.; Perdew, J. P. *J. Chem. Phys.* **2014,** *140*, 121103). We have developed and refined an in-house (i.e., from scratch) implementation of FO-SIC in NWChem. We have chosen to use the NWChem open-source platform for our initial implementation due to its extensive support/use by other DOE CTC PIs as well as its established, massively-parallelized libraries that the FO-SIC approach fully utilizes for maximum efficiency. In addition, we decided to first implement the FO-SIC approach in an all-electron DFT code to both verify and understand all the subtle intricacies of this formalism before proceeding to the more difficult task of modifying this new formalism for DFTB. As a recap for the general reader, the specific procedure for implementing the FO-SIC approach in our NWChem implementation is summarized in **Figure 1** and given as follows: (1) For a set of DFT orbitals, $\{\psi_\alpha\}$, N centroid positions $\{\mathbf{a}_1, \mathbf{a}_1, \cdots, \mathbf{a}_N\}$ (see **Figure 2**) are found which provides a set of N normalized linearly independent (but not orthogonal) FOs, $\{F_1, F_2, \cdots, F_N\}$. Within our NWChem implementation, we obtain initial guesses of these centroids via a Foster-Boys localization method. (2) Löwdin's method of symmetric orthonormalization is then used to construct a set of localized orthonormal orbitals, $\{\phi_1, \phi_2, \cdots, \phi_N\}$ and construct the SIC-DFT energy from the set of FOs; (3) the SIC-DFTB energy is minimized as a function of the DFT orbitals and the FO centroids. Within our specific NWChem implementation, we have found that a Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm gives enhanced (or, at the very least, comparable) convergence to the original conjugate gradient approach used previously. In a manuscript submitted recently (and still under review), we have also re-formulated some of the original expressions in the FO-SIC description to take advantage of the underlying symmetries in the expressions for $\Delta^1_{lk,m}$ and $\Delta^3_{lk,m}$, which give additional physical insight into the convergence properties of this approach. Most importantly, the FO-SIC approach circumvents the original Perdew-Zunger localization equations which scale as $O(N^6)$ and will also be of paramount importance when it is implemented in the DFTB formalism. To validate our FO-SIC implementation, we have carried out detailed comparisons between total electronic energies, atomization energies, and ionization potentials from a very recent arXiv publication by Perdew and co-workers (arXiv: 1703.10742v1 [physics.comp-ph]). After several extensive benchmark comparisons between centroid positions, electronic energies atomization

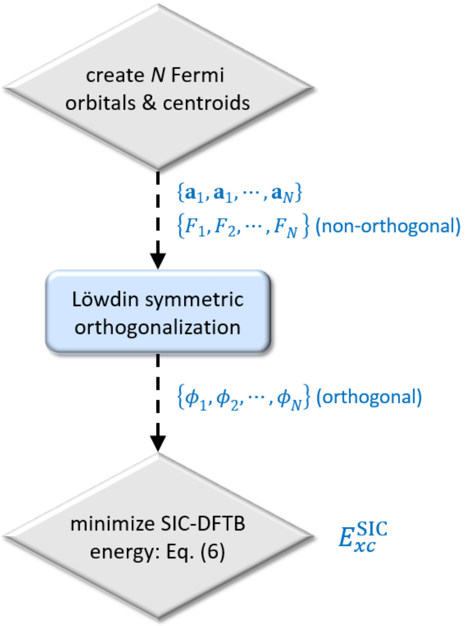


Figure 1. Simplified algorithmic flowchart for our NWChem implementation of FO-SIC. The computed outputs of each block are listed next to the dotted arrows, which are later used in subsequent blocks.

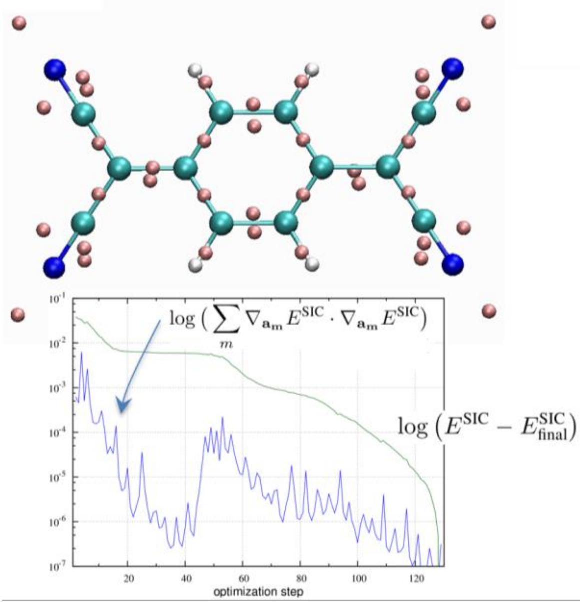


Figure 2. (top) converged FO centroid positions (pink) overlaid on a TCNQ molecule; (bottom) convergence behavior for both the gradient modulus (blue) and the total SIC energy (green).

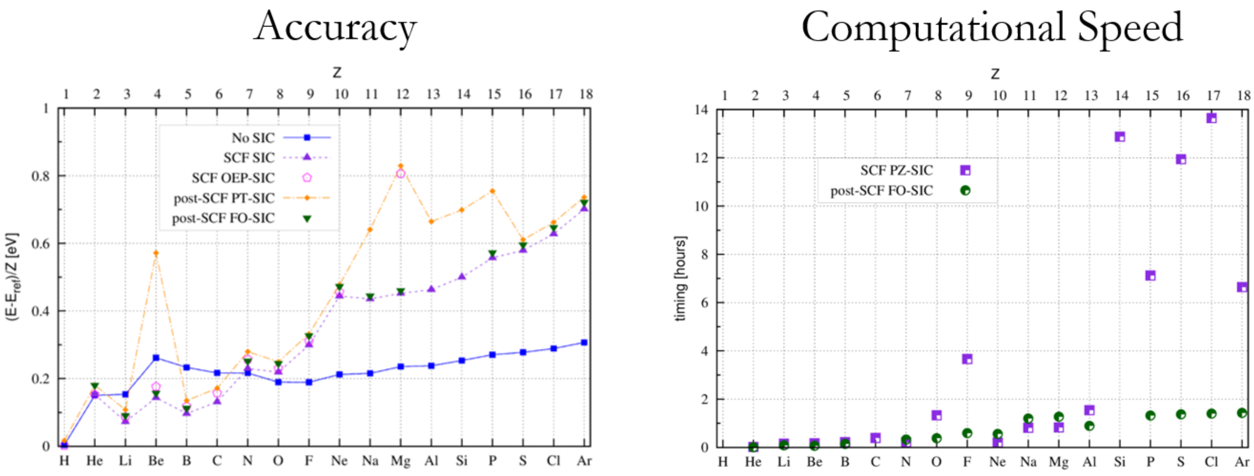


Figure 3. (left) Relative errors in computing the total energy of atoms using various SIC approaches: LDA (No SIC), fully self-consistent SIC (SCF-SIC), optimized effective potential SIC (OEP-SIC), perturbative SIC (post-SCF PT-SIC), and Fermi Orbital (post-SCF FO-SIC); (right) computational timings of fully self-consistent SIC vs. the post-SCF FO-SIC approach.

energies, and ionization potentials benchmarks provided by Dr. Zeng-hui Yang and Prof. Alan Jackson, we have confirmed that our FO-SIC approach is fully functional. With this approach properly benchmarked, we have also carried out additional studies comparing the accuracy of FO-SIC against other SIC variants, including fully self-consistent PZ-SIC (SCF SIC), optimized effective potential (OEP-SIC), as well as other perturbative versions of SIC (post-SCF PT-SIC), as shown in **Figure 3**. Our extensive comparisons show that FO-SIC achieves similar accuracy to the more computationally-expensive SCF SIC and is more accurate than some of the other perturbative post-SCF SIC approaches. These results are particularly encouraging since they show that FO-SIC has the same accuracy as higher levels of theory but is fast enough (**Figure 3**) to not degrade the overall efficiency when it will be implemented in the DFTB approach.

As mentioned previously, Niranjan Ilawe, a graduate student funded by this DOE project, is scheduled to graduate in June 2018. Between the last DOE update in April 2017 and this abstract submission, a recent 2017 manuscript was published in the *Journal of Chemical Theory and Computation* that utilizes real-time, time-dependent DFTB (RT-TDDFTB) to understand energy transfer in large plasmonic nanoantennas (shown schematically in **Figure 4**). The RT-TDDFTB approach was utilized to provide a quantum-mechanical description (at an electronic/atomistic level of detail) for characterizing and analyzing these systems without using commonly-used classical approximations. This recent work demonstrated highly long-range electronic couplings in these complex systems and showed that the range of

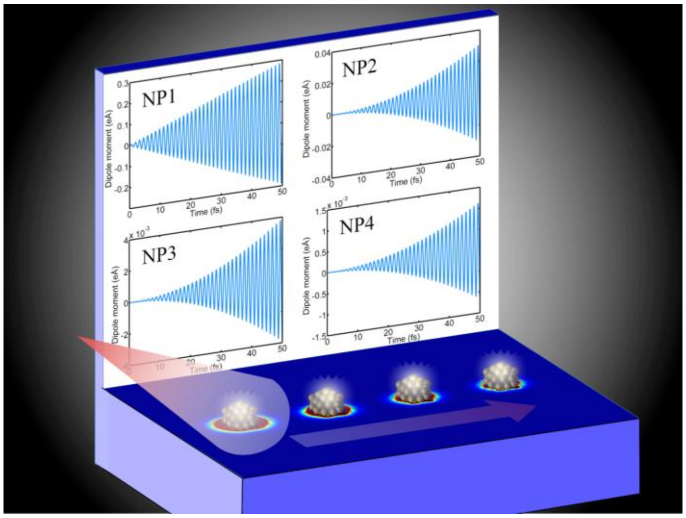


Figure 4. Electronically-excited dipole moments of individual nanoparticles (NP1 – NP4) in a plasmonic nanoantenna as NP1 is excited by monochromatic light.

these couplings was more than twice the conventional cutoff limit considered by FRET based approaches. Furthermore, these unusually long-ranged electronic couplings were attributed to the coherent oscillations of conduction electrons in plasmonic nanoparticles. This long-range nature of plasmonic interactions has important ramifications for electronic excitation transfer – in particular, this published study showed that the commonly used "nearest-neighbor" FRET model is inadequate for accurately characterizing electronic excitation transfer even in simple plasmonic antenna systems. These findings provide a real-time, quantum-mechanical perspective for understanding electronic excitation transfer mechanisms and provide guidance in enhancing plasmonic properties in artificial light-harvesting systems. A follow-up paper to this study was recently submitted to *J. Mater. Chem. C* and, at the time of this abstract submission, is undergoing a first revision.

3. Future Plans

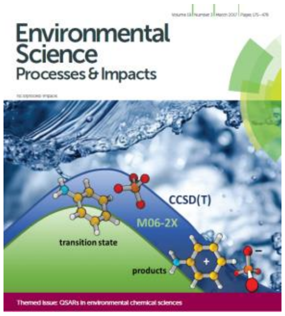
With the FO-SIC all-electron DFT code fully-working and functional, we intend to focus all our effort into modifying this formalism in both the DFTB and a real-time DFTB dynamics approach. In addition, we are making exciting progress in utilizing new computational hardware for massive parallelization of the real-time DFTB approach. Two MS theses were supported by this DOE grant, and a total of 3 manuscripts by these MS students have been published (see below). A PhD thesis (and two associated manuscripts) is expected to be completed by June 2018.

Grant Number and Title: DE-SC0016269: ***"**Non-Empirical and Self-Interaction Corrections for DFTB: Towards Accurate Quantum Simulations for Large Mesoscale Systems**"***

Postdoc: Dr. Fredy W. Aquino
Students: Mr. Niranjan Ilawe, Ms. Sangavi Pari, and Ms. Lindsey N. Anderson

Publications acknowledging DOE grant in the last 18 months:

1. A. A. Barragan, N. V. Ilawe, L. Zhong, B. M. Wong, and L. Mangolini, *"A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles."* Journal of Physical Chemistry C, **121**, 2316 (2017).
2. S. Pari, I. A. Wang, H. Liu, and B. M. Wong, *"Sulfate Radical Oxidation of Aromatic Contaminants: A Detailed Assessment of Density Functional Theory and High-Level Quantum Chemical Methods."* *Environmental Science: Processes & Impacts*, **19**, 395 (2017). **(Invited Paper)**
    - **Featured as the** front cover **for the** March 2017 themed collection on QSARs and Computational Chemistry Methods in Environmental Chemical Sciences **of** *Environmental Science: Processes & Impacts* (Issue 3)
    - **Featured as one of the "top 10 most downloaded articles" in** *Environmental Science: Processes & Impacts* in 2017



3. L. N. Anderson, M. B. Oviedo, and B. M. Wong, *"Accurate Electron Affinities and Orbital Energies of Anions from a Non-Empirically Tuned Range-Separated Density Functional Theory Approach."* *Journal of Chemical Theory and Computation*, **13**, 1656 (2017).
4. N. V. Ilawe, M. B. Oviedo, and B. M. Wong, *"Real-Time Quantum Dynamics of Long-Range Electronic Excitation Transfer in Plasmonic Nanoantennas."* Journal of Chemical Theory and Computation, **13**, 3442 (2017).
5. L. N. Anderson, F. W. Aquino, A. E. Raeber, X. Chen, and B. M. Wong, *"Halogen Bonding Interactions: Revised Benchmarks and a New Assessment of Exchange vs Dispersion."* *Journal of Chemical Theory and Computation*, **14**, 180 (2018).

Francesco A. Evangelista

Driven similarity renormalization group: Extension to electronically excited states

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Abstract

The goal of our project is the development of new multireference many-body theories based on the driven similarity renormalization group (DSRG).[1] In the past, we have developed state-specific multireference DSRG (MRDSRG) methods to treat dynamical electron correlation effects in molecular systems. We have shown that the MRDSRG provides a convenient framework to derive numerically-robust multireference theories with electron correlation treated perturbatively (second- and third-order)[2–4] or at a level comparable to that of coupled cluster methods.[5] Another advantage of the DSRG is that it leads to equations that are relatively simple, and therefore, can be implemented in efficient algorithms that are amenable to parallelization.

In this talk, I will give an overview of recent developments, focusing on new economical schemes to treat electronically-excited states and state-averaged methods that for near-degenerate states and conical intersections.

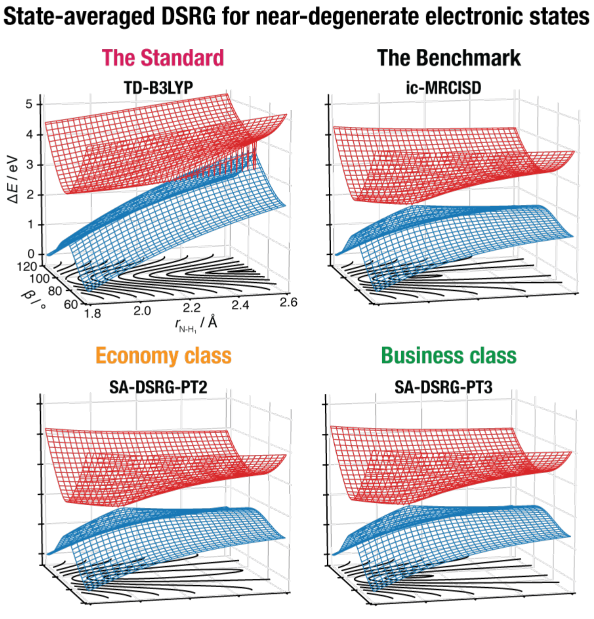

Figure 1. Potential energy surfaces (PESs) for the lowest two singlet states of NH_3 computed using various methods and the aug-cc-pVTZ basis set. $r_{N\text{-}H}$: N-H_1 bond distance, β: pyramidalization angle.

Recent progress

In the past year, we have worked on extensions of the DSRG formalism to treat excited states. In our first paper (Ref. 6), we developed low-cost state-specific approaches based on valence configuration interaction (VCI) zeroth-order wave functions. Starting from a Hartree–Fock reference, we construct the space of all singly or singly and doubly excited determinant within a set of active orbitals. These zeroth-order wave functions are then corrected for missing electron correlation effects using the DSRG truncated to second order in perturbation theory (DSRG-PT2). The resulting VCIS/VCISD-DSRG-PT2 methods were benchmarked on a set of over 100 excitation energies of 28 organic molecules. Interestingly, we found that these simple approaches can predict excitation energies with accuracy that compares very favorably with other TD-DFT and wave function methods. Excitation energies computed at the VCIS-DSRG-PT2 level deviate on average from reference CC3 values by 0.32 eV (absolute deviations) matching the accuracy of TD-B3LYP. By adding doubles (VCISD), the accuracy of this approach improves and the mean absolute deviation is reduced to 0.22 eV, a number comparable to that of equation-of-motion coupled cluster theory with singles and doubles (EOM-CCSD).

One of the major limitations of state-specific theories is their inability to correctly describe near-degenerate electronic states. For example, the avoided crossing between the first two $^1\Sigma^+$ states of LiF is incorrectly described by many state-specific methods as a double crossing. To treat such problems with the DSRG, we have recently developed a state-averaged formalism. Our new approach is described in a second paper (Ref. 7) where we generalize the DSRG to study an ensemble of electronic states. In the state-averaged multireference DSRG (SA-MRDSRG), we perform a *single* unitary transformation of the Hamiltonian to decouple a chosen ensemble of states from excited configurations. This corresponds to treating dynamical correlation effects in an averaged way for all the states of interest. We have currently examined the SA-MRDSRG truncated to second- and third-order in perturbation theory (SA-DSRG-PT2/3). These methods are advantageous because they can treat a manifold of near-degenerate states at the cost of a single state-specific computation. We have benchmarked the SA-DSRG-PT2/3 methods on the potential energy curve of LiF, the conical intersection between the ground and first singlet excited states of NH_3, a prototype of the retinal protonated Schiff base, and the challenging low-lying states of the (E,E)-1,3,5,7-octatetraene molecule. The accuracy of SA-DSRG-PT2 is found to be similar to other second-order multi-state second-order perturbation theories. Instead, the third-order approach SA-DSRG-PT3 is in very good agreement with the Werner-Knowles version of internally-contracted MRCISD.

Future plans

- Develop excited state methods that combine features of the state-averaged formalism with the accuracy of state-specific approaches.
- Derive and implement analytic energy gradients of the DSRG-MRPT2.
- Realize a density-fitted implementation of the nonperturbative MR-DSRG truncated to one- and two-body excitations with computational and memory scaling equivalent to that of CCSD.

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Grant Numbers and Grant Titles

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

Postdoc(s): Chenyang Li

Student(s): Jeffrey B. Schriber, Tianyuan Zhang

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

a) Li, C.; Evangelista, F. A., Driven Similarity Renormalization Group: Third-Order Multireference Perturbation Theory. *J. Chem. Phys.* **146**, 124132 (2017).
b) Li, C.; Verma, P.; Hannon, K. P.; Evangelista, F. A., A low-cost approach to electronic excitation energies based on the driven similarity renormalization group. *J. Chem. Phys.* **147**, 074107 (2017).
c) Parrish, R. M.; Smith, D.; L. Burns *et al*., Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. *J. Chem. Theory Comput.* **13**, 3185 (2017).
d) Li, C.; Evangelista, F. A. Driven similarity renormalization group for excited states: A state-averaged perturbation theory, *J. Chem. Phys.* **148**, 124106 (2018).
e) Smith, D.; L. Burns; D. Sirianni *et al*., Psi4NumPy: An Interactive Quantum Chemistry Programming Environment for Reference Implementations and Rapid Development (*submitted*).

Accurate wave functions expressed as polynomial product states

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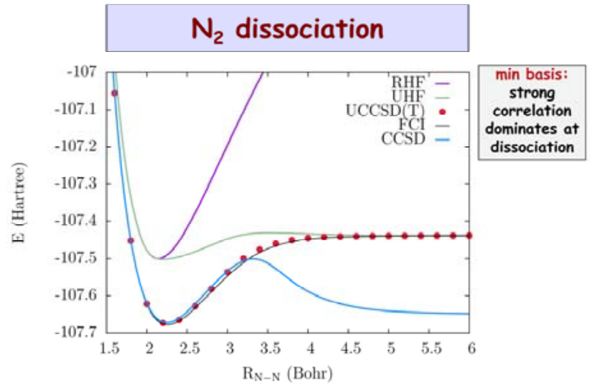
Abstract

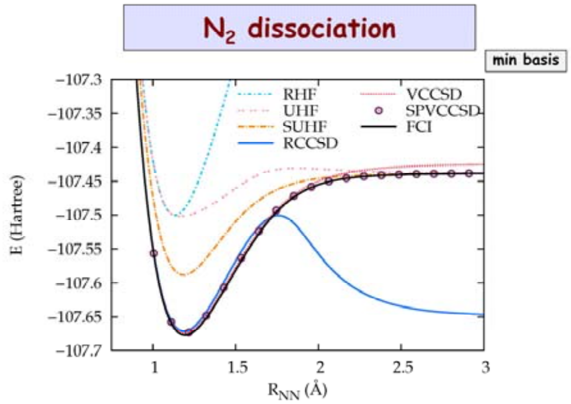
A precise accounting for electronic correlation effects is necessary for quantum mechanical calculations to reliably yield accurate results in molecular and solid-state systems. Correlation can be conceptually divided into weak correlations due to electrons avoiding one another because of the repulsive Coulombic interaction, and strong correlations which arise from 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.

In this project, 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 two 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 responsible for the catastrophic failure of restricted coupled cluster under strong correlation. This is bad news. The good news is that these collective excitations factorize (non-exponentially) from lower order ones, so their accurate treatment is plausible. Our current efforts are focused on merging exponential and non-exponential polynomials of particle-hole excitations for treating weak and strong correlations, respectively.



CCSD has an unphysical bump

UCCSD(T) : right energy but wrong wavefunction



VCCSD does not get the right answer at dissociation
SPVCCSD = **SUHF+VCCSD** is very accurate everywhere

Grant Number and Grant Title

DE-FG02-09ER16053 Computational and Theoretical Chemistry
Accurate Ground and Excited States via Symmetry Projection Combined with Coupled Cluster Theory

Personnel

Thomas M. Henderson (Senior Research Associate, 50%), Matthew R. Hermes (Postdoc, 50%),
Yiheng ("Ethan") Qiu (Graduate Student, 100%)

Ten Publications Acknowledging this Grant

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Theoretical Studies of Elementary Hydrocarbon Species and their Reactions

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Abstract

Fast construction of the exchange operator in an atom-centered basis with concentric atomic density fitting

An algorithm is presented for computing the Hartree–Fock exchange matrix using concentric atomic density fitting with *O(N)* data and instruction count complexities. The algorithm exploits the asymptotic distance dependence of the three-center Coulomb integrals along with the rapid decay of the density matrix to accelerate the construction of the exchange matrix. The new algorithm is tested with computations on systems with up to 1536 atoms and a quadruple-zeta basis set (up to 15585 basis functions). Our method handles screening of high angular momentum contributions in a particularly efficient manner, allowing the use of larger basis sets for large molecules without a prohibitive increase in cost.

Computation of the so-called exchange operator is often the most expensive step in electronic structure models applicable to large systems, such as the hybrid density functional theory (DFT) and Hartree–Fock (HF), the latter of which serves as the starting point for electron correlation treatment with modern reduced-scaling many-body methods. The exchange matrix, K, is given by

$$K_{\mu\nu} = \sum_{\lambda\sigma} D^{\lambda\sigma}(\mu\lambda|\nu\sigma)\,, \tag{1}$$

Where μ, ν, λ, σ,… denote basis functions, **D** is the density matrix, and

$$(\mu\nu|\nu\sigma) = \int \chi_{\mu}(\vec{r}_1)\,\chi_{\lambda}(\vec{r}_1)\frac{1}{|\vec{r}_1 - \vec{r}_2|}\,\chi_{\nu}(\vec{r}_2)\chi_{\sigma}(\vec{r}_2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{2}$$

are the electron repulsion integrals (ERIs) in the Mulliken 'bra–ket' notation. Here we consider atom-centered basis functions $\chi(\vec{r})$, typically represented by (contracted) Gaussian-type orbitals. Although $(\mu\lambda|\nu\sigma)$ decays with the bra–ket distance R only as R^{-1} (i.e. slowly), the decay of the density matrix $D^{\lambda\sigma}$ in a finite system (and, generally, any system with a nonzero band gap) is exponential with the distance between λ and σ. Therefore, as first noted by Almlöf, the number of nontrivial elements of the exchange matrix **K** grows linearly with system size – that is, **K** has $O(N)$ significant elements ($N \propto$ system size). A number of linear-scaling methods for the computation of **K** have been investigated over the years, with pioneering work done in chemistry in the mid-

1990s by Schwegler, Challacombe and Head-Gordon and Burant, Scuseria and Frisch. Several related algorithms have been developed, e.g. ONX by Challacombe et al. and LinK by Ochsenfeld, White and Head-Gordon.

The aforementioned $O(N)$ algorithms for exchange take advantage of the element-wise sparsity of the ERI and density matrix tensors in Equation (1). Some effort has gone into utilization of rank sparsity of the ERI tensor, as revealed by the multipole expansion of the Coulomb operator, by the pseudospectral and related factorizations of ERI, or, as done here, by the density fitting approximation of ERIs. The density fitting approximation (DF, also called resolution of the identity) expresses the two-center products in the bra and the ket of the ERI tensor (often called 'densities,' not to be confused with the density matrix **D**) as linear combinations of one-center functions from an auxiliary basis:

$$|\mu\nu) = \sum_X C_{\mu\nu}^X \, |X) \, , \tag{3}$$

where X, Y, … are indices in an auxiliary basis set. To obtain the coefficients $C_{\mu\nu}^X$, one must left-project with the auxiliary basis to obtain a system of linear equations:

$$(Y|\mu\nu) = \sum_X C_{\mu\nu}^X \, (Y|X) \, . \tag{4}$$

The solution of these equations in their full form requires $O(N^3)$ effort and is thus untenable for large molecular systems. Moreover, substitution of the form in Equation (3) into the exchange matrix expression in Equation (1) does not reduce the formal scaling of the exchange matrix build; nevertheless, for small systems and/or large basis sets the use of density fitting for the exchange evaluation can be worthwhile. Consequently, significant work has been done on methods of reducing the scaling of Equation (3), by using local fitting metrics and/or by using 'local' subsets of the fitting bases. Here, we employ the most extreme local density fitting variant, namely where an AO product density is expanded in terms of the fitting functions concentric with any of the AOs in the product. Although the idea is as old as the density fitting itself, recently it has been revived under the name pair atomic resolution of the identity (PARI) by Merlot and co-workers; we referred to this approach as concentric atomic density fitting (CADF) to emphasize the underlying robust density fitting approximation, which is critical to the viability of the approach, as well as to permit extensibility beyond binary product densities. This paper presents a formulation of HF exchange based on CADF with rigorously linear storage and operation complexities. The algorithm has been implemented in a massively parallel fashion in a publicly available open-source Massively Parallel Quantum Chemistry (MPQC) software suite.

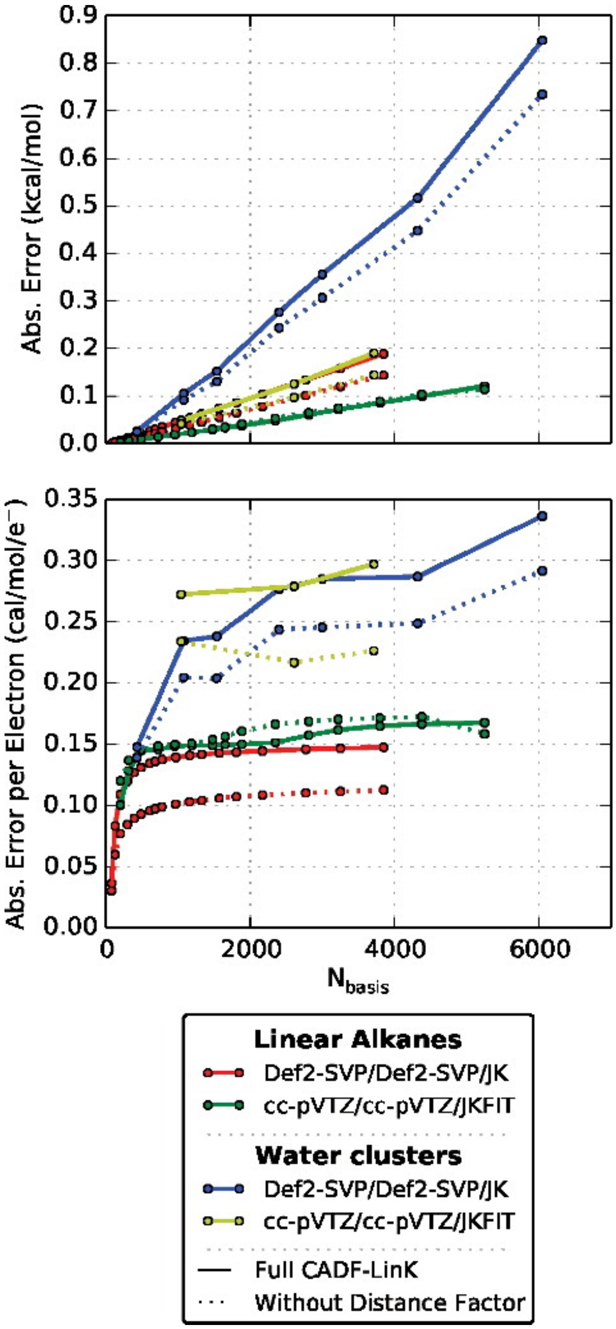

Figure. Errors in absolute energies arising from the CADF-LinK approximation, relative to CADF-based exchange using only Schwarz screening. Errors per electron are given in the bottom plot to show that the CADF-LinK errors increase linearly with system size.

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Theoretical and Experimental Studies of Elementary Hydrocarbon Species and Their Reactions

Students: Adam S. Abbott, Andreas V. Copan, Sarah N. Elliott, Marissa L. Estep, Jonathon Misiewicz, Kevin B. Moore, Whitney J. Morgan, Avery E. Wiens, Boyi Zhang

Ten Recent DOE Sponsored Publications

1. D. S. Hollman, H. F. Schaefer, and E. F. Valeev, "Fast Construction of the Exchange Operator in an Atom-Centered Basis with Concentric Atomic Density Fitting," *Molecular Quantum Mechanics Special Issue, Mol. Phys.* **115,** 2065 (2017).

2. A. Gao, G. Li, B. Peng, Y. Xie, and H. F. Schaefer, "The Water Dimer Reaction $OH + (H_2O)_2 \rightarrow (H_2O) - OH + H_2O$," *Phys. Chem. Chem. Phys.* **19,** 18279 (2017).

3. L. Li, M. Lei, Y. Xie, H. F. Schaefer, B. Chen, and R. Hoffmann, "Stabilizing a Different Cyclooctatetraene Stereoisomer," *Prof. Nat. Acad. Sci. USA* **114**, 9803 (2017).

4. M. L. Estep, W. J. Morgan, A. T. Winkles, A. S. Abbott, N. A. Villegas-Escobar, J. W. Mullinax, W. E. Turner, X. Wang, J. M. Turney, and H. F. Schaefer, "Radicals Derived from Acetaldehyde and Vinyl Alcohol," *Phys. Chem. Chem. Phys.* **19,** 27275 (2017).

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Machine Learning for Evaluating Global Reaction Coordinates from Nonadiabatic Molecular Dynamics Simulations

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Program Scope

We have successfully developed and implemented machine-driven algorithms to evaluate reaction coordinates from non-adiabatic molecular dynamics (NAMD) simulations. The methodology can be easily applied to *any* molecular dynamics simulation package. The benefits of our approach is that we evaluate reaction coordinates with **zero** human bias influencing the results. The efficiency of our NAMD approach means that we can also explore significantly statistical ensembles of excitation processes.

RECENT PROGRESS

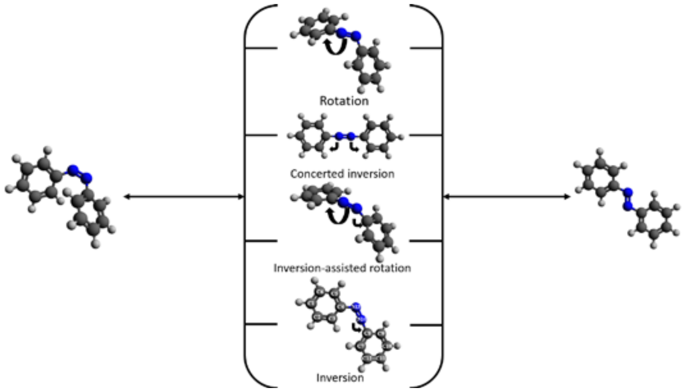

Figure 1. Four reported mechanisms in azobenzene photoisomerization.

Structurally, azobenzene molecules exist in closed and open forms, which can be interconverted between their *cis*- and *trans*-isomers via light irradiation (photoisomerization). There are four proposed mechanisms for isomerization in azobenzene based on experimental and theoretical observations: rotation, inversion, concerted inversion, and inversion-assisted rotation. In the rotational pathway (shown in Fig. 1), the N=N π-bond breaks, allowing for free rotation around the N−N bond, and the C−N=N−C dihedral angle changes, while the N=N−C angles remain fixed at ~120°. In the inversion mechanism (also shown in Fig. 1), the C−N=N−C angle remains fixed at 0°, but one of the N=N−C angles increases to 180°. A linear transition state is produced in the concerted inversion mechanism when both N=N−C bond angles increase to 180°. Finally, in the inversion-assisted rotation mechanism, there are large changes in both the C−N=N−C angle and the N=N−C angles, simultaneously. No barrier exists along the rotational pathway after excitation into the S1 state. According to previous computational research, the conical intersection between the S0 and S1 states exists when the C−N=N−C dihedral angle is ~90° and the N=N−C angle is ~140°. These facts have prompted the acceptance of rotation as the dominant mechanism with concerted inversion occurring under rotation-restricted conditions.

The greatest challenge in determining reaction coordinates from chemical processes is to sort through the complexity of the reaction pathway. Experimental spectroscopic techniques may pinpoint one or two internal coordinates that contribute to a specific reaction pathway; but, it is impossible to probe the contributions of all internal coordinates to the reaction coordinate. We have recently reported (*J. Am. Chem. Soc.* 2018) on a *comprehensive* reaction coordinate describing the photoisomerization reaction mechanism of azobenzene. There are 116 internal coordinates (bonds, angles, and dihedral angles) within azobenzene; and, through a series of machine-driven algorithms, we rank order all of these internal coordinates and quantify their contribution to the reaction mechanism of photoisomerization.

Thereby, in this work, we are present a reaction mechanism profile that is based on *all degrees of freedom* of azobenzene.

In our machine-driven hunt for global reaction coordinates, we have developed the following procedure (details are discuss in Ref. 1, *J. Am. Chem. Soc.* 2018): 1) calculate the mutual information between energy and coordinate datasets generated from nonadiabatic molecular dynamics simulations – this will quantitatively yield a weight of how each internal coordinate participates in the global reaction coordinate; 2) filter out redundancies of internal coordinate participation in the global reaction coordinate utilizing principal component analysis; 3) build nodes belonging to a network where each node is multi-dimensionally represented by the HOMO energy and that energy's corresponding internal coordinates weighted by the mutual information.; 4) determine global reaction coordinates along the network following the paths of least action. We follow trajectories along these nodes that represent points from molecular dynamics simulations; however, these simulations do not connect one node to another node – the nodes are independent.

From our mutual information rankings, we discover the following – 1) the largest contribution to the change in the HOMO potential energy surface is the C8-N14=N13-C4 dihedral angle (atom labels defined in Fig. 1) with MI = 0.320; 2) the next higher values are the adjacent dihedral angles N13=N14-C8-C7, N13=N14-C8-C9, N14=N13-C4-C5, and N14=N13-C4-C3, all with MI ~ 0.18. Utilizing principle component analysis (discussed in the Supplemental Information), we determine that there is are redundancies found in the four dihedral angles – the dihedral angle N13=N14-C8-C9 is redundant to the dihedral angle N13=N14-C8-C7 and the dihedral angle N14=N13-C4-C3 is redundant to the dihedral angle N14=N13-C4-C5; 3) the third ranking internal coordinates are the angles C4-N13=N14 and C8-N14=N13 with MI ~ 0.18; 4) the fourth ranking internal coordinates are the double N=N bond and the neighboring N-C bonds, all with MI ~0.14.

These results are remarkable in that by merely considering entropic correlations the primary reaction coordinate for the photoisomerization consists of the C8-N14=N13-C4 dihedral angle – this result is well known and verified by experiment and theory. However, more than this putative result, our machine-driven results also suggest that there are two other mechanisms involved and rank high in the MI correlations – one mechanism is a concerted motion including the dihedral angle N13=N14-C8-C7 (or its redundant dihedral angle N13=N14-C8-C9) with the angle C8-N14=N13; the second mechanism is a concerted motion including the dihedral angles N14=N13-C4-C5 (or its redundant dihedral angle N14=N13-C4-C3) together with the angle C4-N13=N14. That is, using mutual information, we are able to predict that the global reaction coordinate mainly includes a rotation around the C8-N14=N13-C4 dihedral angle as well as the rotation-inversion mechanism involving the two angles C4-N13=N14 and C8-N14=N13 and their corresponding dihedral angle. We previously reported, in our ensemble simulations for azo-functional systems, that there is statistically significant assistance from an inversion-assisted rotation (the nonadiabatic coupling vectors of these angles are not negligible) and results of this inversion-assisted rotation mechanism are also reported from experimental observations. Finally, by calculating the mutual information, we are also able to explicitly evaluate the contribution of each internal coordinate to the reaction coordinate. All 116 internal coordinates of azobenzene do contribute something to the reaction coordinate; however, the value of MI for the remaining internal coordinate contributions are greatly reduced compared to the first seven internal coordinates discussed above.

Calculating the mutual information and filtering using principle component analysis only recommends which of the internal coordinates are involved in the reaction mechanisms and their degree of participation (correlation) to the potential energy surface. All 166 internal coordinates contribute to the photoisomerization reaction coordinate of azobenzene and we can represent the potential energy surface with respect to all 116 degrees of freedom. However, we greatly reduce the dimensionality for representing the potential energy surface by choosing only the top five internal coordinates that contribute the most significantly after calculating mutual information and principle component analysis – the dihedral angle C8-N14=N13-C4, the dihedral angles N13=N14-C8-C7 and N14=N13-C4-C5 (or redundant partners, the dihedral angles N13=N14-C8-C9 and N14=N13-C4-C3), and the two angles C4-

N13=N14 and C8-N14=N13. From this reduced dimensionality, we have built a network representing the potential energy surface as a function of this five-fold dimensionality. As an example, Fig. 2 shows a reduced potential energy surface for the energy surface projected in the direction of the two primary internal coordinates.

Once we have built a network with nodes and edges, we can find the nodes corresponding to two optimized structures for local minima and use well known algorithms to find the path of least action between minima. We note three regions in the HOMO energy level in Fig. 3 - two are minima and one is a maximum. The minima of the HOMO correspond to the two forms of azobenzene, *cis* and *trans*. The maximum of the HOMO is the point corresponding to the transition between *cis* and *trans*. The structure at this transition point is a representative structure correspond to the intermediate state as *cis* photoisomerizes to *trans* or vice versa. If we follow the path of least action along the HOMO energy (described in the Supplemental Information – we build a surface network and following the least action gradients), then we arrive at the pathways shown in Fig. 3. Only the five primary, and non-redundant, internal coordinates responsible for the photoisomerization mechanism are plotted. The top plot of Fig. 3 also shows how the C8-N14=N13-C4 dihedral changes with respect to the change in the HOMO energy level. Looking at the C8-N14=N13-C4 dihedral, we find that the dihedral tends to 0° for the *cis*-azobenzene, tends to 180° for the *trans*-azobenzene, and ~90° for the transition structure – these results are exactly what is supported from experiment.

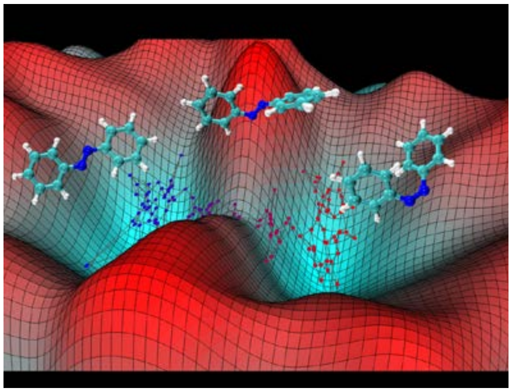

Figure 2. Two-dimensional representation of the multi-dimensional nodal network for the reaction pathways in azobenzene photoisomerization.

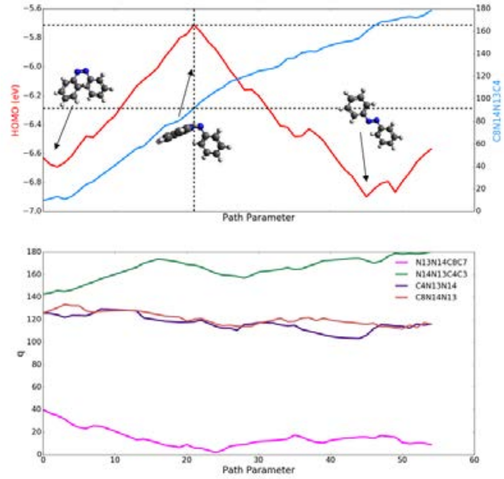

Figure 3. Results of the machine-learning network. (*top*) Plot of the HOMO versus the C8-N14=N13-C4 dihedral angle, one of the reactions coordinates found in the photoisomerization of azobenzene. (*bottom*) Plot of the HOMO versus reaction coordinates – the dihedral angles, N13=N14-C8-C7 and N14=N13-C4-C3, and the angles, C4-N13=N14 and C8-N14=N13.

The changing dihedral angle is the primary mechanism anticipated; however, from the plots, we see that other internal coordinates are also contributing to the reaction mechanism. For instance, there are noticeable changes in the two dihedral angles, N13=N14-C8-C7 and N14=N13-C4-C3, and the two angles, C4-N13=N14 and C8-N14=N13 (and, by symmetry, the two dihedral angles N13=N14-C8-C9 and N14=N13-C4-C5) which is supported by the mutual information ranking. However, these dihedral angles and principle angles, near the central dihedral, do not change significantly as we note in Fig. 3. The two dihedrals (N13=N14-C8-C7 and N14=N13-C4-C3) only change by roughly 20° and the two angles (C4-N13=N14 and C8-N14=N13) change only by roughly 10°. According to the mutual information ranking, these internal coordinates indeed contribute to the global reaction coordinate; however, the internal coordinates do not change significantly. This suggests that there certainly is an inversion-assisted rotation mechanism (a concerted motion of the dihedral angles and principal angles); however, this mechanism is not as strongly pronounced as suggested in previous observations. Our results do not support a purely inversion or a concerted inversion mechanism; there is nothing in the reaction coordinate plots of Fig. 3 to support these mechanisms.

In conclusion, what we propose is unique in that our method evaluates a global reaction coordinate that is *absolutely unbiased* - we merely take *n* datasets which are results from nonadiabatic molecular simulations and run machine-learning algorithms on this data. The reaction coordinates of the system are automated output. There are "human-free" decisions made within our approach other than to decide at the threshold of the mutual information for building the network. Algorithms can easily be put into place to remove this threshold decision. Finally, it is very important to note that the reaction coordinates are temperature dependent – we can easily run the simulations at different temperatures to evaluate temperature dependencies. Our results from mutual information shows the capability of choosing the importance of bonds in a reaction as N=N bond and C-N bonds. The applicability of this method to any other type of transition such as bond break depends on the output of the simulation package. Our approach is independent of DFT package, as long as the electronic structure calculations can provide an ensemble of simulations with the designated type of transition of interest can be calculated.

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

Postdoctoral Associates Supported: Guillermo Avendano Franco and Hong Wang
Students Supported: Arturo Hernandez, Amanda J. Neukirch, Olivia Pavlic, and Pedram Tavozohi

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1. P. Tavadze, G. Avenaño-Franco, P. Ren, X. Wen, Y. Li, and J.P. Lewis. **2018**. "A machine-driven hunt for global reaction coordinates of azobenzene photoisomerization," *J. Am. Chem. Soc.* 140: 285-290.
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Improving Density Functional Theory Methods for Spin-Related Molecular Properties

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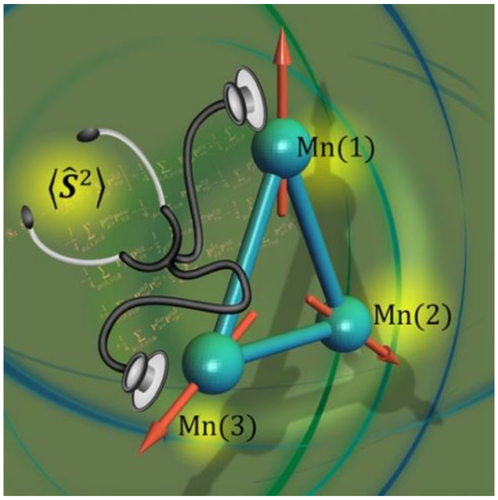
Abstract

Recent Progress:

(a) Even though several programs can be used today to perform noncollinear spin DFT calculations, none provides analysis tools for the solutions beyond one-particle spin operators. In view of this, we provided a generalization of the local spin analysis of Clark and Davidson [J. Chem. Phys. 115, 7382 (2001)] for the partitioning of the expectation value of the molecular spin square operator, $\langle S^2 \rangle$, into atomic contributions, $\langle S_A \cdot S_B \rangle$, to the noncollinear spin case in the framework of DFT. We also employed this local spin partitioning for a practical application: To extract $\langle S_A \cdot S_B \rangle$ as a function of the interatomic spin orientation given by the angle θ, which combined with the dependence of the electronic energy with θ, provides a methodology to extract magnetic exchange couplings J_{AB} from DFT calculations that, in contrast to conventional energy differences-based methods, does not require the use of *ad hoc* S_A and S_B nominal values.



(b) Self-interaction error (SIE) in DFT has been well known for a long time, and its potential effect on calculated molecular and solid-state properties have been discussed in the literature. For example, the reduction of SIE has been extensively used to justify the success of DFT+U for magnetic properties. Perhaps the most widely accepted framework for removing SIE in DFT is due to Perdew and Zunger (PZ) [Phys. Rev. B 23, 5048 (1981)]. However, due to the high computational cost associated with minimizing the PZ energy expression, the calculation of explicitly self-interaction free magnetic properties remains elusive. Recently, an efficient implementation for SIE removal based on Fermi orbitals was proposed (FLOSIC) [JCP 140, 121103 (2014)]. Using this method, we analyzed the effect of removing the SIE on magnetic exchange couplings using a small set of hydrocarbon radical molecules and model transition metal complexes. These calculations were carried out by independently relaxing the Fermi orbital descriptors (used in the FLOSIC method to localize the orbitals) for both high-spin and broken-symmetry configurations. In line with previous observations for small model systems, we find that removing SIE from LSDA improves calculated exchange couplings (Table 1). This can be interpreted in terms of the localization of the spin density produced by removing SIE.

Table 1: Magnetic exchange couplings (in cm^{-1}) calculated with standard DFT approximations and LSDA-based FLOSIC.

Method	model H-He-H			C_4H_4	TMM	$Cu_2Cl_6^{2-}$
	1.250 Å	1.625 Å	2.000 Å			
LSDA	-12,493	-1,494	-159	7,382	4,800	-493
PBEh	-7,275	-763	-73	-3,563	9,871	-22
SIC*	-5,414	-614	-62	-	-	-
FLOSIC	-5,503	-632	-61	-6,965	11,487	-198
Reference†	-4,860	-544	-50	-7,131	11,192	0 to -40

* From Ruiz *et al*. JCP 123, 164110 (2005).
† From different sources.

Future Plans:

- Improve efficiency in the relaxation of the Fermi orbital descriptors and in the FOSIC code. This will allow us to perform calculations on larger transition metal complexes.
- Test GGA and meta-GGA functionals in FLOSIC for magnetic properties.
- Implement a general two-component formalism combined with FLOSIC.
- Combine the local spin analysis with the two-components time propagation code. This is important to analyze the response of general magnetic systems, including spin-orbit and magnetic perturbations. We are currently developing an externally driven non-unitary propagation code to model systems out of equilibrium. The purpose is to develop a code that can model the electron and spin conduction through molecular junctions.

DE-SC0018331: FLO-SIC: Efficient Density Functional Theory Calculations without Self-Interaction and DE-SC0005027: Computational Methods Based on Density Functional Theory for Reactions and Processes Involving Electronic Spin.

Postdoc(s): Kamal Sharkas (since Jan. 2018) supported from DE-SC0018331.

Student(s): Suresh Thapa (2016-2017) R. P. Joshi (2018-) supported from DE-SC0005027.

Publications Acknowledging this DOE sponsored research (2014-2018)

- On the Question of the Total Energy in the Fermi-Löwdin Orbital Self-interaction Correction Method, K. P. K. Withanage, K. Trepte, J. E. Peralta, T. Baruah, R. Zope, and K. A. Jackson (submitted).
- Magnetic Properties of Mononuclear Co(II) Complexes with Carborane Ligands, D. R. Alcoba, O. B. Oña, G. E. Massaccesi, A. Torre, L. Lain, J. I. Melo, J. E. Peralta, and J. M. Oliva-Enrich (submitted)
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Program Title: Theoretical and Code Developments and Applications to Surface Science, Heterogeneous Catalysis, and Intermolecular Interactions

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Program Scope. Our research effort combines new theory and code developments with applications to a variety of problems in surface science and heterogeneous catalysis, 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.

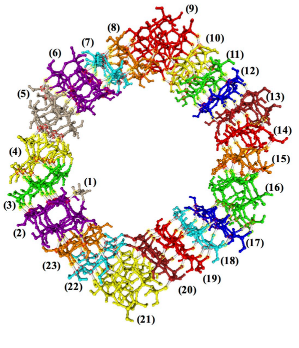
Recent Progress. A significant effort involves the development of efficient methods that can be applied to large systems, such as surfaces, nanoparticles and liquids. One such method is the effective fragment potential (EFP) method whose accuracy for intermolecular interactions rivals that of second 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 also been combined with our spin-flip TDDFT method to study solvent effects on the location and energy profile of conical intersections, which have a profound effect on excited states, photochemistry and photobiology. EFP molecular dynamics (MD) simulations have been employed to study the aqueous solvation of the hydronium ion[3] and to predict the melting temperature of ice[1]. In the latter study, the EFP method was shown to outperform density functional theory (DFT) methods.

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[3,5]. We have shown previously that one can do FMO/HF MD simulations with periodic boundary conditions and that fully analytic gradients are absolutely essential. An invited review of fragmentation methods has appeared in a high impact journal.[1] The FMO method is also highly scalable, because the calculation for each fragment can be performed on a separate compute node. Advances have also been made in high performance computational chemistry. An INCITE grant has 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)[5]. 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[5]. Also, a new method, the effective fragment molecular orbital (EFMO) method has been developed that replaces the bath potential with the EFP[6]. This incorporates the EFP induction component that includes many body interactions. It has been shown that the EFMO method is both more accurate and faster than the FMO2 method. Fully analytic EFMO gradients have been derived and implemented[6].

Another approach to making high-level electronic structure calculations is to use localized molecular orbitals (LMOs), because correlation is local. Another LMO-based fragmentation method, developed by the Piecuch group, called cluster-in-molecule (CIM) has been implemented in GAMESS. The CIM method is primarily intended to work with MP2 and coupled cluster methods, such as CCSD(T) and CR-CC(2,3). The bottleneck in the CIM method is the need to perform a HF calculation on the entire system to obtain the LMOs. This problem has been alleviated by the development of a combined FMO-CIM method, so that only the orbitals on each fragment need to be localized[2].

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

Mesoporous silica nanoparticles (MSN) have received increasing attention due to their catalytic capabilities. Because the MSN species are very important for their selective heterogeneous catalytic capability, we have an ongoing effort to model these complex species, in collaboration with the Evans and Slowing groups. Electronic structure theory calculations have been combined with the non-equilibrium statistical mechanics methods of the Evans group to provide insights about processes that occur within a MSN. The FMO method has been used to study the formation of carbinolamine, catalyzed by a section of MSN[4].



Fragmentation scheme for 1700-atom MSN

The GAMESS development group is part of the Department of Energy Exascale Computing Project (ECP). 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 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**[10]**.

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

A collaboration with the Evans group at the Ames Laboratory on reactions that occur on the Pd surface combines accurate electronic structure theory with kinetic Monte Carlo studies. These studies are complicated by the existence of several spin states of varying multiplicities, even for large Pd clusters. So, we have carried out a systematic analysis of the binding of substrates on metal clusters as a function of the spin state and the size of the cluster**[8]**. These calculations set the stage for the more extensive calculations of Co on Pd surfaces.

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

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

The interface of GAMESS with the quantum Monte Carlo (QMC) code QMCPACK is in progress, with the goal of combining QMC with our EFMO method. This will allow QMC calculations to take advantage of the multi-level parallelism associated with our fragmentation methods. Initial calculations on water clusters are very encouraging.

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Density functional simulations in the presence of environment

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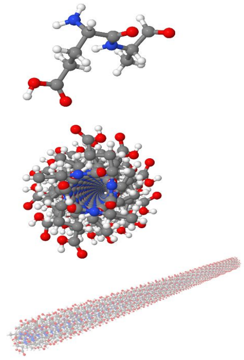

Component and views of 11,650 atom Glu-Ala Helix (67,2014 basis functions)

The project aims to improve the scalability of UTEP-NRLMOL electronic structure software for investigation of ground and excited state properties of molecular systems in the presence of an environment. The MPI+MPI parallelization using the shared memory features has been utilized to simulate systems as large as 11,650 atoms and 67,204 basis functions using 960 cores (2.66 Gb/core) on the Edison computational system at NERSC. The QM/MM model is implemented and parallelized where MM is the non-empirical effective fragment potential for simulations of large number of atoms. In the forthcoming year we will apply for large computational resources to examine the performance scaling of the code in detail and to carry out a few applications on systems in the presence of environments.

Technical progress and future work:

The work is primarily focused on improving the scalability in memory for the UTEP-NRLMOL electronic structure code for simulations in the presence of environment. This is needed for example to obtain accurate estimates of energetics such as redox potentials or solvent shifts or to model large molecules in vacuum. The largest memory consuming part in the code is the storage of Hamiltonian and Overlap matrices, and storage of the eigenvectors or density matrix. Besides these a number of arrays are needed to store various component of the Kohn-Sham potentials or its gradients on numerical grids. Numerical grids are needed due to the complexity of the exchange-correlation functional forms.

In the last PI meeting we presented two alternative approaches. The first approach, which we call cluster mesh approach, the parallelization was performed by breaking down the total systems into clusters for each atom by including all the atoms in a sphere whose radius depends on the most diffuse basis function (the basis function with the smallest exponent) for that atom. Thus the total system is broken down into subsystems to facilitate parallelization for reducing memory bottlenecks. The Kohn-Sham problem is still solved for the full system. In the second approach that we have pursued during the last year the mesh is divided into the blocks and the Hamiltonian matrix is stored in sparse format on each node using shared memory features of MPI-3. In this blockmesh approach, a group of processors work on building the Hamiltonian for each block of mesh. This idea is illustrated in the figure on the left. The figure shows the paraview rendering of the numerical grid used in DFT calculations on a multi-chromophoric heptad molecule. The mesh is divided into 8 blocks shown in different colors in the figure. All DFT calculations, that is, construction of DFT potentials and the Hamiltonian matrix elements for a given block of mesh are performed on a given node. The Hamiltonian matrix is stored on a node in a compressed sparse row format using shared memory features of MPI. The total Hamiltonian is obtained by

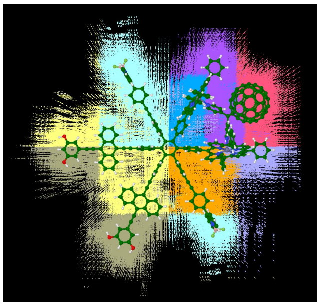

Illustration of parallelization by partitioning numerical mesh of Heptad molecule reducing the Hamiltonians calculated on each block of mesh. In this MPI+MPI approach internode communication occurs only during the reduction of Hamiltonians for each block of mesh and during the ScaLapack diagonalization. This implementation also leads to a scalable code. Over the past year subsequent memory bottlenecks were similarly identified and eliminated using shared memory features, including the calculated wavefunctions (expansion coefficients) and mesh-dependent arrays. The block-cyclic distribution is also used to store arrays when the full array is not needed on a node. An example of this are the eigenvectors returned after solving the generalized eigenvalue problem using ScaLapack. Likewise, the arrays required for mixing the potential for accelerating SCF convergence using Broyden-Johnson method are distributed across the nodes and used in such a way that no or minimal communication is required. We have studied a number of water balls using this blockmesh version of UTEP-NRLMOL code. With large system sizes, even a small serial section of the code which otherwise requires insignificant computing time begins to become a bottleneck. A number of such sections have been parallelized. A number of loops or parts of the code have been rewritten so that linear algebra routines from LAPACK/BLAS could be used. With this version we can simulate systems containing over **50,000** basis functions depending on the grid size. The largest system we have modeled using this system is Glu-Ala helix consisting of **11,650** atoms and **67,204** basis functions. This calculation was run on 40 nodes using 960 cores with 10 groups of 96 processors. All these calculations were performed on Edison at NERSC utilizing all available cores. It may be possible to simulate systems larger than this but our limited computational budget restricted us from going beyond this limit.

Additionally, to model the systems in the presence of very large number of atoms the QM/MM model has been introduced into the code. The MM model here is the non-empirical polarizable effective fragment potential (EFP) developed by Mark Gordon and coworkers. We have interfaced the *libefp* developed by Slipchenko and coworkers with UTEP-NRLMOL. This requires calculations of electric field at the multipoles sites which was obtained by differentiating the Coulomb potential by finite difference method. The implementation was tested on a number of small systems against the PSI4 and Q-Chem codes. The interface was parallelized and used to simulate the C_{60} fullerene-porphyrin-carotenoid triad immersed in 16,000 water molecules. Here the triad was treated at the DFT level and the water molecules using EFP.

DE-SC0006818: Improving scalability of electronic structure code for molecular simulations in the presence of environment

Postdoc(s): Luis Basurto

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

RECENT PROGRESS

Photoelectron Spectra of Copper Oxide Cluster Anions

We computed and analyzed the photoelectron spectra of copper oxide cluster anions, CuO^-, CuO_2^-, CuO_3^-, and Cu_2O^-. The spectra were computed using various techniques including DFT with semi-local, global hybrid, and optimally-tuned range-separated hybrid (OT-RSH) functionals, as well as many-body perturbation theory within the *GW* approximation based on various DFT starting points. The results were compared with each other and with available experimental data. We concluded that, as in many metal-organic systems, self-interaction errors are a major issue which is mitigated by hybrid functionals. However, these need to be balanced against a strong role of non-dynamical correlation – especially in smaller, more symmetric systems – where errors are alleviated by semi-local functionals. We investigated the relative importance of the two phenomena, including practical ways of balancing the two constraints.

The computed photoelectron spectra of the CuO$^-$ cluster show interesting variations across different levels of theory (Fig. 1). The ground state of CuO$^-$ is a closed shell singlet ($^1\Sigma^+$) that could be roughly described as $3d^{10}2p\sigma^2 2p\pi^4$. The first two photoelectron peaks [X and Y states in Fig. 1] can be interpreted as arising from the removal of $pd\pi^*$and $pd\sigma^*$ electrons from anti-bonding orbitals of significant O 2p character leading to the X$^2\Pi$ ground state and Y$^2\Sigma^+$ excited states of CuO, respectively. The broad and noisy band in the 4-6 eV energy range can be interpreted as the detachment of electrons from orbitals of primarily 3d character (bonding $pd\sigma$, $pd\pi$ and non-bonding Cu 3d). A comparison of the computed spectra with experimental data surprisingly shows that PBE provides the best predictions (within 50 meV of experiment) for the positions of the first two peaks. The PBE0 and OT-RSH (with exact exchange fraction α = 0.2) predictions are virtually the same, but they significantly underestimate both the ionization potential and the X-Y separation by ~0.5 eV. G_0W_0@PBE results are strikingly poor, with both X and Y peaks underestimated by ~1.4 eV. The use of a PBE0 starting point for G_0W_0 calculations significantly improves the quasiparticle energies, but the X and Y levels are still underestimated by ~0.4 eV compared to experiment. Better agreement with experiment can be obtained at the G_0W_0@BHLYP level, where the X and Y peaks are predicted to be 0.07 and 0.32 eV below the experimental values. Due to the broad and noisy nature of the Z band, it is not straightforward to make direct comparisons with experiment for states with higher binding energies (BEs). Using the results from recent EOM-CCSD calculations as a rough guide (which predict three peaks in the 4.5-5.5 eV range, in agreement with experiment), we observe that for these states PBE severely underestimates their BEs, while hybrid functionals (either within DFT or as starting point for the ensuing G0W0 calculations) do better. Overall taking all five peaks (with BEs less than 6 eV) into account, G_0W_0@BHLYP results are in good agreement with experiment and quantum chemistry results. PBE predictions are very good for the two most loosely bound states, but they perform poorly for states with higher BEs, while the opposite trend is observed for the case of hybrid functionals.

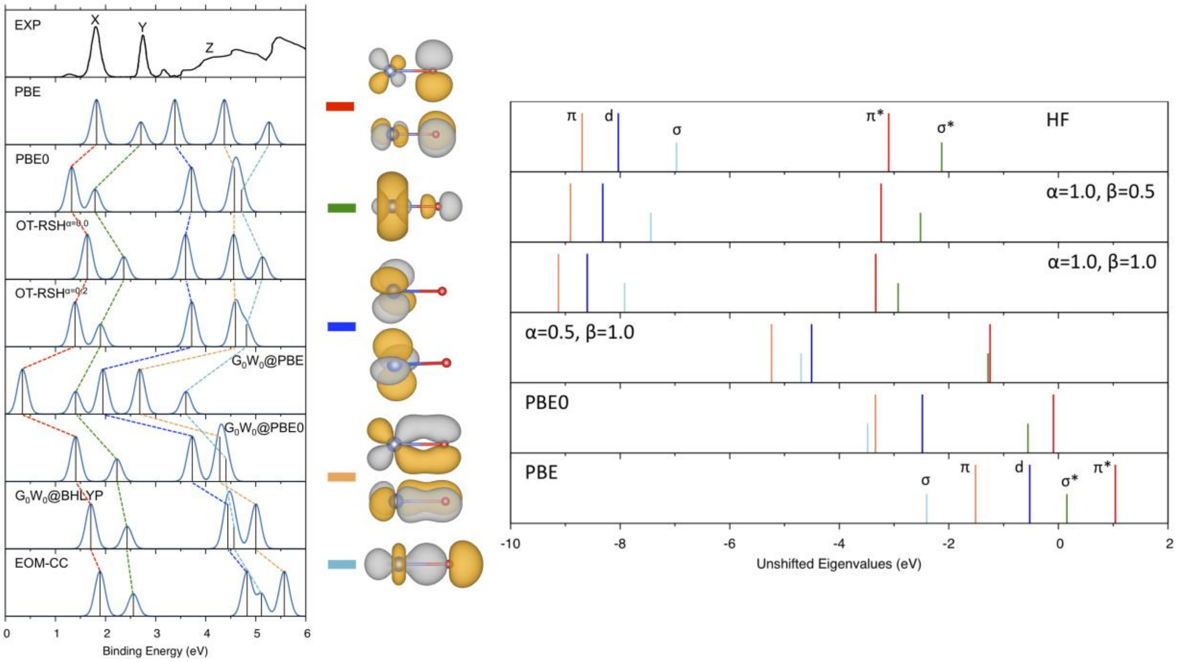

Fig. 1: (Left) Computed binding energies at various levels of theory for CuO$^-$ along with experimental data. Isosurfaces for $pd\pi^*$, $pd\sigma^*$, non-bonding Cu 3d, $pd\pi$, and $pd\sigma$ orbitals at the PBE level are also shown. (Right) Unshifted eigenvalues computed with differing amounts of Fock exchange and PBE correlation. To arrive at the binding energies plotted on the left within DFT, the eigenvalues need to be shifted to align the first peak with the vertical ionization potential of the CuO$^-$.

The increase in the BE of orbitals at the hybrid functional level compared to PBE for orbitals of large Cu 3*d* character can be understood in terms of mitigation of the self-interaction error by hybrid functionals for localized orbitals via the introduction of a fraction of the Fock exchange. The observation that PBE outperforms PBE0 for the position of the first two (X,Y) peaks is unexpected at first sight, but further analysis allowed us to interpret this finding in terms of the compatibility of exact exchange and correlation: Using an exchange-correlation $E_{\mathrm{xc}} = \alpha E_{\mathrm{x,HF}} + (1-\alpha)E_{\mathrm{x,PBE}} + \beta E_{\mathrm{c,PBE}}$ where $E_{\mathrm{x,HF}}$ is the Hartree-Fock (HF) exchange, and $E_{\mathrm{x,PBE}}$ $E_{\mathrm{c,PBE}}$ are semilocal PBE exchange and correlation, respectively, we performed a series of DFT computations varying α and β from 0 to 1 [Fig. 1(right)]. Of particular importance is the ordering of the orbitals at the HF level (α=1, β=0), where the (non-degenerate) HOMO is incorrectly predicted to be of σ^* character, and the doubly degenerate HOMO-1/HOMO-2 has π^* character. Adding more semilocal correlation to HF decreases the magnitude of the σ^*- π^* separation slightly, but HOMO still has σ^* character even at β=1. Upon removing some of the exact exchange, however, the σ^*- π^* ordering gets reversed, and $\alpha \leq 0.5$, HOMO has π^* character, in agreement with experimental data. Therefore, the small π^*- σ^*separation predicted by PBE0 (α=0.25, β=1) can be traced to the incorrect description of the ordering at the HF level, with PBE0 having "too much" exact exchange or "not enough" semilocal exchange. Since semilocal exchange is known to mimic non-dynamical correlation, we attributed the apparent success of the PBE predictions (for the first two peaks) to a more accurate accounting of non-dynamical correlation in PBE compared to PBE0.

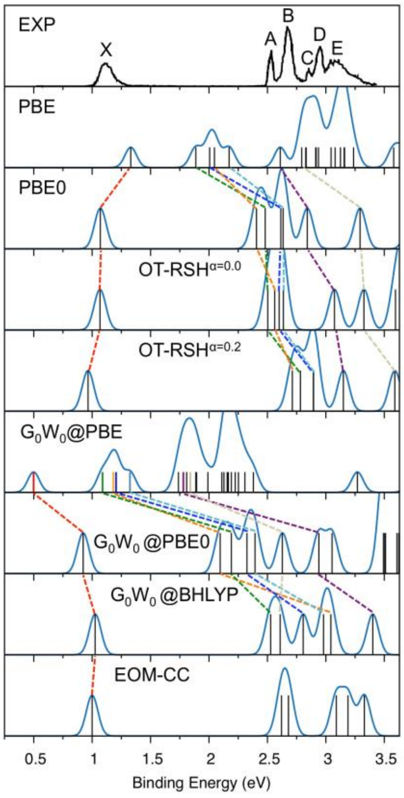

Fig. 2: Computed binding energies at various levels of theory for Cu_2O. The top panel shows the experimental data.

For a cluster with a larger Cu content, such as Cu_2O (Fig. 2 on the left), on the other hand, the spectra computed with hybrid functionals within DFT, or within the G_0W_0 approximation with hybrid functional starting points, are in much better agreement with experimental data and EOM-CCSD results as compared to PBE (or G_0W_0@PBE) predictions. This is due to mitigation of self-interaction error via the introduction of exact exchange and the significantly smaller role of non-dynamical correlation in this larger and less-symmetric cluster.

One of the important findings that resulted from our studies on copper oxide anion clusters is that the one-shot *GW* approximation with a DFT starting point using a semi-local exchange-correlation functional leads to strikingly poor predictions with typical errors larger than 1 eV (as shown in Figs. 1 and 2 for the case of G_0W_0@PBE). As also shown in Figs. 1 and 2, it is possible to obtain very good agreement with experimental data by performing G_0W_0 calculations on top of hybrid functionals. However, the level of agreement depends crucially on the amount of exact exchange in the starting point DFT as well as the Cu content of the cluster, as shown in Fig. 3 below. For clusters with relatively large Cu content, such as Cu_2O and CuO, G_0W_0@BHLYP (with 50% exact exchange) leads to very good agreement with experiment. For clusters with less Cu content, such as CuO_2 and CuO_3, a PBE0 starting point with 25% exact exchange leads to much better agreement.

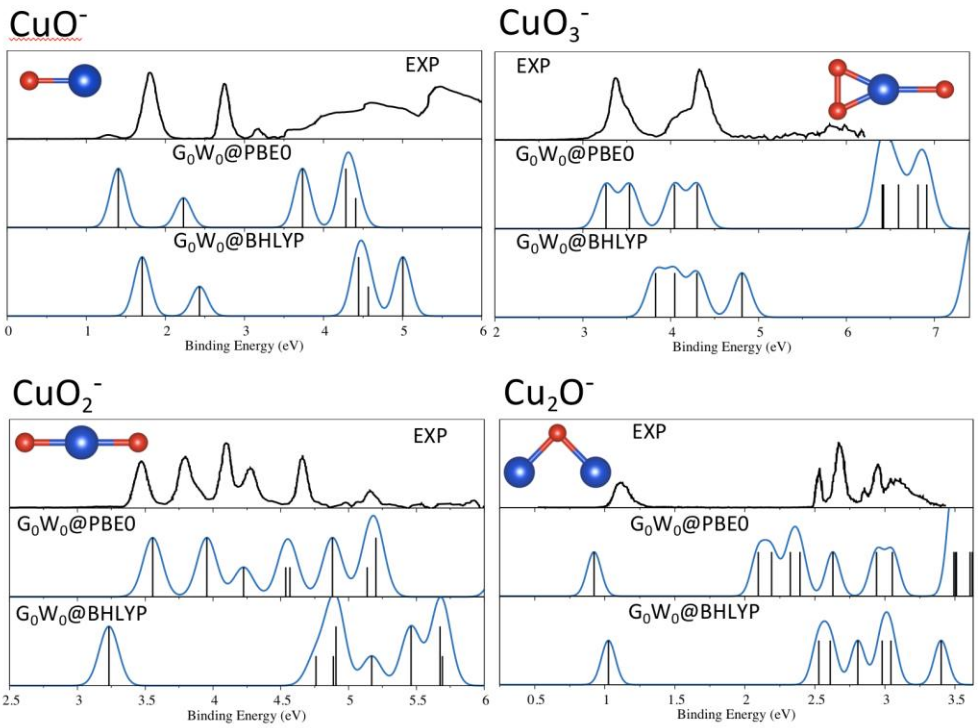

Fig. 3: G_0W_0 quasiparticle energies computed with PBE0 and BHLYP starting points along with experimental data.

FUTURE PLANS

Our ongoing research and future plans in first-principles investigations of electronic and optical properties of transition-metal oxide nanostructures include (i) the effects of eigenvalue and quasiparticle self-consistency in the computed spectra of Cu_xO_y cluster anions, and (ii) applications of *GW*-based theories to the 3*d* transition metal monoxide anions. We have obtained preliminary results for early (ScO, TiO) and late (ZnO) transition metal oxides and are currently analyzing the trends.

PUBLICATIONS ACKNOWLEDGING THIS GRANT

1) Hung, L; da Jornada, F. H.; Souto-Caseras, J.; Chelikowsky, J. R.; Louie, S. G.; Ogut, S. Excitation spectra of aromatic molecules within a real-space *GW*-BSE formalism: Role of self-consistency and vertex corrections. *Phys. Rev*. B **2016**, *94*, 085125.
2) Hung, L; Bruneval, F.; Baishya, K.; Ogut, S. Benchmarking the *GW* approximation and Bethe-Salpeter Equation for Groups IB and IIB Atoms and Monoxides. *J. Chem. Theory Comput*. **2017**, 13, 2135-2146.
3) Hung, L; Bruneval, F.; Baishya, K.; Ogut, S. Correction to Benchmarking the *GW* approximation and Bethe-Salpeter Equation for Groups IB and IIB Atoms and Monoxides. *J. Chem. Theory Comput*. **2017**, 13, 5820-5821.
4) Hung, L; Ogut, S. Modeling Excited States of Confined Systems, submitted (February **2018**) to *Handbook of Materials Modeling. Volume 2 Applications: Current and Emerging Materials* (Springer).
5) Gao, W; Hung, L; Ogut, S; Chelikowsky J. R. The stability, Electronic Structure, and Optical Absorption of Boron-Nitride Diamondoids from First-Principles Calculations, submitted (April **2018**) to *Physical Chemistry Chemical Physics*.
6) Shi, B; Weissman, S; Bruneval, F; Kronik, L; Ogut, S. Photoelectron Spectra of Copper Oxide Cluster Anions from First Principles Methods, submitted (April **2018**) to *Journal of Chemical Theory and Computation*.

2018 CTC PI MEETING May 22 - 24, 2018

ABSTRACT

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

Our comprehensive program for the current project starts from investigations of 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. We also plan to continue studies of transport through clusters. The requested DOE program will involve four interrelated areas of study, namely: A) motivated by our preliminary findings, we will investigate magnetic anisotropy in mixed transition metal carbide $TM1_nTM2_mC_l$ (TM=Cr, Mn, Fe, Co, Ni) clusters to identify those with unusually high MAE. We will investigate transition metal clusters supported on reduced graphene following our preliminary studies that indicate that such a support could considerably increase the MAE; B) investigate the origin of stability of metal chalcogenide superatoms including electron donors $Co_6Se_8(PEt_3)_6$, $Cr_6Se_8(PEt_3)_6$, $Ni_9Te_6(PEt_3)_8$, $Ni_9Te_6(PMe_3)_8$, $Co_6Te_8(PEt_3)_6$, $Co_6Te_8(PEt_2Ph)_6$ and electron acceptor clusters $Co_{11}Te_7(CO)_{10}$, and $Co_9Te_6(CO)_8$. We shall investigate how the donor/acceptor characteristics and magnetic character can be transformed by the choice of ligands. Finally, we will carry out theoretical studies on the doping of MoS_2 and WSe_2 semiconductors with metal chalcogenide superatoms not only to provide insight into the recent experiments in the group on 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) development of computational codes to carry out electronic transport in ligated systems including the effect of excess charge and spin ordering.

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

(1) $Co_6Se_8(PEt_3)_6$ Clusters as Tunable Chemical Dopants for Novel Two-Dimensional Semiconductors

Semiconductors used in most technological applications are doped with impurities whose kind, concentration, and location of impurity level determine the electronic, optical, and transport characteristics of the semiconductor. For bulk materials, the doping is generally carried out by implanting the impurities in an intrinsic material where the dopants can occupy interstitial sites or substitute for host atoms. This has limitations, as not all semiconductors allow an unlimited pathway to incorporation of any impurity in any amount. For two dimensional or thin film semiconductors, an alternative approach to overcome this limitation is to deposit dopants on surface that can chemically bind to surface sites and change the carrier density either through fields and/or donation of carriers.

We have recently proposed that ligated chalcogenide clusters can be used as dopants to create novel semiconductors where the impurity level could be manipulated and the clusters could donate multiple electrons. Our theoretical studies were aimed at understanding how the donor and acceptor behaviors of selected chalcogenide clusters bound to a semiconductor surface can be affected through ligand exchange, ligand removal, and through the doping of the semiconductor. Our work was motivated in part by the experimental study of Yu *et al.* at Columbia University who found that by depositing $Co_6Se_8(PEt_3)_6$ clusters on a p-type WSe_2 support, the WSe_2 was transformed from a p-type to an n-type semiconductor. These materials could be made air stable and offer a simple strategy for the doping of two-dimensional semiconductors. Our studies not only complemented the experimental work in demonstrating how a cluster can be used as a super donor to transform the nature of carriers but how they can be used to modulate the location of the impurity level and even induce magnetic carriers.

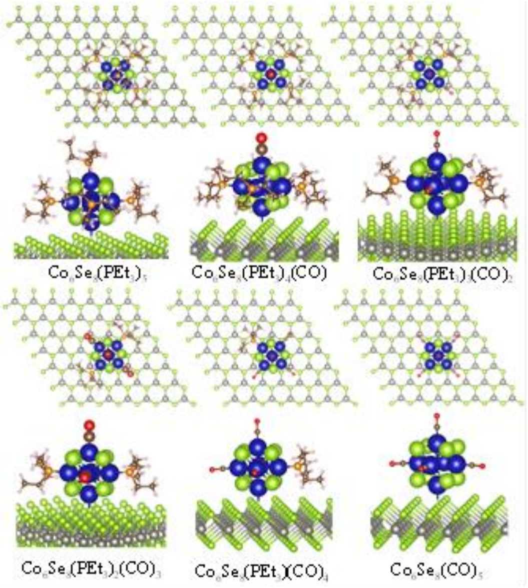

Figure 1. Structure of $Co_6Se_8(PEt_3)_{5-n}(CO)_n$ clusters on WSe_2.

Our investigations involved a WSe_2 surface doped with ligated metal chalcogenide $Co_6Se_8(PEt_3)_5$ clusters. We showed that the WSe_2 support binds more strongly to the Co_6Se_8 cluster than the PEt_3 ligand, so ligand exchange between the phosphine ligand and the WSe_2 support is energetically favorable. The metal chalcogenide clusters serves as donors that may transform the

WSe_2 p-type film into an n-type semiconductor. We further show that by replacing the PEt_3 ligands by CO ligands, one can control the electronic character of the surface and deposited species.

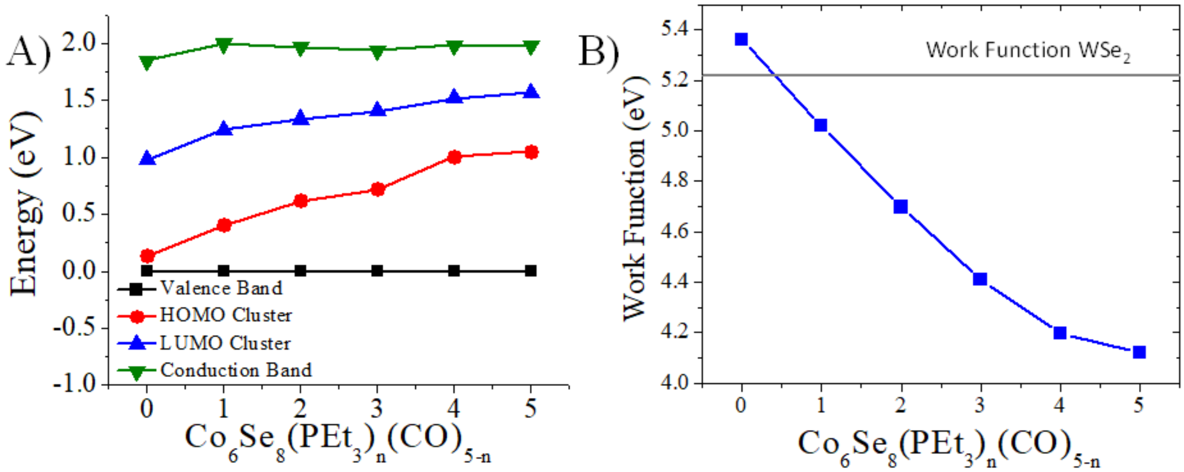

Figure 2. Energies of the valence band, Fermi energy, LUMO of the Cluster, and the Conduction band, and Work function of $Co_6Se_8(PEt_3)_n(CO)_{5-n}$ on WSe_2.

In fact, the Fermi energy of the doped system can be varied over a wide range by selectively replacing the PEt_3 ligands by CO ligands. Such a control is important for optoelectronic properties and even for creating semiconductors where the dopants carry magnetic moments. We also show that the variation in the binding energy of $Co_6Se_8(PEt_3)_5$ and $Co_6Se_8(CO)_5$ units can be used to characterize the change from p- to n-type in the semiconductor surface, offering a chemical probe to n- or p- type characteriztion. These findings have been submitted and a complete report will be presented in the next year report.

(2) **Towards Magnetic Silicon based Motifs for Magnetic Semiconductors. : Electronic and Magnetic Properties of Fe2Sin (0≤n≤12)+/0/- Clusters:**

Carbon and silicon belong to the same group of the periodic table, and the discovery of fullerenes inspired a search for stable silicon based cages that could be constructed into nano-assemblies. Implanting transition metal atoms into a silicon cage can stabilize the caged structure. These results have inspired numerous studies on silicon cages containing endohedral transition metal atoms with an eye towards creating magnetic silicon based materials. Studies on silicon cages with a single endohedral atom, however, indicated that while the transition metal atom did stabilize the cage, the silicon cage generally quenches the magnetic moment of the transition metal atom.

Our studies were directed towards silicon cages containing multiple transition metal atoms as a way to stabilize magnetic species. First principles studies on the geometry, electronic structure and magnetic properties of neutral, cationic, and anionic Fe_2Si_n ($0 \leq n \leq 12$) have been performed to better understand magnetic dopants in silicon. The doubly-Fe doped clusters in the size range $0 \leq n \leq 12$ are marked by finite spin moments at the Fe sites, and Fe_2Si_3, Fe_2Si_4, and Fe_2Si_7 are found to exhibit antiferromagnetic coupling. Fe_2Si_3 and Fe_2Si_{12} are relatively stable. We find that short Fe-Fe bond distances correlate with ferromagnetic coupling due to the destabilization of antibonding orbitals between the iron sites, while longer Fe-Fe bond distances lead to nonbonding atomic orbitals that favor antiferromagnetic coupling.

(3). **Palladium Clusters supported on graphene as catalysts for cross-coupling reactions:**

While the primary role of supports in catalysis has been to anchor metal particles to prevent sintering, supports can also activate catalytic processes. We have carried out computational studies that support the experimental results in providing a fundamental understanding of how a graphene support may activate both oxidative and reductive reaction steps in the catalytic cycle of Suzuki-Miyaura palladium-catalyzed cross-coupling reactions. Theoretical investigations reveal that the observed high catalytic activity is linked to the ability of a graphene support to act as both an efficient charge donor and acceptor in oxidation and reduction reaction steps. We compare the activation energy and turn over frequency for a series of supported and homogeneous catalysts and find that exposing palladium-graphene to defect inducing microwave radiation results in dramatically lower activation energies and higher turnover frequencies. These results explain why a defected graphene support may catalyze reaction steps that require both charge donation, and charge acceptance.

- **Future Plans**:

We are proceeding along several directions to identify potential magnetic building blocks and properties of their assemblies. We are currently exploring the potential of other ligated clusters as dopants to create novel semiconductors. Here, we plan to investigate different kind of dopants to create n- and p- type materials. The eventual goal is to have magnetic dopants that can lead to semiconductors with magnetic units. We are also studying metal silicon clusters containing multiple transition metal atoms to stabilize magnetic units.

- **Selected Publications:**

1. "Magnetic Behavior of Superatomic-Fullerene Assemblies", Pallabi Sutradhar, Vikas Chauhan, Shiv N Khanna, and Jayasimha Atulasimha, *Phys. Chem. Chem. Phys.* 19, 996-1002 (2017).
2. "The Effect of Substituted Benzene Dicarboxylic Acid linkers on the Optical Band Gap Energy and Magnetic Coupling in Manganese Trimer Metal Organic Frameworks", S. Mandal, K.S. Asha, A.C. Reber, N. Ahmed, R.C. Nath, and S.N Khanna, *J. Mater. Chem.* ***C*** **5**, 539-548 (2017).
3. "Symmetry and magnetism in Ni_9Te_6 clusters ligated by CO or phosphine ligands", A.C. Reber, V. Chauhan, and S.N. Khanna, *J. Chem. Phys.* **146,** 024302 (2017).
4. "Metal Chalcogenide Clusters with Closed Electronic Shells and the Electronic Properties of Alkalis and Halogens", V. Chauhan, A.C. Reber, and S.N. Khanna. *J. Amer. Chem. Soc.* **139**, 1871-1877 (2017).
5. "Superatoms: Electronic and Geometric Effects on Reactivity", A.C. Reber and S.N. Khanna, *Acc. Chem. Res.* 50, 255-263 (2017).
6. "Evolution of the Spin Magnetic Moments and Atomic Valence of Vanadium in VCu_x^+, VAg_x^+, and VAu_x^+ Clusters (x = 3 - 14)", W.H. Blades, A.C. Reber, S.N. Khanna, L. Lopez-Sosa, P. Calaminici, A. Koester. *J. Phys. Chem. A.* **121**, 2990-2990 (2017).
7. "Ionic and Metallic Bonding in Al_nNa_m and Al_nMg_m ($3<n+m<15$) clusters", C.J. Grover, A.C. Reber, and S.N. Khanna. *J. Chem. Phys.* **146**, 224301 (2017).
8. "The Complete $Ag_4M_2(DMSA)_4$ (M = Ni, Pd, Pt, DMSA = Dimercaptosuccinic Acid) Cluster Series: Optical Properties, Stability, and Structural Characterization", S.R. Biltek, A.C. Reber, S.N. Khanna, and A. Sen, *J. Phys. Chem* ***A*** **121**, 5324-5331 (2017).
9. "CO Ligands Stabilize Metal Chalcogenide Co_6Se_8 Clusters via Demagnetization", V. Chauhan, A.C. Reber, and S.N. Khanna, *Phys. Chem. Chem. Phys.* **19**, 31940-3194 (2017).
10. "More than Just a Support: Graphene as a Solid-State Ligand for Palladium-Catalyzed Cross-Coupling Reactions", Yuan Yang, Arthur C. Reber, Stanley E. Gilliland III, Carlos E. Castano, B. Frank Gupton, and Shiv N. Khanna, *Journal of Catalysis*, **360**, 20-26 (2018).

Shiv N. Khanna

Transform Metal Chalcogenide Clusters into Donors or Acceptors Via Ligands and Using $Co_6Se_8(PEt_3)_6$ Superatoms as Tunable Chemical Dopants for Two-Dimensional Semiconductors

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Physics Department, Virginia Commonwealth University, Richmond, VA 23284-2000

Abstract

A promising direction in the research on clusters is to design nanomaterials with size selected clusters or the nanoparticles as the building blocks. Since the properties of clusters/nanoparticles change with size and composition, nano-assemblies offer the unique prospect of designing nanoscale materials with controlled properties. The presentation will focus on our recent effort in designing metal-chalcogenide clusters that can have lower ionization potentials for multiple ionization and how such units can be used to design novel semiconductors where the location of Fermi energy and n- and p-characteristics can be controlled.

Nanostructured Metal chalcogenides are well known for their applications in efficient energy conversion and as non-linear optical and magnetic materials. It has recently been possible to synthesize atom precise nanoscale solids (Roy et al. (SCIENCE 341, 157 (2013)) from an assembly of individually synthesized chalcogenide superatoms that exchange charge with counterions to form ionic solids. These assemblies built from different transition metal chalcogenides and counter ions offer potential for photovoltaics, spintronics, and single molecule electrical circuits. In a recent work, the group of Nuckolls et al. at Columbia University showed that the chalcogenide clusters can offer potential for novel semiconductots. In their experiments, they doped two-dimensional transition metal chalcogenides using Co_6Se_8 $(PEt_3)_6$ superatoms as electron donors. Their experiments indicate that electron-rich superatom could be used as a tunable and controllable surface dopant for the semiconductors. For example, their experiments show that they could transform MoS_2 from moderately to heavily electron dope-states by controlling the concentration of superatoms in the solution. Even more interesting was that for WSe_2, the characteristics of the film changed from hole transporting to electron transporting upon doping.

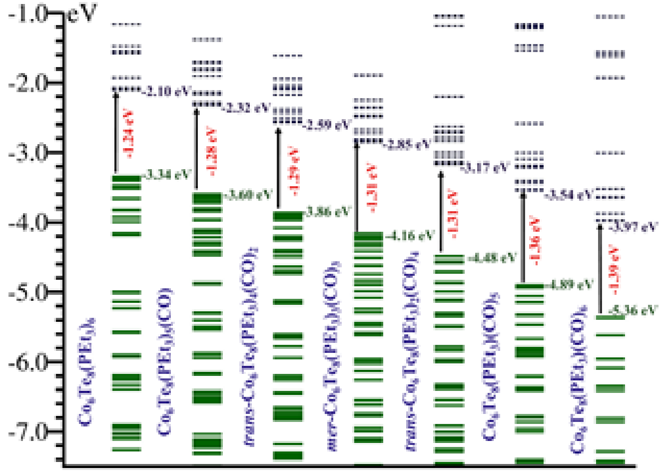

Figure 1. One electron energy levels of ligated $Co_6Te_8(PEt_3)_m(CO)_n$; (m+n=6) clusters. Solid and dashed lines represent the occupied and empty energy levels. The values of HOMO, LUMO and HOMO-LUMO gap are also given.

In this work, I will first talk about how the ligands can be used to control the ionization and electron affinity of metal chalcogenide clusters. Clusters with filled electronic shells and a large gap between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are generally energetically and chemically stable. Enabling clusters to become electron donors with low ionization potentials or electron acceptors with high electron affinities usually requires changing the valence electron count. I will demonstrate that a metallic cluster may be transformed from an electron donor to an acceptor by exchanging ligands while the neutral form of the clusters has closed electronic shells. Our studies on $Co_6Te_8(PEt_3)_m(CO)_n$ (m+n=6) clusters show that $Co_6Te_8(PEt_3)_6$ has a closed electronic shell and a low ionization potential of 4.74 eV, and that the successive replacement of PEt_3 by CO ligands ends with $Co_6Te_8(CO)_6$ exhibiting halogen-like behavior. Both the low ionization potential $Co_6Te_8(PEt_3)_6$ and high electron affinity $Co_6Te_8(CO)_6$ have closed electronic shells marked by high HOMO-LUMO gaps of 1.24 eV and 1.39 eV respectively. Such units have the potential to act as donors or acceptors of **multiple electrons**.

I will then present results of our recent work on using $Co_6Se_8(PEt_3)_5$ clusters as donors to dope a WSe_2 film by binding dopants to the surface. Our investigations show such a doping allows several new features for the doped species. First, the Fermi energy of the doped system can be varied over a wide range by selectively replacing the PEt_3 ligands by CO ligands. Such a control is important for optoelectronic properties and even for creating semiconductors where the dopants carry magnetic moments.

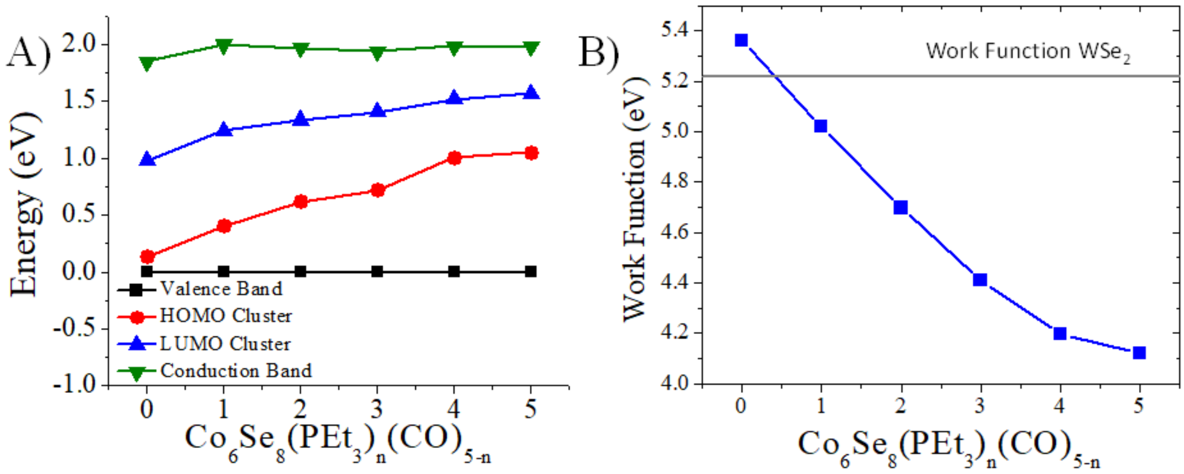

Figure 2. Energies of the valence band, Fermi energy, LUMO of the Cluster, and the Conduction band, and Work function of $Co_6Se_8(PEt_3)_n(CO)_{5-n}$ on WSe_2.

Secondly, I will show that the superatomic clusters can provide a chemical probe to identify the n- or p- nature of the underlying semiconductor. To demonstrate this fascinating aspect, we first created a p-type semiconductor by replacing one to four W sites by Nb atoms. We similarily created an n-type semiconductor by replacing 1-4 W sites with Re atoms. $Co_6Se_8(PEt_3)_5$ is a donor superatom while $Co_6Se_8(CO)_5$ is an acceptor superatom. I will show that the donor superatom binds strongly to a p-type semiconductor while an acceptor superatom binds more strongly to a n-type semiconductor. One can therefore identify a p- or n- type semiconductor by monitoring the binding energy of $Co_6Se_8(PEt_3)_5$ and $Co_6Se_8(CO)_5$ offering a chemical way to detect n- and p- character of semiconductors.

We are now exploring more dopants and the possibility of stabilizing magnetic dopants to create magnetic semiconductors.

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

Student:	Albert Armstrong	Graduate Student (Partial)
	Dinesh Bista	Graduate Student (Partial)
	Ryan Lambert	Graduate Student (Partial)

Selected Publications:

1. “Magnetic Behavior of Superatomic-Fullerene Assemblies”, Pallabi Sutradhar, Vikas Chauhan, Shiv N Khanna, and Jayasimha Atulasimha, *Phys. Chem. Chem. Phys.* 19, 996-1002 (2017).
2. “The Effect of Substituted Benzene Dicarboxylic Acid linkers on the Optical Band Gap Energy and Magnetic Coupling in Manganese Trimer Metal Organic Frameworks”, S. Mandal, K.S. Asha, A.C. Reber, N. Ahmed, R.C. Nath, and S.N Khanna, *J. Mater. Chem.* ***C*** **5**, 539-548 (2017).
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10. “More than Just a Support: Graphene as a Solid-State Ligand for Palladium-Catalyzed Cross-Coupling Reactions”, Yuan Yang, Arthur C. Reber, Stanley E. Gilliland III, Carlos E. Castano, B. Frank Gupton, and Shiv N. Khanna, *Journal of Catalysis*, **360**, 20-26 (2018).

Quantum Monte Carlo calculations for chemical bonding and reactions

Henry Krakauer and Shiwei Zhang

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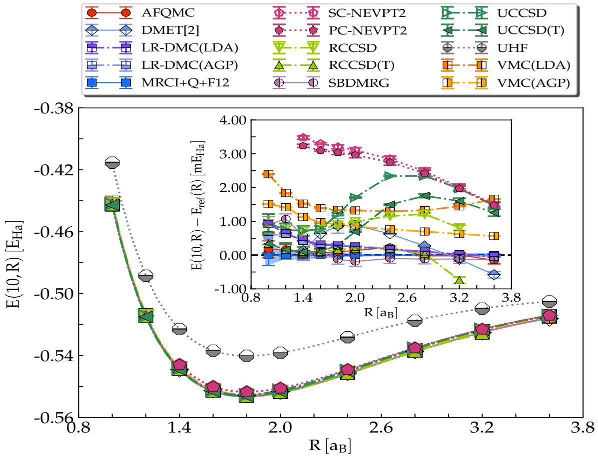
Abstract

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

Recent progress includes:

- the development of a downfolding approach which allows realistic quantum-chemistry-like calculations in solids, including transition metal oxides
- implemented recently developed multiple-projector pseudopotentials into the plane-wave-based AFQMC, which achieves all-electron accuracy while reducing planewave cutoffs, increasing its reach to larger and more complicated systems
- embedding AFQMC in DFT to extend length scales and speed up many-body calculations, with which we were able to determine the stability and magnetic state of Co adsorption on graphene
- systematic improvement with constraint release in AFQMC, which enabled near-



Benchmark results in Hydrogen chain. *Energy per particle of H_{10} in the complete basis set (CBS) limit, versus the distance R between two consecutive H atoms, from a comprehensive benchmark study with state-of-the-art many-body methods [M. Motta et. al., Phys. Rev. X 7, 31059 (2017)] Inset: comparison of the H_{10} energies per particle, using MRCI+Q+F12 results at CBS as reference. The excellent agreement between AFQMC and MRCI+Q+F12 confirms the uniform and overall high accuracy of the AFQMC method.*

exact calculations in the chromium dimer in large basis sets

- excited state method development and calculations of band gaps in solids
- the introduction of frozen-core with the framework of AFQMC which eliminated pseudopotential errors in quantum Monte Carlo
- development of a correlated sampling approach to improve AFQMC efficiency for chemical transformations
- an algorithm for accurate, systematic and scalable computation of interatomic forces and the optimization of molecular geometry within AFQMC

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

In this talk, I will give a general overview of stochastic wave function methods, quantum Monte Carlo, in the context of quantum chemistry, and describe our recent progress with AFQMC. We highlight strong connections with standard quantum chemistry approaches, and the synergy and cross-fertilization. Results on applications in molecular systems will be discussed, including recent developments in the computation of density, atomic forces, and geometry optimization, and rapid acceleration of AFQMC calculations in molecular systems on GPUs.

Grant Numbers and Grant Titles

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

[Also part of CMCSN team DOE DE-SC0006650 "Quantum chemistry via walks in determinant space" with Cyrus Umrigar (PI, Cornell), Gustavo Scuseria (Rice), and Miguel Morales (LLNL), 2011-15]

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

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

Student(s): Brandon Eskridge; Yudistera Virgus

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

1. Motta, Mario, and Shiwei Zhang. 2018. "Calculation of Interatomic Forces and Optimization of Molecular Geometry with Auxiliary-Field Quantum Monte Carlo," March. Preprint: http://arxiv.org/abs/1803.05599.
2. Shee, James, Shiwei Zhang, David R. Reichman, and Richard A. Friesner. 2017. "Chemical Transformations Approaching Chemical Accuracy via Correlated Sampling in Auxiliary-Field Quantum Monte Carlo." Journal of Chemical Theory and Computation, May. American Chemical Society, acs.jctc.7b00224. doi:10.1021/acs.jctc.7b00224.
3. Motta, Mario, David M. Ceperley, Garnet Kin-Lic Chan, John A. Gomez, Emanuel Gull, Sheng Guo, Carlos A. Jiménez-Hoyos, et al. 2017. "Towards the Solution of the Many-Electron Problem in Real Materials: Equation of State of the Hydrogen Chain with State-of-the-Art Many-Body Methods." Physical Review X 7 (3). American Physical Society: 31059. doi:10.1103/PhysRevX.7.031059.
4. Ma, Fengjie, Shiwei Zhang, and Henry Krakauer, 2017. "Auxiliary-Field Quantum Monte Carlo Calculations with Multiple-Projector Pseudopotentials." *Physical Review B* 95 (16). American Physical Society: 165103. doi:10.1103/PhysRevB.95.165103.
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Advances in Many-Body Green's Function Theory

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Abstract

Objective: Looking broadly at physics, a Green's function is more essential than a wave function. It computes the probability of a particle propagating from one spacetime point to another. This particle could be one mediating an interaction and, therefore, a Green's-function-based formalism can describe retardation of the interaction and particle creation and annihilation, and is indispensable in quantum electrodynamics and beyond. In chemistry and materials science, one-particle many-body Green's function (MBGF) methods can directly calculate correlated electron-detachment and attachment energies and quasiparticle energy bands, key to chemical and materials properties and transformations. It is also the mathematical basis of scattering, transport, and embedding. The overarching objective of the project is to deepen our understanding of MBGF and advance numerical methods of calculating and utilizing MBGF.

Highlight 1: Just like wave functions, MBGF can be computed by the methods of configuration-interaction, coupled-cluster, or many-body perturbation theory (MBPT). While introduced first, the Feynman-Dyson perturbation expansion of MBGF is the least well understood and the least well developed in chemistry, with the highest order implemented so far being only the third order. This is traced to the absence of an algebraic recursive definition of MBGF, which would enable a general-order implementation and a rigorous time-independent justification of diagrammatic rules. We thus conduct a thorough analytical and numerical characterization of the whole Feynman-Dyson perturbation series of MBGF. It

- introduces 3 distinct, but mathematically equivalent algebraic recursive definitions of the Green's function in the style of the Rayleigh-Schrödinger recursion for MBPT;
- proves the linked-diagram theorem of the Green's function and self-energy, purely in the time-independent framework, utilizing the factorization theorem of Frantz and Mills, asserting their linkedness and thus size-consistency;
- also proves the irreducible-diagram theorem in a time-independent logic, justifying the removal of reducible diagrams and of dangling lines in a Green's function diagram to expose a self-energy (**Figure 1**);

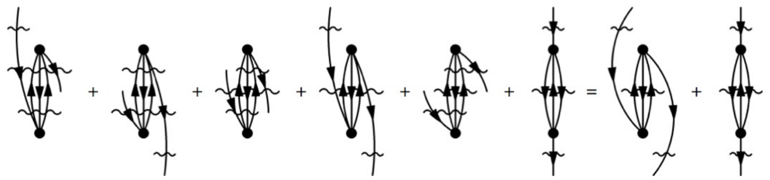

Figure 1. Factorization of denominators.

- shows the equivalence of ΔMP*n* [a method developed in support of this grant and reported in S. Hirata *et al.* J. Chem. Theory Comput. **11**, 1595 (2015)] and MBGF(*n*) in the diagonal, frequency-independent approximation at $n < 4$, confirming our earlier assignments of the difference at $n = 4$ to the semi-reducible and linked-disconnected diagrams;

- implements as many as 6 general-order algorithms of MBGF (3 recursions, automatic generation of Feynman–Dyson diagrams, λ-variation method, and ΔMP*n* method), all but the last yielding the same, nondivergent series of electron binding energies;
- presents for the first time the benchmark result of a full MBGF(n) calculation for $n > 4$ up to $n = 20$;
- quantifies the impact of the perturbation, diagonal, frequency-independent, and ΔMP*n* approximations on electron binding energies of Koopmans and non-Koopmans states;
- illustrates, both analytically (via the theorems mentioned above) and numerically, the full equivalence of the diagrammatic definition of the Feynman–Dyson perturbation series of the self-energy with the algebraic definitions including the λ-variation (the derivative of the exact basis-set result with a perturbation-scaled Hamiltonian).

Highlight 2: The gravest shortcoming of *ab initio* perturbation methods for energies (MBPT) and MBGF is that their implementations are usually a series of dense matrix multiplications, which are nonscalable with respect to system size or computer size. This is compounded by the slow convergence of correlation energies with the size of one-particle basis set. We proposed a novel algorithm that solves all these problems by marrying the scalable Monte Carlo method with the *ab initio* methods. It

- transforms the usual MBPT/MBGF expressions of sum-of-products of transformed two-electron integrals into a single high-dimensional integral by a Laplace transform of the denominators, and evaluates the integral by a Metropolis Monte Carlo algorithm with a suitable weight function;
- can calculate directly MBPT(2) and MBPT(3) correlation energies, MBPT(2) energy and MBGF(2) energy bands of one-dimensional solids (**Figure 2**), and MBGF(2) and MBGF(3) electron-detachment and attachment energies;
- can also evaluate the basis-set extension error by the explicit correlation (F12) ansatz for MBPT(2) and MBGF(2) using virtually any correlation factor with no auxiliary basis set or resolution-of-identity approximation;
- requires no analytical evaluation, transformation, or storage of numerous two-electron integrals either in the atomic-orbital or molecular-orbital basis;
- is free of disk I/O;
- is scalable with system size [$O(n^3)$ scaling of Monte Carlo MBPT(2) as opposed to $O(n^5)$];
- is highly scalable with computer size (easily up to thousands of CPUs and hundreds of GPUs);
- is a new branch of quantum Monte Carlo (QMC), which does not suffer from the sign problem and is thus free of fixed-node errors, is systematically convergent at exactness with perturbation rank and basis-set extension, is rigorously size-consistent and can calculate the energy bands in the whole reciprocal space, having no finite-size error or the need for thermodynamic extrapolation, can directly calculate energy differences (not as small differences of noisy total energies), and is free of pseudopotentials.

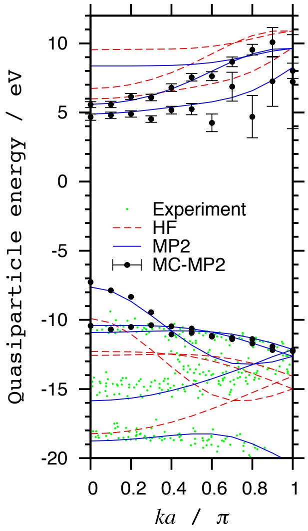

Figure 2. Energy bands of polyethylene.

Computational Chemical Sciences (2017-)

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

Postdocs: Jun Zhang, Alexander Kunitsa

Students: Alexander E. Doran; Cole M. Johnson; Punit Jha

DE-FG02-11ER16211 (-2018)

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

Postdocs: Alexander Kunitsa; Tomonori Yamada

Students: Alexander E. Doran; Jacob A. Faucheaux; Cole M. Johnson; Matthew R. Hermes

Ten Publications Acknowledging the Grant in the Last 3 Years

1. J. A. Faucheaux, M. Nooijen, and S. Hirata,
The Journal of Chemical Physics **148**, 054104 (2018) (24 pages),
"Similarity-transformed equation-of-motion vibrational coupled-cluster theory."
2. S. Hirata, A. E. Doran, P. J. Knowles, and J. V. Ortiz,
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."
3. C. M. Johnson, S. Hirata, and S. Ten-no,
Chemical Physics Letters **683**, 247-252 (2017) [Ahmed Zewail Commemoration Issue],
"Explicit correlation factors."
4. C. M. Johnson, A. E. Doran, J. Zhang, E. F. Valeev, and S. Hirata,
The Journal of Chemical Physics **145**, 154115 (2016) (19 pages),
"Monte Carlo explicitly correlated second-order many-body perturbation theory."
5. A. E. Doran and S. Hirata,
Journal of Chemical Theory and Computation **12**, 4821-4832 (2016),
"Monte Carlo MP2 on many graphical processing units."
6. S. Hirata, T. Shiozaki, C. M. Johnson, and J. D. Talman,
Molecular Physics **115**, 510-525 (2017) [Sanibel Symposium Special Issue],
"Numerical solution of the Sinanoğlu equation using a multicentre radial-angular grid."
7. J. A. Faucheaux and S. Hirata,
The Journal of Chemical Physics **143**, 134105 (2015) (21 pages),
"Higher-order diagrammatic vibrational coupled-cluster theory."
8. T. Yamada and S. Hirata,
The Journal of Chemical Physics **143**, 114112 (2015) (7 pages),
"Singlet and triplet instability theorems."
9. M. R. Hermes and S. Hirata,
The Journal of Chemical Physics **143**, 102818 (2015) (11 pages),
"Finite-temperature coupled-cluster, many-body perturbation, and restricted and unrestricted Hartree-Fock study on one-dimensional solids: Luttinger liquids, Peierls transitions, and spin- and charge-density waves."
10. S. Hirata, M. R. Hermes, J. Simons, and J. V. Ortiz,
Journal of Chemical Theory and Computation **11**, 1595-1606 (2015),
"General-order many-body Green's function method."