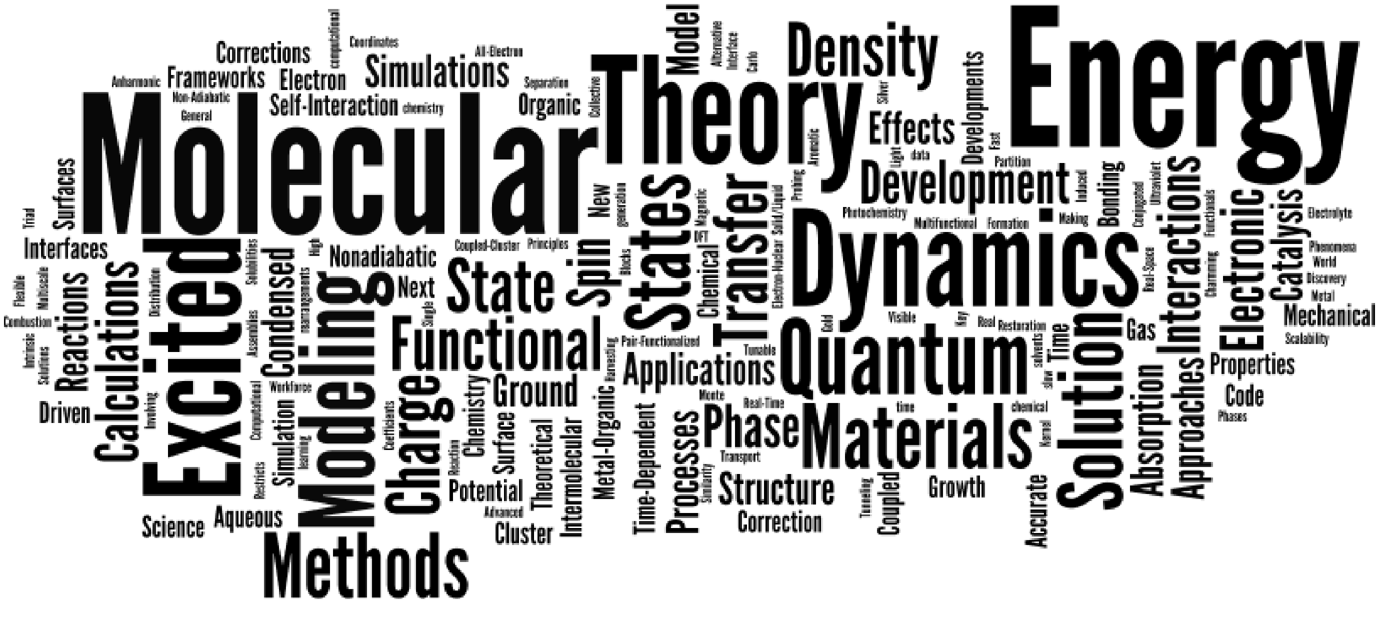
Computational and Theoretical Chemistry PI Meeting
Marriott Washingtonian
Gaithersburg Maryland
15-18 May 2017



FORWARD

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

The objective of this meeting is to provide an interactive environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually complementary expertise, will identify needs of the research community, and will focus on opportunities for future research directions. In addition to organized lunch time topical group discussions, there should be ample time during the evenings for detailed follow-up discussions and the meeting room is available during this time for informal breakout sessions.

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

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

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

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

15-May 2017

SHORT AGENDA 2017 CTC PI Meeting

Marriott Washingtonian – Gaithersburg

9751 Washingtonian Boulevard Gaithersburg Maryland 20878 USA
For more information and registration: http://www.orau.gov/ctc2017/
Abstracts: http://science.energy.gov/bes/csgb/principal-investigators-meetings/

15 May 3-6 PM	**Registration**	
Evening	Self-organized dinner at nearby restaurants	
16 May 7:30AM	**Breakfast -- Topical Group Discussions by Table (Everyone)** **See table below for assignments to topical groups.**	
8:55AM	Welcome	**Mark Pederson**
9:00AM	BES/CSGB/CTC Update and Outlook	**Mark Pederson**
9:45AM	Break	
	1st Principles Methods for Sustainable Energy Solutions **CHAIR: Francesco Evangelista**	
10:00AM	**PLENARY: Sustainable energy solutions from first principles**	**Emily Carter**
	Electrolytes and Solvents **CHAIR: Margaret Cheung**	
11:00AM	Polarizable models for water and electrolyte solutions	**Thanos Panagiotopoulos**
11:30AM	Excited-state charge/energy transfer via master equations	**Thomas Markland**
11:50AM	Realistic depictions of aqueous chromophore UV-VIS absorption.	**Aurora Clark**
12:10PM	**Working Lunch – Topic Group Discussions by Table**	Everyone
	Challenges in Computational & Theoretical Chemistry **CHAIR: Sotiris Xantheus**	
1:30PM	New theory & codes for surface science & heterogeneous catalysis	**Mark Gordon**
2:00PM	Merging symmetry restoration and coupled cluster theories	**Gus Scuseria**
2:30PM	Beyond KS-DFT: Challenge of excited states & transition-metal systems	**Laura Gagliardi**
3:00PM	Quasi-atom-based resolution of molecular electronic wave functions	**Klaus Ruedenberg**
3:30PM	**Coffee**	Everyone
	Gas-Phase Chemical Physics **CHAIR: Judit Zador**	
4:00PM	Quantum mechanical and semiclassical simulations of photochemistry	**Don Truhlar**
4:20PM	Accurate coupled potential energy surfaces & nonadiabatic dynamics	**David Yarkony**
4:40PM	Nonadiabatic tunneling: Geometric phase and diagonal BO correction	**Hua Guo**
5:00PM	Methods for collisional energy transfer & pressure dependent kinetics	**Ahren Jasper**
5:30PM	**Food For Thought - A working dinner (Moderated by Mark Pederson)**	
5:40PM	2-slide report – Charge, spin, matter and energy transfer	**Emily Carter**
6:20PM	2-slide report – Simulating chemistry in generalized solvents	**Margaret Cheung**
6:30PM	2-slide report – Driven chemical reactions	**George Schatz**
6:40PM	2-slide report – ASCR/Exascale Couplings	**Theresa Windus**

17 May 7:30	**Breakfast**	
	Driven Chemical Reactions & Dielectric Media I1 **Chair: Neepa Maitra**	
9:00	1st Principles photo- & voltage- biased charge transfer & transport	**Barry Dunietz**
9:20	Post-Marcus simulation of interfacial charge transfer dynamics	**Eitan Geva**
9:40	Scalable methods for simulations on molecule-solute systems	**Rajendre Zope**
10:10AM	**Coffee**	
	Frontiers in Larger Length- and Time Scale Simulations **CHAIR: Alenka Luzar**	
10:30	Enhancements in DFTB: GPU acceleration & self-interaction corrections	**Brian Wong**
11:00	Next generation first principles molecular dynamics	**Anders Niklasson**
11:30	Sampling rare events in molecular simulations	**Sapna Sarupria**
Noon	**Food For Thought - A working lunch (MRP)**	
	Two-Slide 5-Minute Report – QM Accuracy with pair-potential speed	**So Hirata**
	Two-Slide 5-Minute Report – Fast and slow time scales	**Chris Mundy**
	Two-Slide 5-Minute Report – Methods, data, & machine learning	**Alan Aspuru-Guzik**
	Two-Slide 5-Minute Report – Next generation computational spectra	**Greg Schenter**
	Simulation of Radiative Processes **Chair: Marivi Fernandez-Serra**	
1:30	Quantum & coarse-grained modeling of excitons in LH complexes	**Seogjoo Jang**
2:00	Impact of passivation on radiative/non-radiative processes in q-Dots	**Svetlana Kilina**
2:30	Real-time excited-state absorption & spin-orbit effects	**Niri Govind**
3:00	**Coffee**	
	Chemical Rearrangements **Chair: Jordan Schmidt**	
3:30	NMGC: methods & software to store, separate & convert gases	**Ilja Siepmann**
4:00	Web-enabled molecular simulation and multiscale modeling.	**Lee Woodcock**
4:30	Chemisorption & catalysis on metals: Stat. mech. & energetics	**Jim Evans**
5:00	Continued discussion and/or Topic group Reports	**Mark Pederson**
17 May Evening	**DINNER ON YOUR OWN**	
18 May 7:30	**Breakfast – Sessions for next year**	
	Electron-rearrangments and Reactions **CHAIR: Xiaosong LI**	
8:30AM	Gas/condensed phase photo- ionization & detachment modeling	**Anna Krylov**
9:00AM	1-particle MBGFT: Linked, irreducible and general-order diagramatics	**So Hirata**
9:30AM	Theoretical studies of elementary hydrocarbon species & reactions	**Henry Schaefer**
10:00AM	**Coffee**	
	Driven Chemical Reactions & Dielectric Media II **CHAIR: Vikram Gavini**	
10:30AM	New semiempirical methods for plasmonics	**George Schatz**
11:00AM	DG methods for Li-ion battery anode-electrolyte simulations	**John Pask**
11:30AM	Polarizability trends in clusters & new self-interaction corrected results	**Koblar Jackson**
Noon	**Closing Remarks**	**Mark Pederson**

Dear Colleagues:
As part of continued strategy session, you have been assigned to topic groups that will meet during the working lunches and at other times if necessary. Please meet with your topic groups at breakfast and lunch and work toward developing a two-slide synopsis of the current state of your topic area, on detail-oriented and grand challenges for this topic area, and on why it is important for the BES mission. If you prefer to provide additional input to a different session, please advise.
Thanks,
Mark

Topic Area	**(Chair), Scribe, & Participants**
Crosscutting - ACSR/Exascale	**(Windus)** Gordon, Siepmann, Baruah, Fernandez-Serra, Clark
Fast and slow time scales, complexity & mesoscopicity	**(Mundy)** Sarupria, Niklasson, Wong, Clark, Mebel, Evans
Driven chemical rearrangements	**(Schatz)** Truhlar, Yarkony, Gua, Jasper, Shuford, Galperin, Aikens, Geva, Zador, Maitra, Greeley, Jackson, Klippenstein
Simulating chemistry in general solvents	**(Cheung)** Panagiotopoulos**,** Markland, Luzar, Herbert, Xantheas, Pask, Siepmann, Schmidt
QM accuracy with pair-potential speed	**(Hirata)** Gavini, Dawes, Krakauer, Shiozaki, Ruedenberg, Scuseria, Schaefer, Isborn, Gordon, Windus, Piecuch, Zgid, Evangelista, Papaconstantopoulos, Wasserman
Charge, spin, matter and energy transfer	**(Carter)** Gagliardi, Dunietz, Schmidt, Jang, Krylov, Baruah, Khanna, Paesani, Li, Peralta
Methods, data, & machine learning	**(Aspuru-Guzik)** Hanwell**,** Woodcock, Lewis, Fernandez-Serra, Shao
Next generation computational spectroscopies	**(Schenter)** Zope, Zhang, Furche, Ogut, Kilina, Govind, Windus

After listening to the talks and discussion, please complete the table below and return them to Mark Pederson (by 18-May 2017) to help organize sessions for next year's CTC PI meeting. You may complete this during the working meals. Your input as a primary or seconding recommender is strongly encouraged.

Sessions is recommend by (please list 2-3 recommenders):

Title of Session	Title of Session Title of Session.
	Chair Person: Speaker 1: Speaker 2: Speaker 3:

Emily A. Carter

Quantum Mechanical Evaluation of Alternative Photovoltaic Materials

Nima Alidoust,[1] Kuang Yu,[2] Thomas P. Senftle,[2] and Emily A Carter[2,3,4]

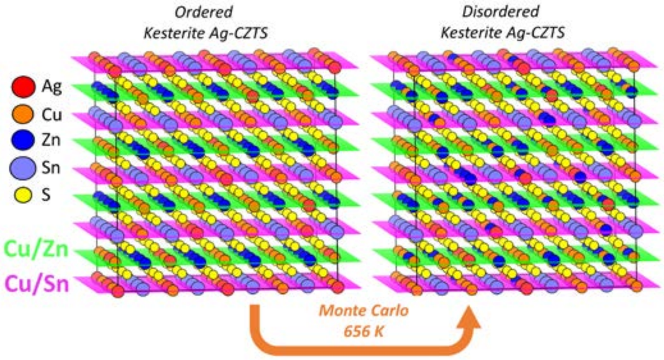
Departments of Electrical Engineering[1] and Mechanical and Aerospace Engineering,[2] Program in Applied and Computational Mathematics,[3] and the School of Engineering and Applied Science[4]

Princeton University, Princeton, NJ 08544-5263

eac@princeton.edu

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 continue 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 talk will present some of our recent theoretical work aimed at accurate evaluation of key materials properties associated with optimizing alternative photovoltaic materials components, including potential new light absorbers and transparent conductors in devices ranging from tandem dye-sensitized solar cells to intermediate band photovoltaics. Key experimental and theoretical challenges will be highlighted throughout. The talk will focus on two materials families: those based on NiO and Cu_2ZnSnS_4 (CZTS), both of which are p-type semiconductors that have been explored as inexpensive solar cell components. NiO is a wide band gap insulator whereas CZTS has an optimal band gap (~1.5 eV) for a single junction cell light absorber. Both feature abundant elements and can be manufactured by low-temperature processing techniques. However, NiO exhibits poor photoconductivity while CZTS-based solar cells suffer from low efficiency because of poor crystal quality. We analyze these weaknesses, create and validate accurate theoretical frameworks for studying each of these material types and their relevant properties, and ultimately suggest design principles to improve their performance.



The rest of this abstract provides further details regarding some of the work above, based on some of the papers listed at the end; to keep within the page limits, we focus on CZTS results. We begin with theoretical advances in electronic structure methods, which enabled some of the applications presented in the talk.

Density functional theory (DFT) + U is an efficient, effective means to calculate ground-state properties of strongly correlated transition-metal compounds, with effective U parameters often determined empirically. Two *ab initio* schemes to compute U were developed over the years, based on either constrained DFT (CDFT) or electrostatically embedded unrestricted Hartree-Fock (UHF) theory. The latter scheme – from the Carter group - offers the advantage of utilizing exact exchange whereas CDFT does not and therefore can lead to unphysical trends. Moreover, numerical instability issues arise for CDFT – which is based on a linear response formalism that breaks down – when applied to closed-shell transition metal cations such as ZnO and Cu_2O. By contrast, the embedded UHF method behaves robustly for both closed- and open-shell cations in materials, making it more suitable for deriving U for all elements. (*J. Chem. Phys.* 2014, **140**, 121105)

The density functional embedding theory (DFET) developed by Huang, Pavone, and Carter in 2011 offers the means to locally refine periodic DFT to include accurate exchange-correlation via wavefunction methods. We recently implemented DFET within the projector-augmented-wave (PAW) formalism as implemented in the VASP code. This advance allows efficient generation of embedding potentials using optimized effective potential theory. These embedding potentials are robust and physically correct, as demonstrated for several test semiconductor systems (and later for metals). This advance allowed the study of, e.g., point defects in bulk semiconductors, using VASP and its systematic PAW potential library, wide selection of functionals, and computational speed, with DFET. (*J. Chem. Phys.* 2015, **143**, 102806)

The poor crystal quality of CZTS is partly caused by secondary phase formation during synthesis. We used DFT +U to confirm that three CZTS phases - kesterite, stannite, and wurtzite - have very similar formation energies. This finding is consistent with the known difficulties in synthesizing pure kesterite CZTS, the phase most desirable for photovoltaics. To overcome this problem, we characterized surfaces and interfaces of CZTS and identified certain “beneficial surfaces” that could be exploited to provide extra stability to the kesterite phase. We proposed the zinc-blende ZnS (001) surface as a substrate to induce formation of these beneficial surfaces and to stabilize the kesterite phase, thereby serving as an effective crystallization template for fabrication of high-performance CZTS solar cells. (*Chem. Mater.* 2015, **27**, 2920)

CZTS suffers from a low open-circuit voltage (V_{OC}) thought to be due to local potential fluctuations caused by a disordered Cu/Zn sublattice. This aspect is difficult to study experimentally and had been universally neglected in simulations. We developed a cluster expansion (CE) model that enabled Monte Carlo (MC) simulations of the order-disorder phase transition in CZTS. With a proper atomic structure of the disordered phase, we investigated the temperature-dependent voltage loss in CZTS, illustrating intrinsic limitations of existing synthesis methods and suggesting an optimal annealing temperature. We also offered an explanation why Cu-poor CZTS is optimally efficient, as Cu vacancies increase the band gap via interactions between free carriers and the disordered, as-grown CZTS. Accordingly, increasing carrier concentrations may be an effective strategy to flatten the fluctuating potentials. (*Chem. Mater.* 2016, **28**, 864)

We continued to investigate CZTS non-stoichiometry under various experimental conditions using first-principles quantum mechanics combined with grand canonical Monte Carlo simulations. We developed an approach to predicting the optimal CZTS stoichiometry, explaining the physical origin of Zn-enrichment observed in experiments. We further proposed practical ways to introduce more free carriers into CZTS in order to screen observed local potential fluctuations, increase conductivity, and ultimately improve the efficiency of CZTS. (*Chem. Mater.* 2016, **28**, 4415)

Recent experiments have shown that Ag and Cd dopants enhance the efficiency of CZTS (see *ACS Energy Lett.* 2016, **1**, 1256 and *Chem. Mater.* 2016, **28**, 5821). These authors hypothesized that substitution of heavy elements (i.e., Ag^+ for Cu^+ and Cd^{2+} for Zn^{2+}) stabilizes the Cu/Zn sub-lattice, thus inhibiting the order-disorder transitions responsible for band-edge fluctuations that cause V_{OC} loss and decreased efficiency. We recently extended our previous CE model to describe mixed $(Cu,Ag)_2ZnSnS_4$ and $Cu_2(Zn,Cd)SnS_4$ phases, to assess the impact of Ag and Cd on the order-disorder transition temperature in CZTS. MC simulations with the newly derived CE models reveal that Ag substitution indeed stabilizes the Cu/Zn sub-lattice, as the order-disorder transition temperature increases from 558 K at 0% Ag to 601 K and 656 K at 6.25% and 12.5% Ag, respectively. Initial DFT+U calculations on small supercells suggest that Ag substitution also increases the band gap, which improves the V_{OC} of the material. The same MC procedure, however, suggests that Cd substitution *does not* stabilize the Cu/Zn sub-lattice, as the order-disorder transition temperature *decreases* to 514 K and 496 K at 12.5% Cd and 25% Cd, respectively. Furthermore, the magnitude of the band gap *decreases* with Cd substitution, thus demonstrating that Cd must impact CZTS in a manner fundamentally different than Ag. DFT+U calculations on $(Cu,Ag)_2ZnSnS_4$ and $Cu_2(Zn,Cd)SnS_4$ in large supercell structures derived from equilibrated MC ensembles were completed to assess the impact of Cd and Ag on long-range band edge fluctuations. Initial results suggest that the fluctuations responsible for band-gap narrowing are related to separate domains of ordered and disordered Cu/Zn sub-lattices within the nanometer-sized unit cell. We therefore hypothesize that Cd doping enhances efficiency by *destabilizing* the Cu/Zn sub-lattice, therefore preventing the formation of separate ordered and disordered domains that are primarily responsible for band gap narrowing. (T. P. Senftle and E. A. Carter, manuscript in preparation)

In addition to Ag and Cd doping, numerous reports demonstrate that the band gap of CZTS-based materials can be further tuned by the introduction of Se (see *MRS Comm.* 2014, **4**, 159). Initial work has been completed to extend the CE model to allow for varying S:Se ratios in the CZTSSe lattice. MC simulations with the CZTSe CE model demonstrate that Se addition lowers the order-disorder transition temperature compared to CZTS, in agreement with experiment (*Phys. Stat. Solid.* 2016, **253**, 1890). Ongoing efforts utilize structures derived from MC ensembles at varying temperatures to investigate the effects of Se addition on long-range fluctuations and band-gap narrowing. Future work will seek to develop a generalized CE approach that simultaneously treats varying levels of Ag/Cd/Se doping within one framework. This will enable MC investigations to assess emergent properties arising from interactions between varying substituents in the multi-component system, thus providing design principles aiding the search for an optimized $(Cu,Ag)_2(Zn,Cd)Sn(S,Se)_4$ absorber material. (T. P. Senftle and E. A. Carter, work in progress)

Grant Number, Titles, and Personnel Supported

DOE-BES Grant No. DE-SC0002120

Quantum Mechanical Evaluation of CZTS Properties for Photovoltaic Applications

Postdocs: Kuang Yu and Thomas P. Senftle

Student: Nima Alidoust

Optimizing New Materials for Solar Energy Conversion via Quantum Mechanics

Postdoc: Maytal C. Toroker

Student: Nima Alidoust

Ten Selected Recent Publications

Method Development

K. Yu and E. A. Carter, "Communication: Comparing *Ab initio* Methods of Obtaining Effective U Parameters for Closed-Shell Materials," *J. Chem. Phys.* **140**, 121105 (2014). doi: 10.1063/1.4869718

K. Yu, F. Libisch, and E. A. Carter, "Implementation of density functional embedding theory within the projector-augmented-wave method and applications to semiconductor defect states," *J. Chem. Phys.* **143**, 102806 (2015). doi: 10.1063/1.4922260

NiO Band Gap Engineering

N. Alidoust, M. C. Toroker, and E. A. Carter, "Revisiting photoemission and inverse photoemission spectra of nickel oxide from first principles: implications for solar energy conversion," *J. Phys. Chem. B* **118**, 7963 (2014). doi: 10.1021/jp500878s

N. Alidoust, M. C. Toroker, J. A. Keith, and E. A. Carter, “Significant Reduction in Nickel(II) Oxide Band Gap Upon Alloying with Lithium Oxide: Applications to Solar Energy Conversion,” *ChemSusChem* **7**, 195 (2014). doi: 10.1002/cssc.201300595

NiO Carrier Transport Engineering

N. Alidoust and E. A. Carter, “First-principles assessment of hole transport in pure and Li-doped NiO,” *Phys. Chem. Chem. Phys.* **17**, 18098 (2015). doi: 10.1039/C5CP03429A

N. Alidoust and E. A. Carter, “Three-Dimensional Hole Transport in Nickel Oxide by Alloying with MgO or ZnO,” *J. Appl. Phys.* **118**, 185102 (2015). doi: 10.1063/1.4935478

Intermediate Band Semiconductor for Multispectral Photovoltaics

N. Alidoust, M. Lessio, and E. A. Carter, “Cobalt (II) oxide and nickel (II) oxide alloys as potential intermediate-band semiconductors: A theoretical study,” *J. Appl. Phys.* **119**, 025102 (2016). doi: 10.1063/1.4939286

Optimization of Structure and Stoichiometry of CZTS

K. Yu and E. A. Carter, “A Strategy to Stabilize Kesterite CZTS for High-Performance Solar Cells,” *Chem. Mater.* **27**, 2920 (2015). doi: 10.1021/acs.chemmater.5b00172

K. Yu and E. A. Carter, “Elucidating Structural Disorder and the Effects of Cu Vacancies on the Electronic Properties of Cu_2ZnSnS_4 Photovoltaics,” *Chem. Mater.* **28**, 864 (2016). doi: 10.1021/acs.chemmater.5b04351

K. Yu and E. A. Carter, “Determining and Controlling the Stoichiometry of Cu_2ZnSnS_4 Photovoltaics: the Physics and Its Implications,” *Chem. Mater.* **28**, 4415 (2016). doi: 10.1021/acs.chemmater.6b01612

Simulations of Solubilities and Activity Coefficients in Aqueous Electrolyte Solutions

Athanassios Z. Panagiotopoulos

Department of Chemical and Biological Engineering
Princeton University, Princeton, NJ 08544
Electronic mail: azp@princeton.edu

Presentation Abstract

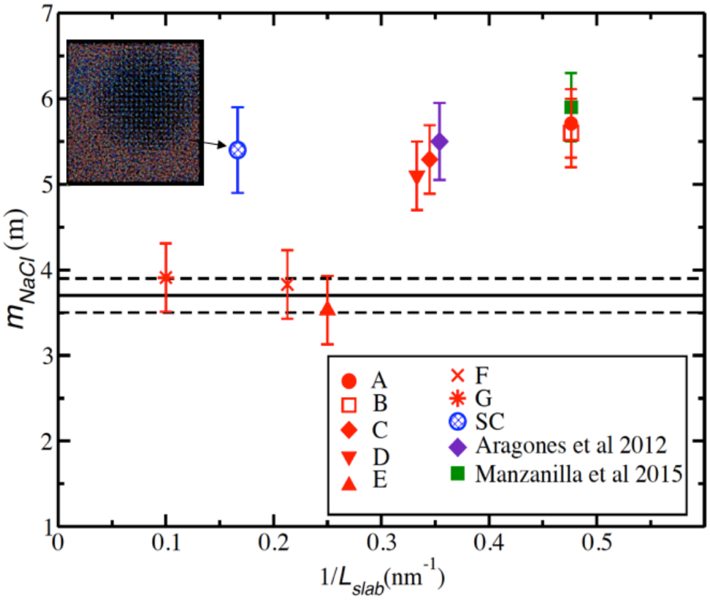


Fig. 1. NaCl solubility as a function of the inverse width of the crystal slab. Red symbols are our results for direct coexistence simulations, black lines indicate the value and error obtained by chemical potential simulations [8].

Aqueous electrolyte solutions play an important role in chemical engineering separations, and also in geochemical environments and for biophysics. The mean ionic activity coefficients quantify the deviation of salt chemical potential from ideal solution behavior; experimental measurements are available for many salts over broad ranges of concentration and temperature, but there have been practically no prior simulation results of these quantities, because if sampling difficulties for explicit-solvent electrolyte solutions. We have developed a new approach for determination of activity coefficients of aqueous electrolytes. Common fixed-point-charge models for water and ions are unable to reproduce simultaneously activity coefficients and solubilities, especially at elevated temperatures. Polarizable models perform better, but still predict an incorrect temperature dependence of these properties. To complicate matters even more, direct coexistence simulations of salt solubilities systematically overpredict salt solubilities when compared to free-energy calculations using the same molecular models. Work in the group that has identified the origin of these discrepancies will be described.

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 (Hispanic-American); Jeffrey Young.

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, in order to address the major sampling challenges encountered for these strongly interacting systems. 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 fixed-point-charge models for water and ions, which result in large errors in modeling activity coefficients and solubilities. Promising polarizable models are being developed and explored in detail. In the area of ionic 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 two years, 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 1 in the publication list of section 4]. We find that the temperature dependence of the activity coefficients and solubilities does not match experiments, even for the polarizable models. We also obtained thermodynamic and transport properties of the binary H_2O + NaCl system [2,3,10] in order to compare polarizable force fields against fixed-point-charge (non-polarizable) models. Most of the properties of interest are better represented by the polarizable models, which also remain physically realistic at elevated temperatures. New polarizable models were developed for water and CO_2 [5,9]. In addition, we leveraged prior expertise by Dr. Hao Jiang to obtain molecular-thermodynamics models for the activity coefficients [6]. An unresolved discrepancy in calculated solubility values between direct interfacial calculations and thermodynamic integration methods was resolved in [6] by identifying interface charging effects that lead to solubility values with strong dependence on lab thickness in the interfacial calculations.

In the area of computational methodologies for the study of self-assembly, a long-standing question has been that many prior simulations of micellizing systems have observed a decrease in the free surfactant concentration with overall surfactant loading for both ionic and nonionic surfactants, contrary to theoretical expectations from mass-action models of aggregation. We investigate a simple lattice nonionic surfactant model in implicit solvent [4] and proposed an algorithm for the precise calculation of the excluded volume and effective concentration of unassociated surfactant molecules in the accessible volume of the solution.

Finally, the PI has been involved in a multi-author major review [7] on properties of (metastable) liquid water at low temperatures and the possible existence of a liquid-liquid transition.

3 FUTURE PLANS

For activity coefficient calculations, it is necessary to perform simulations with relatively few ion pairs in solution. In the coming year, we plan to investigate methods to correct for finite-size effects that are present in such calculations. We also would like to obtain reliable methods for extrapolating free ionic surfactant concentrations observed in the presence of micellar aggregates down to the critical micelle concentration. Finally, we would like to obtain reliable methods for calculation of interfacial free energies for electrolyte solutions in contact with polar surfaces.

4 PUBLICATIONS FROM THIS AWARD (PAST 2 YEARS)

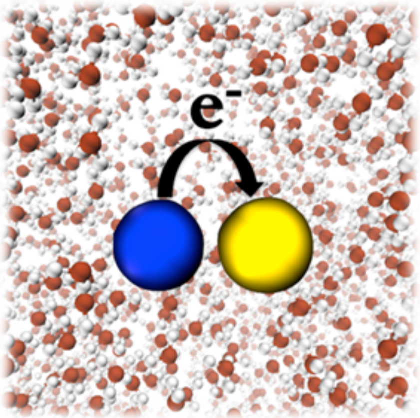
1. Z. Mester and A. Z. Panagiotopoulos, "Temperature-Dependent Solubilities and Mean Ionic Activity Coefficients of Alkali Halides in Aqueous Solutions from Molecular Dynamics Simulations," *J. Chem. Phys.* **143**: 044505, 10 pp (2015). DOI: 10.1063/1.4926840
2. H. Jiang, Z. Mester, O. A. Moultos, I. G. Economou, and A. Z. Panagiotopoulos, "Thermodynamic and Transport Properties of H_2O+NaCl from Polarizable Force Fields," *J. Chem. Theory Comput.* **11**: 3802-3810 (2015). DOI: 10.1021/acs.jctc.5b00421
3. E. Tsai, H. Jiang, and A. Z. Panagiotopoulos, "Monte Carlo Simulations of H_2O-$CaCl_2$ and H_2O-$CaCl_2$-CO_2 Mixtures," *Fluid Phase Equil.* **407**: 262-68 (2016). DOI: 10.1016/j.fluid.2015.05.036
4. A. P. Santos and A. Z. Panagiotopoulos, "Determination of the critical micelle concentration in simulations of surfactant systems," *J. Chem. Phys.* **144**: 044709, 10 pp (2016). DOI: 10.1063/1.4940687
5. H. Jiang, O. A. Moultos, I. G. Economou, and A. Z. Panagiotopoulos, "Gaussian-Charge Polarizable and Non-Polarizable Models for $CO_{2,}$" *J. Phys. Chem. B* **120**: 984-994 (2016). DOI: 10.1021/acs.jpcb.5b11701
6. H. Jiang, A. Z. Panagiotopoulos and I. G. Economou, "Modeling of CO_2 Solubility in Single and Mixed Electrolyte Solutions Using Statistical Associating Fluid Theory," *Geochim. Cosmochim. Acta* **176**: 185-197 (2016). DOI: 10.1016/j.gca.2015.12.023
7. P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, "Water: A Tale of Two Liquids," *Chem. Rev.* **116**: 7463-7500 (2016). DOI: 10.1021/acs.chemrev.5b00750
8. J. R. Espinosa, J. M. Young, H. Jiang, D. Gupta, C. Vega, E. Sanz, P. G. Debenedetti, and A. Z. Panagiotopoulos, "On the calculation of solubilities via direct coexistence simulations: Investigation of NaCl aqueous solutions and Lennard-Jones binary mixtures," *J. Chem. Phys.,* **145**: 154111, 7 pp (2016). DOI: 10.1063/1.4964725
9. H. Jiang, O. A. Moultos, I. G. Economou, A. Z. Panagiotopoulos, "A Hydrogen-Bonding Polarizable Intermolecular Potential Model for Water," *J. Phys. Chem. B*, **120**: 12358-70 (2016). DOI: 10.1021/acs.jpcb.6b08205
10. H. Jiang, I. G. Economou, and A. Z. Panagiotopoulos, "Phase Equilibria of Water/CO_2 and Water/n-Alkane Mixtures from Polarizable Models," *J. Phys. Chem. B*, **121**: 1386-1395 (2017). DOI: 10.1021/acs.jpcb.6b12791

DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION: ACCURATE DYNAMICS ON THE CHEAP - MAKING THE MOST OF QUANTUM-CLASSICAL THEORY WITH MASTER EQUATIONS

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

Andres Montoya-Castillo, William C. Pfalzgraff, Aaron Kelly, Thomas E. Markland
Department of Chemistry, Stanford University, Stanford, California, USA

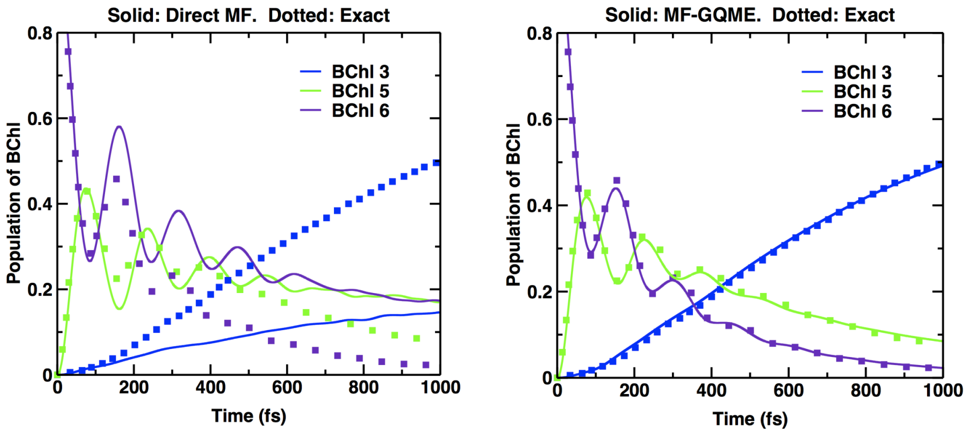
The development of next generation energy conversion and catalytic systems requires fundamental understanding of the interplay between photo-excitation and the resulting proton and electron transfer processes that occur in solution. To address these challenges requires accurate and efficient methods 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. In this talk, I will discuss our recent research showing 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 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. In our recent research, we have applied the MF-GQME method to study the non-equilibrium quantum dynamics of an atomistic model of electron transfer incorporating two molecules that can exchange charge in a fully atomistic environment (liquid water) [7]. This demonstrates that proceeding via the GQME to generate quantum dynamics offers efficiency and accuracy benefits beyond the assumptions of harmonic environments and linear subsystem-environment coupling [7]. The successful treatment of electron transfer builds towards the further objective of accurately treating proton coupled electron transfer (PCET) in solution and at electrode interfaces.

We have also shown analytically the cases where a GQME approach is likely to be able to give a more accurate solution than direct application of the approximate method [2]. When approximate methods, such as those arising from the quantum-classical and semiclassical hierarchies, are used to calculate the memory kernel, significant improvements in accuracy have been observed when compared to their direct application. However, such improvements sensitively depend on how one calculates the projection-free partial kernels that are used to construct the memory kernel. These observations naturally raise questions as to why this is and when proceeding via the projection operator formalism will be advantageous. In our recent work we have demonstrated the conditions which must be satisfied to obtain gains in accuracy when proceeding via the GQME formalism. However, one can also use manipulations that are satisfied by exact quantum mechanics (but which may not be satisfied by an approximate method), to cast the expression for the memory kernel into a different form. We show that this alternate form of the memory kernel is *guaranteed* to give an identical result to that obtained from the direct dynamics. By considering the connections between these forms of the kernel, we derive the conditions that approximate methods must satisfy if they are to offer different results when used in conjunction with the GQME formalism. This research thus uncovers the origins of why the GQME approach is able to improve the accuracy of some approaches and hence informs the application of these approaches.

A concern that has been raised about the ability to use the GQME formalism to accelerate and improve the accuracy of quantum classical methods is that, for a system with N_s subsystem states, the size of the memory kernel that must be generated formally grows as N_s^4. One might imagine that this unfavorable scaling would present a barrier to applying the same approach to problems with larger numbers of subsystem states. Recently, we have therefore shown how quantum-classical methods can be used to evaluate the memory kernel in the GQME can be scaled to problems with many subsystem states. The figure below shows our results obtained for the Fenna Mathews Olsen complex (FMO) with 7 subsystem states. Although for this problem there are 2,401 memory kernel elements, one can show that one can generate them with Ehrenfest trajectories with only 28 different initial conditions. As we saw for systems with smaller numbers of subsystem states, proceeding via the memory kernel formalism recovers the exact result almost perfectly, even though a direct application of mean-field theory is qualitatively incorrect. In addition, we are currently investigating how one can use importance sampling to preferentially sample initial conditions that are needed to capture the particular initial excitation of the system which one is interested in. Our initial tests using an importance sampling algorithm for the memory kernel elements already indicate that, in FMO, one can obtain more than an order of magnitude acceleration by using such an approach, making MF-GQME less computationally expensive than even direct mean-field theory, even for this many-level system. With these advanced sampling algorithms implemented, we intend to demonstrate the ability to scale MF-GQME to large subsystems by applying it to electronic energy transfer in the LHC-II light harvesting complex, which has a 14 state quantum subsystem and thus presents a significant challenge to many nonadiabatic quantum dynamics methods.



These extensions 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. In the next stage of this research we are using our insights into when GQME methods can offer accuracy advantages to provide similar improvements for nonequilibrium systems as well as treating problems incorporating vibrational modes that are strongly coupled to the electronic subsystem. These developments are essential for PCET 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 (since September 2015), Markland Group

[1.] 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)*

[2.] 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)*

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

[4.] 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)*

[5.] Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges. *M. Ceriotti, W. Fang, P. G. Kusalik, R. H. McKenzie, M. A. Morales, A. Michaelides and T. E. Markland, Chem. Rev., 116 (13), 7529-7550 (2016)*

[6.] Ab initio molecular dynamics with nuclear quantum effects at classical cost: ring polymer contraction for density functional theory. *O. Marsalek and T. E. Markland, J. Chem. Phys. 144, 054112 (2016)*

[7.] Nonadiabatic dynamics in atomistic environments: harnessing quantum-classical theory with generalized quantum master equations. *W. C. Pfalzgraff, A. Kelly and T. E. Markland, J. Phys. Chem. Lett., 6, 4743-4748 (2015)*

DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION: CLASSICAL AND QUANTUM SOLVENT ENSEMBLES - REALISTIC DEPICTIONS OF AQUEOUS CHROMOPHORE UV-VIS ABSORPTION.

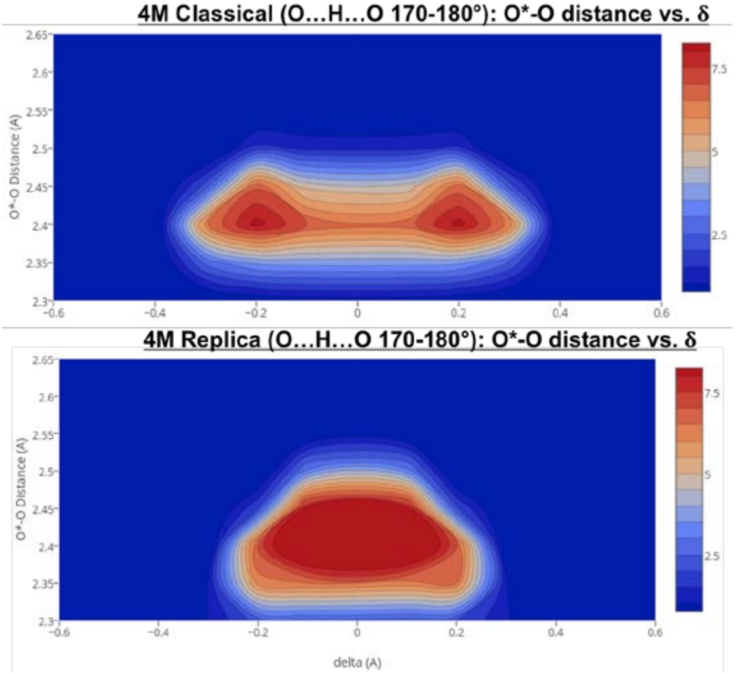
Christine Isborn[1] (PI), Aurora Clark (co-PI)[2], Thomas Markland (co-PI)[3]
1. University of California Merced, Email: cisborn@ucmerced.edu
2. Washington State University, Email: auclark@wsu.edu
3. Stanford University, Email: tmarkland@stanford.edu

Lelee Ounkham, Lance Edens, Aurora E. Clark
Department of Chemistry, Washington State University, Pullman, Wa

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. In the latter, analysis of solvent dynamics within a quantum dynamics framework presents new challenges and previously unafforded opportunities to understand the role of quantum behavior within classes of reactions that span solvent mediated proton, energy and electron transfer. In the past year Clark has focused upon developing a quantitative understanding of the differences of solvent organization and dynamics within classical and QM dynamics regimes using graph theoretical methods applied to the networks of intermolecular interactions in solution. In the first project, we have compared classical and quantum dynamics trajectories of pure water wherein we have determined that there is a remarkable similarity in the rotational dynamics of classical and QM water, however, the added uncertainty associated with hydrogen atom distributions in the latter leads to notable changes in the ability to cleanly identify of rotational mechanisms (Clark-Markland collaborative work). One paper will be submitted in the next 1-2 months.

In the second project, model solutions of aqueous HCl have been employed to determine the algorithms necessary to analyze ion speciation, solvation dynamics and reactivity pathways associated with proton transfer. This has enabled the development of an efficient code for determining ion speciation and reaction coordinates for transformations of solvation environments, and ion configurations. Using this approach, the role of quantum nuclear effects associated with delocalization of proton position can clearly be observed in configurations that are ‘pre-organized’ for proton-sharing character, where the quantum-dynamics trajectories have greater shared or zundel characteristics as opposed to classical trajectories.



In the third project, we have begun to analyze solvation of the PCT anion chromophores being studied by the Isborn and Markland groups, paying special attention to whether quantum nuclear effects lead to subtle changes in hydrogen bonding patterns that affect the UV-Vis spectrum and energy transfer from solute to solvent. Preliminary results indicate a slightly broader range of solvent configurations obtained from the quantum nuclear dynamics trajectories relative to the classical simulations. Sampling of the configurations that have varying density within 3 Å of the solute atoms does not indicate large spectral shifts. Ongoing work to be discussed will highlight changes in organizational patterns associated with different “hydrophobic” versus “hydrophilic” regions of PCT^- obtained from the quantum dynamics and classical trajectories.

As an important extension of the funded work, we have enhanced the parallelization of the ChemNetworks software program and received Directors Discretionary funding at OLCF to develop real-time analytics capabilities of the quantum dynamics trajectories. This will decrease total compute time and enable potentially new means by which to explore the system PES for PCET processes.

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)

Clark Group Postdoc (50%): Lance Edens **Clark Group Student:** Lelee Ounkham

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

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

Program Scope. Our research effort combines new theory and 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. Recently, the EFP method has been combined with nonlinear time-dependent density functional theory to facilitate the investigation of solvent effects on nonlinear optical properties[1]. 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[5]. In the latter study, the EFP method was shown to outperform density functional theory (DFT) methods.

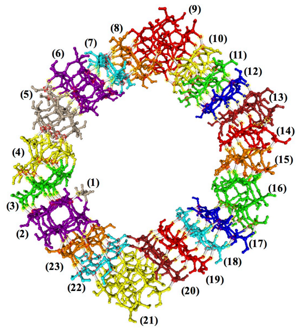
Another (fully quantum) fragmentation approach is the fragment molecular orbital (FMO) method. The FMO method divides a large species into fragments to facilitate accurate QM calculations on very large systems. The FMO method can be used in concert with any electronic structure method in GAMESS. In order 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[7,9]. 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.[5] 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)[9]. 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[9]. Also, a new method, the effective fragment molecular orbital (EFMO) method has been developed that replaces the bath potential with the EFP[10]. 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[10].

Another approach to making high-level electronic structure calculations is to use localized molecular orbitals (LMOs), because correlation is local. So, one can design LMO domains or subsystems and only perform the correlation calculation within those domains. Carter (Princeton) has developed a multi-configurational (MR) configuration interaction (CI) code called TigerCI to perform such calculations. In collaboration with the Carter group, a preliminary parallel version of TigerCI code has been implemented[2]. The TigerCI code has now been incorporated into GAMESS. A manuscript that describes this effort is in preparation. 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[6].

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[4]. The FMO method has been used to study the formation of carbinolamine, catalyzed by a section of MSN[8].



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.

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

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

A collaboration with the Evans group at the Ames Laboratory on reactions that occur on the Pd surface will combine 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 are carrying 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.

References to 10 recent publications of DOE sponsored research

1. F. Zahariev and M.S. Gordon, "Non-linear Response Time-Dependent Density Functional Theory combined with the Effective Fragment Potential Method", J. Chem. Phys., 140, 18A523 (2014)
2. J. Dieterich, D. Krisiloff, A Gaenko, F.Libisch, T. Windus, M. Gordon, E. Carter, "Shared-memory parallelization of a local correlation multi-reference CI program", Comp. Phys. Comm., 185, 3175 (2014)
3. K.R. Brorsen, S.R. Pruitt, and M.S. Gordon, "Surface affinity of the hydronium ion: The effective fragment potential and umbrella sampling", J. Phys. Chem B., 118, 14382 (2014).
4. J. Wang, A. Garcia, D.M. Ackerman, M.S. Gordon, I.I. Slowing, T. Kobayashi, M. Pruski, and J.W. Evans, "Multi-functionalization of nanoporous catalytic materials to enhance reaction yield: Statistical mechanical modeling for conversion reactions with restricted diffusive transport", Mater. Res. Soc. Symp. Proc. Vol. 1641 (2014)
5. K.R. Brorsen, S.Y. Willow, S.S. Xantheas, and M.S. Gordon, "The melting temperature of liquid water with the effective fragment potential", J. Phys. Chem. Lett., 6, 3555 (2015).
6. A. Findlater, F. Zahariev, and M.S. Gordon, "A Combined Fragment Molecular Orbital-Cluster in Molecule Approach to Massively Parallel Electron Correlation Calculations for Large Systems", J. Phys. Chem. A, 119, 3587 (2015)
7. H. Nakata, D.G. Fedorov, F. Zahariev, M.W. Schmidt, M.S. Gordon, and S. Nakamura, "Analytic second derivative of the energy for density functional theory based on the three-body fragment molecular orbital theory", J. Chem. Phys., 142, 124101 (2015)
8. Ana P. de Lima Batista**,** Federico Zahariev, Igor I. Slowing, Ataualpa A. C. Braga, Fernando R. Ornellas, Mark S. Gordon, "Silanol-Assisted Carbinolamine Formation in an Amine-Functionalized Mesoporous Silica Surface: Theoretical Investigation by Fragmentation Methods", J. Phys. Chem. B, 120, 1660 (2016).
9. S.R. Pruitt, H. Nakata, T. Nagata, M. Mayes, Y. Alexeev, G.D. Fletcher, D.G. Fedorov, K. Kitaura, and M.S. Gordon, "The Importance of Three-Body Interactions in Molecular Dynamics Simulations of Water", J. Chem. Theory Comp., 12, 1423 (2016)
10. C. Bertoni and M.S. Gordon, "Analytic gradients for the Effective Fragment Molecular Orbital method", J. Chem. Theory Comp., in press.

Merging symmetry restoration with Coupled Cluster theory

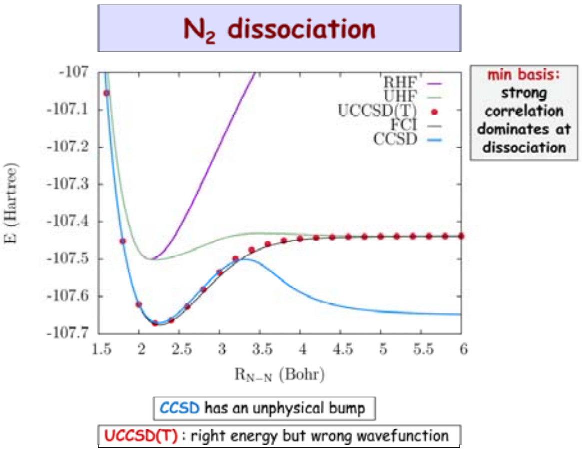
Gustavo E. Scuseria

Department of Chemistry
Department of Physics & Astronomy
Department of Materials Science and Nano Engineering
Rice University, Houston, Texas, USA
`guscus@rice.edu`

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.

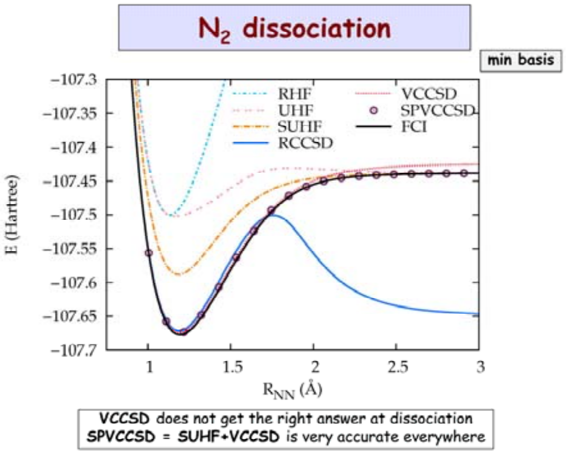
In this project, we are exploring novel routes toward combining techniques developed over the years to describe these two separate kinds of correlation into one powerful tool capable of treating all correlation effects on an equal footing. Strong correlations are taken into account by symmetry-projected mean-field methods, and the residual weak correlations are included using coupled cluster theory. Major progress was made in our group during the past year 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. In this presentation, I will discuss our current efforts for understanding the problems of restricted coupled cluster theory under strong correlation and designing a meaningful solution using these polynomial of particle-hole excitations.



min basis: strong correlation dominates at dissociation

CCSD has an unphysical bump

UCCSD(T) : right energy but wrong wavefunction



min basis

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

1. Quasiparticle coupled cluster theory for pairing interactions, T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, *Phys. Rev*. **C 89**, 054305 (2014); http://link.aps.org/doi/10.1103/PhysRevC.89.054305

2. Analytic energy gradient for the projected Hartree-Fock method, R. Schutski, C. A. Jiménez-Hoyos, and G. E. Scuseria, *J. Chem. Phys*. **140**, 204101 (2014); http://scitation.aip.org/content/aip/journal/jcp/140/20/10.1063/1.4876490

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

4. Variational description of the ground state of the repulsive two-dimensional Hubbard model in terms of non-orthogonal symmetry-projected Slater determinants, R. R. Rodríguez-Guzmán, C. A. Jiménez-Hoyos, and G. E. Scuseria, *Phys. Rev*. **B 90**, 195110 (2014); http://journals.aps.org/prb/abstract/10.1103/PhysRevB.90.195110

5. Cluster-based mean-field and perturbative description of strongly correlated fermion systems: Application to the one- and two-dimensional Hubbard model, C. A. Jiménez-Hoyos and G. E. Scuseria, *Phys. Rev*. B **92**, 085101 (2015); http://link.aps.org/doi/10.1103/PhysRevB.92.085101

6. Polynomial Similarity Transformation Theory: A smooth interpolation between coupled cluster doubles and projected BCS applied to the reduced BCS Hamiltonian, M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, *Phys. Rev*. **B 93**, 125124 (2016); http://link.aps.org/doi/10.1103/PhysRevB.93.125124

7. Projected Hartree Fock Theory as a Polynomial Similarity Transformation Theory of Single Excitations, Y. Qiu, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **145**, 111102 (2016); http://dx.doi.org/10.1063/1.4963082

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

9. Projected Hartree-Fock as a polynomial of particle-hole excitations and its combination with variational coupled cluster theory, Yiheng Qiu, T. M. Henderson, and G. E. Scuseria; https://arxiv.org/abs/1702.08578

10. Combining symmetry collective states with coupled cluster theory: Lessons from the Agassi model Hamiltonian, M. R. Hermes, J. Dukelsky, and G. E. Scuseria; https://arxiv.org/abs/1703.02123

Laura Gagliardi

Beyond KS-DFT: Challenge of excited states & transition-metal systems

Christopher J. Cramer, Jason Goodpaster, Donald G. Truhlar, Laura Gagliardi

Department of Chemistry, Chemical Theory Center, Supercomputing Institute, University of Minnesota,
207 Pleasant Street SE, Minneapolis, MN 55455-0431,

Abstract

We recently worked together on a Scientific Discovery through Advanced Computing (SciDAC-3) Application Partnership in Materials and Chemical Sciences entitled *Charge Transfer and Charge Transport in Photoactivated Systems — Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite* supported for the period September 1, 2012 to August 31, 2017. As part of that project, methods, algorithms, and software tools needed for the reliable treatment of the underlying physics of charge transfer and charge transport were developed. This research was motivated by the recognition that charge transfer and charge transport in photoactivated systems are fundamental processes that underlie solar energy capture, solar energy conversion, and photoactivated catalysis, both organometallic and enzymatic.

The SciDAC-3 project involved substantial work dedicated to rewriting of the existing MCSCF code in the open-source *NWChem*software. Additionally, optimization of various code sections in order to speed-up electronic structure calculations[1] in release and development versions of *NWChem* was accomplished thanks to collaborations between UMN, Pacific Northwest National Laboratories, and the SciDAC Institutes SUPER and FastMATH. We integrated the vertical electrostatic model (VEM) for the nonequilibrium solvation of excited states with *NWChem*'s time-dependent density functional theory (TDDFT) capabilities and incorporated surface hopping approaches for non-adiabatic molecular dynamics simulations as well as an interface between *NWChem* and the Minnesota dynamics code *ANT,* which includes beyond-surface-hopping methods, of which the coherent switches with decay of mixing algorithm is of particular importance.

Substantial progress was made on a number of topics, including:

- Improving the range and efficiency of CASSCF and CI calculations in *NWChem*
- Development and implementation of MC-PDFT and early applications to a variety of problems
- Development and implementation of new diabatization schemes for multistate dynamics
- Development and implementation of general approaches for combining molecular-mechanics treatments for spectator degrees of freedom with quantum mechanical approaches for reactive degrees of freedom in dynamical simulations
- Computational characterization of the photochemical reactions of complex organic molecules
- Characterization of charge-transport mechanisms in molecular wires ranging from tunneling to site hopping as a function of chemical composition and wire length
- Exploitation of real-time TDDFT approaches to predict excited-state (transient) absorptions and optical limiting behavior for various chromophores

Next we highlight one specific example.

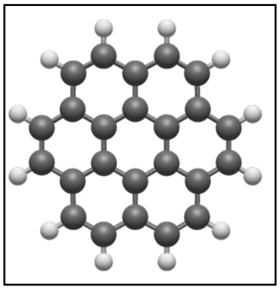


Figure **1**: the structure of coronene

In order to explore the limits of the newly implemented MCSCF code in

NWChem, CASSCF calculations were performed on coronene (Figure **1**), including all 24 p electrons in 24 orbitals. This calculation involved half a trillion Slater determinants (3.6 trillion determinants were symmetry not to have been exploited), which was a record calculation that far exceeded what had previously been feasible. The highly scalable MCSCF algorithm ran a single CI iteration on 7680 processors in 15 minutes and work is ongoing with scalability testing and additional load-balancing improvements to increase the number of processors that can be used to get an even faster time-to-solution.

Our future plans is to **model inherently multireference materials and extended chemical systems** with powerful embedding methods that will enable the calculation of multireference dynamic correlation energy for extended systems. These methods will describe all aspects of electron correlation in a balanced fashion and thus predict accurate solid-state, thin-film, and catalytic properties of these systems. Specifically we propose to extend density matrix embedding theory (DMET) and density embedding theory (DET) to treat large and periodic systems with multireference character. We propose to do this by treating the primary subsystem by a recently developed multireference method, namely multi-configuration pair-density functional theory, (MC-PDFT). The MC-PDFT method has two steps: first an MCSCF calculation to include non-dynamic correlation, which may also be called static correlation in this context, and then a density functional step to treat dynamic correlation. The MC-PDFT method has been developed as a way to combine the advantages of wave function theory and density functional theory to provide a better treatment of multireference systems because it addresses *both* static and dynamic correlation but without the high cost of wave function methods for dynamic correlation. We will explore complete-active-space multiconfiguration wave functions for the MCSCF step, but we expect that practical calculations will eventually involve generalized-active-space (GAS) multiconfiguration self-consistent-field (GASSCF) wave functions because they allow the treatment of a larger number of active electrons and active orbitals by removing large portions of the deadwood in the configuration space. The separated-pair approximation for ground-state properties and frontier partitioning for excited state properties, both of which are special cases of GASSCF, have proven especially promising in molecular systems. Since MC-PDFT requires much less computer time and storage than previous wave function theory (WFT) methods, and at the same time it accounts for dynamic correlation in a formally exact manner (albeit with the limitation that the correlation functionals are not exact), it opens the door for accurate simulations of larger and complex multireference systems.

Grant Numbers and Grant Titles

Scientific Discovery through Advanced Computing (SciDAC-3) Application Partnership in Materials and Chemical Sciences entitled *Charge Transfer and Charge Transport in Photoactivated Systems — Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite*

Postdoc(s): Kostantinos Vogiatziz

Student(s): Chad E. Hoyer

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

1. Vogiatzis, K. D.; Ma, D.; Olsen, J.; Gagliardi, L.; de Jong, W., Pushing Configuration-Interaction to the Limit: Towards Massively Parallel MCSCF Calculations. *Submitted* 2017,

2. Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Galvan, I. F.; Ferre, N.; Frutos, L. M.; Gagliardi, L.; Garavelli, M.; Giussani, A.; Hoyer, C. E.; Li Manni, G.; Lischka, H.; Ma, D. X.; Malmqvist, P. A.; Muller, T.; Nenov, A.; Olivucci, M.; Pedersen, T. B.; Peng, D. L.; Plasser, F.; Pritchard, B.; Reiher, M.; Rivalta, I.; Schapiro, I.; Segarra-Marti, J.; Stenrup, M.; Truhlar, D. G.; Ungur, L.; Valentini, A.; Vancoillie, S.; Veryazov, V.; Vysotskiy, V. P.; Weingart, O.; Zapata, F.; Lindh, R., Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J. Comput. Chem.* 2016, *37* (5), 506-541 (10.1002/jcc.24221).

3. Hoyer, C. E.; Parker, K.; Gagliardi, L.; Truhlar, D. G., The DQ and DQ Phi electronic structure diabatization methods: Validation for general applications. *J. Chem. Phys.* 2016, *144* (19), (10.1063/1.4948728).

4. Li Manni, G.; Carlson, R. K.; Luo, S.; Ma, D.; Olsen, J.; Truhlar, D. G.; Gagliardi, L., Multi-Configuration Pair-Density Functional Theory. *J. Chem. Theory Comp.* 2014, *10* (9), 3669-3690

5. Hoyer, C. E.; Gagliardi, L.; Truhlar, D. G., Multiconfiguration Pair-Density Functional Theory Spectral Calculations Are Stable to Adding Diffuse Basis Functions. *J. Phys. Chem. Lett.* 2015, *6* (21), 4184-4188 (10.1021/acs.jpclett.5b01888).

6. Smith, C. E.; Odoh, S. O.; Ghosh, S.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D., Length-Dependent Nanotransport and Charge Hopping Bottlenecks in Long Thiophene-Containing pi-Conjugated Molecular Wires. *J. Am. Chem. Soc.* 2015, *137* (50), 15732-15741 (10.1021/jacs.5b07400).

7. Vogiatzis, K. D.; Li Manni, G.; Stoneburner, S. J.; Ma, D. X.; Gagliardi, L., Systematic Expansion of Active Spaces beyond the CASSCF Limit: A GASSCF/SplitGAS Benchmark Study. *J. Chem. Theory Comp.* 2015, *11* (7), 3010-3021 (10.1021/acs.jctc.5b00191).

8. Hoyer, C. E.; Ghosh, S.; Truhlar, D. G.; Gagliardi, L., Multiconfiguration Pair-Density Functional Theory Is as Accurate as CASPT2 for Electronic Excitation. *J. Phys. Chem. Lett.* 2016, *7* (3), 586-591 (10.1021/acs.jpclett.5b02773).

9. Miller, D. L.; Siedschlag, R. B.; Clouston, L. J.; Young, V. G.; Chen, Y. S.; Bill, E.; Gagliardi, L.; Lu, C. C., Redox Pairs of Diiron and Iron-Cobalt Complexes with High-Spin Ground States. *Inorg. Chem.* 2016, *55* (19), 9725-9735 (10.1021/acs.inorgchem.6b01487).

10. Taherinia, D.; Smith, C. E.; Ghosh, S.; Odoh, S. O.; Balhorn, L.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D., Charge Transport in 4 nm Molecular Wires with Interrupted Conjugation: Combined Experimental and Computational Evidence for Thermally Assisted Polaron Tunneling. *ACS Nano* 2016, *10* (4), 4372-4383 (10.1021/acsnano.5b08126).

Accurate Calculations and Rigorous Analyses of Electronic Structure, Molecular Bonding and Potential Energy Surfaces

Klaus Ruedenberg
Ames Laboratory USDOE, Iowa State University, Ames, Iowa, 50011
ruedenberg@iastate.edu

Scope

The objective of this work is the development of accurate ab initio molecular wave functions as well as rigorous ab initio analyses that yield theoretically valid concepts for the physical understanding of bonding and bonding changes along reaction paths. Since accurate electronic wave functions have complex structures, rigorous interpretative analyses are also complex, in distinction to unconstrained rationalizations. Since energy changes along reaction paths are dominated by energy changes in the valence space, effective methods are developed for obtaining accurate wave functions in full valence spaces as well as for dynamic correlations.

Recent Work

Dynamic correlation.

In non-equilibrium regions of coordinate space, accurate potential energy surfaces typically require multi-configurational zeroth-order reference functions and dynamical correlation recovery with respect to these reference functions. The correlation energy recovery is challenging when reliable chemical accuracy calls for contributions beyond second order perturbation theory and double excitations with respect to such a reference space. An advance has been the Correlation Energy Extrapolation by Intrinsic Scaling (CEEIS) developed by this group, which greatly reduces the number of excitations that have to be calculated. Thereby correlations of up to eight-tuple excitations for quadruple-zeta basis sets were recovered in diatomic molecules (B_2, C_2, O_2, F_2). In conjunction with complete basis set limit extrapolations, core-valence correlation corrections and relativistic corrections, diatomic potential energy curves were obtained with chemical accuracy, vibration-rotation spectra were obtained with near spectroscopic accuracy and predicted where experimentally unavailable. The method has been generalized to the simultaneous calculation of several states of the same symmetry. The method has also been combined with a many-body expansion.

A recent application, in cooperation with Professor Th. Windus, has been the calculation of the four lowest singlet states [$X^1\Sigma^+{}_g$, $A^1\Pi_u$, $B^1\Delta_g$, and $B'^1\Sigma^+{}_g$] of the carbon atom. These states exhibit several curve crossings due to the $B^1\Delta_g$ state and an avoided crossing between the $^1\Sigma^+{}_g$ states. The agreements between calculation and experiments are within ~0.5 kcal/mol for the dissociation energies, and within ~20 cm^{-1} for the vibrational energy levels.

Another application, in cooperation with Professor Th. Windus, has been to the potential energy surface of Ozone whose ground state has three equivalent open minima and a predicted higher lying closed ring minimum, which has so far eluded experimental detection. The ring isomer is surrounded by a substantial ridge in C_s symmetry on which three saddle points, each in C_{2v} symmetry, provide transition states to the open minima. The ridge is the result of an avoided crossing between the $1^1A'$ ground state and an excited $2^1A'$ state. The two states touch each other along a closed one-dimensional conical intersection seam, which crosses the three C_{2v} symmetry planes in intersections points close to the transition states. The strong interactions between three close atoms and between the two generating diabatic states, as well as the size of the full valence space pose a challenge for accurate calculations.

It was shown that, for reference spaces significantly smaller than the full valence space, achievement of chemical accuracy requires at least sextuple excitations. It was also shown that omission of the correlations of the 2s oxygen orbitals, a widely practiced approximation, in fact introduces uncertainties of about ± 10 mh into the energy differences on the potential energy surfaces and between the surfaces. The elevation of the ring minimum over the open minimum was found to be between 45 and 50 mh. The barrier between the two minima is about 85 to 90 mh with respect to the open minimum. The 1^1A_1 transition state, the minimum of the 2^1A_1 excited state, and the conical intersection are found to lie within a few hundredths of an Angstrom of each other.

Intrinsic ab initio bonding analysis

Since the earliest days of quantum chemistry, it has been recognized that atoms in molecules are different from free atoms and that, therefore, a true understanding of bonding is contingent on understanding the energy *increases* due to the formation of 'quasi-atoms' in a molecule as well as the energy *decreases* resulting from the interactions between the quasi-atoms. An essential prerequisite for the quantification of these counteracting intra- and interatomic energy changes is a quantification of the concept of the quasi-atom in a molecule. Since the electronic wave function contains all electronic structure information, the theoretically valid quantification of the quasi-atom concept should be drawn out of the molecular wave functions. This challenging issue has been universally sidestepped by *postulating* atomic valence states in molecules.

Recent work in this group has addressed this problem without the use of postulated intermediate wave functions. The analysis has shown that a quasi-atomic organization of the electronic structure is embedded in the actual electronic wave function of a molecule. The quasi-atoms that are intrinsic to the wave function have been formulated. The relative roles of the intra-atomic energy changes and the interatomic interactions in bond formation have been deduced from the wave function. Essential for the analysis has been the demonstration that molecular electronic wave functions can be exactly expressed in terms of quasi-atomic orbitals, i.e. orbitals that are slightly deformed free atom orbitals. These orbitals are extracted from the wave function by an unbiased algorithm based on criteria that are independent of the orbital representation. The main bonding interactions have been shown to occur between only a few interacting quasi-atomic orbitals, which represent the rigorous counterparts to the chemical concept of atomic hybrid orbitals.

By expressing the molecular electronic wave function in terms of its quasi-atomic orbitals, the energy has been additively resolved in terms of quasi-atomic energies and interatomic interaction energies. The interatomic interactions energies have been rigorously resolved in terms of classical electrostatic interactions and nonclassical interactions due to electron sharing. By this ab initio analysis of wave functions and energies, bonding patterns in various molecules have been quantitatively elucidated without introducing preconceived rationalizations.

Future Work

Essential prerequisites for efficient molecular calculations are strongly correlated wave functions within full valence spaces. No unbiased self-selecting method currently exists for generating the most efficient wave function in these spaces. A construction of such wave functions has been conceived using quasi-atomic orbitals in conjunction with the effective ORMAS code, which is unique to the GAMESS suite. The formulation will be implemented and further developed.

Several aspects of the bonding analysis require further detailed development and implementation, *viz.*, the detailed relation between quasi-atoms and free atoms, the differentiation between electron sharing with and without charge transfer, and technical improvements for the handling of large molecules. The ab initio analysis will be applied to elucidate disputed bond patterns, such as in C_2, as well as differences between analogous bonding patterns in different molecules, such as H_2CCH_2 versus H_2SiSiH_2.

Publications 2014 to date

Accurate ab initio potential energy curves and spectroscopic properties of the four lowest singlet states of C_2. J. S. Boschen, D. Theis, K. Ruedenberg, T.L. Windus, Theor Chem Acc 33, 1425, 12 pages (2014)

Covalent bonds are created by the drive of electron waves to lower their kinetic energy through expansion. M. W. Schmidt, J. Ivanic, K. Ruedenberg, J. Chem. Phys. 140, 204104, 14 pages (2014)

The Physical Origin of Covalent Binding. M. W. Schmidt, J. Ivanic, K. Ruedenberg, Chapter 1, pp. 1-67 of the book "The Chemical Bond. Fundamental Aspects of Chemical Bonding," (Edited by G. Frenking and S. Shaik, Wiley-VCH, 2014)

A comprehensive analysis in terms of molecule-intrinsic, quasi-atomic orbitals. II. Strongly correlated wave functions. Aaron C. West, Michael W. Schmidt, Mark S. Gordon, Klaus Ruedenberg, J. Phys. Chem. A 119, 10360−10367 (2015), DOI: 10.1021/ acs.jpca.5b03399

A comprehensive analysis in terms of molecule-intrinsic, quasi-atomic orbitals. III. The covalent bonding structure of urea. Aaron C. West, Michael W. Schmidt, Mark S. Gordon, Klaus Ruedenberg, J. Phys. Chem. A 119, 10368−10375 (2015), DOI: 10.1021/ acs.jpca.5b03400

A comprehensive analysis in terms of molecule-intrinsic quasi-atomic orbitals. IV. Bond breaking and bond forming along the dissociative reaction path of dioxetane. Aaron C. West, Michael W. Schmidt, Mark S. Gordon, Klaus Ruedenberg, J. Phys. Chem. A 119, 10376−10389 (2015), DOI: 10.1021/acs.jpca.5b03402

The transition from the open minimum to the ring minimum on the ground state and on the lowest excited state of like symmetry in ozone. A configuration interaction study. Daniel Theis, Joseph Ivanic, Theresa L. Windus, Klaus Ruedenberg, J. Chem. Phys. 144, 104304 (2016), 18 pages, DOI:

Correlation Energy Extrapolation by Many-Body Expansion. Jeffery S. Boschen, Daniel Theis, Klaus Ruedenberg, Theresa L. Windus. J. Phys. Chem, A, 121, 836–844, (2017) DOI: 10.1021/ acs.jpca.6b10953

Intrinsic resolution of molecular electronic wave functions and energies in terms of quasi-atoms and their interactions. Aaron C. West, Michael W. Schmidt, Mark S. Gordon, Klaus Ruedenberg, J. Phys. Chem, A, 121, 1086−1105 (2017) DOI: 10.1021/acs.jpca.6b10911

Nonadiabatic Photochemistry

Donald G. Truhlar

Department of chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute
University of Minnesota, Minneapolis, Mn 55455-0431

truhlar@umn.edu

Program Scope

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

Recent Progress

The local approximations to exchange–correlation functionals that are widely used in Kohn-Sham density functional theory usually underestimate band gaps and molecular excitation energies, and therefore, it becomes necessary to use more expensive hybrid functionals or more empirical DFT+U functionals for accurate predictions and modeling of these properties. We developed two new local approximation to the exchange–correlation functional called HLE16 and HLE17, where HLE denotes high local exchange. The HLE16 functional is a generalized gradient approximation, and the HLE17 functional is a meta generalized gradient approximation. These functionals give good performance for semiconductor band gaps and molecular excitation energies – competitive with hybrid functionals. Unlike the conventional way of using the DFT+U method, one does not need to determine new parameters for every property or system studied. Simultaneously increasing the local exchange and decreasing the local correlation improved electronic excitation energies improved without excessively degrading the ground-state solid-state cohesive energies, molecular bond energies, or chemical reaction barrier heights. The new functional can be useful as is for calculations on semiconductors or excited states where it is essential to control the cost, and it can also be useful in establishing a starting point for developing even better new functionals that perform well for excited states.

We described a diabatic-at-construction (DAC) strategy for defining diabatic states to determine the adiabatic ground and excited electronic states and their potential energy surfaces using the multistate density functional theory (MSDFT). The DAC approach differs in two fundamental ways from the adiabatic-to-diabatic (ATD) procedures that transform a set of pre-selected adiabatic electronic states to a new representation. (1) The DAC states are defined in the first computation step to form an active space, whose configuration interaction produces the adiabatic ground and excited states in the second step of MSDFT. Thus, they do not result from a similarity transformation of the adiabatic states as in the ATD procedure; they are the basis for producing the adiabatic states. The appropriateness and completeness of the DAC active space can be validated by comparison with experimental observables of the ground and excited states. (2) The DAC diabatic states are defined using the valence bond characters of the asymptotic dissociation limits of the adiabatic states of interest, and they are strictly maintained at all molecular geometries. Consequently, DAC diabatic states have specific and well-defined physical and chemical meanings that can be used for understanding the nature of the adiabatic states and their energetic components. We presented results for the four lowest singlet states of LiH and compared them to a well-tested ATD diabatization method, namely the threefold way; the comparison revealed both similarities and differences between the ATD diabatic states and the orthogonalized DAC diabatic states. We showed that MSDFT can provide a quantitative description of the ground and excited states for LiH with multiple strongly and weakly avoided curve crossings spanning over 10 Å of interatomic separation.

We presented a perspective on Kohn-Sham density functional theory (KS-DFT) for electronic structure calculations in chemical physics with part of the review covering topics very important to the current project, especially: 1. The treatment of open-shall and inherently multiconfigurational systems (the later are often called multireference systems and are variously classified as having strong correlation, near-degeneracy correlation, or high static correlation; KS-DFT must treat these systems with broken-symmetry determinants). 2. Time-dependent density functional theory (TDDFT), which is an extension of DFT to treat time-dependent problems and excited states.

The reactions

$$\mathrm{OH}(\mathrm{A}^2\Sigma^+) + \mathrm{H}_2 \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{H} \tag{1}$$

and

$$\mathrm{OH}(\mathrm{A}^2\Sigma^+) + \mathrm{H}_2 \rightarrow \mathrm{OH}(\mathrm{X}^2\Pi) + \mathrm{H} \tag{2}$$

provide enticing targets for theoretical study because of the detailed experimental data available the Lester, Crosley, Heard, and Davis laboratories. Upon the $A\,^2\Sigma \leftarrow X\,^2\Pi$ excitation of isolated OH, only radiative decay is conceivable, but collisions with other molecules open nonradiative de-excitation pathways, such as reactions (1) and (2). The nonradiative pathways are enabled by the presence of conical intersections that couple the ground and the excited states and which have been shown to be ubiquitous in polyatomic molecular systems. The objective of present work is use of the previously developed fourfold way diabatization scheme to calculate full-dimensional global PESs and couplings for the three lowest electronic states for reactions (1) and (2) and their representation in a new form that is convenient for dynamics calculations by either quantal or semiclassical methods. We have used multi-configuration quasidegenerate perturbation theory, fourfold-way diabatic molecular orbitals, and configurational uniformity to develop a global three-state diabatic representation of the potential energy surfaces and their couplings for the electronically nonadiabatic reaction $\mathrm{OH}^* + \mathrm{H}_2 \rightarrow \mathrm{H}_2\mathrm{O} + \mathrm{H}$, where * denotes electronic excitation to the $\mathrm{A}\,^2\Sigma^+$ state. These calculations employ a carefully selected active space for the complete active space self-consistent-field reference calculation, globally applicable diabatic prototype lists, and our recently derived model space diabatization improvement of the fourfold way diabatization scheme. The surfaces and couplings are being fit to permutationally invariant many-body analytic representations that may be used for quantal or semiclassical dynamics calculations. The results are also being used to explore the global nature of the regions of strong interaction of the potential energy surfaces.

The photodissociation of thioanisole, as well as that of similar molecules such as phenol, thiophenol, and anisole, is a prototype of the 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 potential energy surfaces (PESs) and state couplings of the ground and two lowest singlet excited states of thioanisole ($C_6H_5SCH_3$) were constructed in a diabatic representation based on electronic structure calculations including dynamic correlation. They cover all 42 internal degrees of freedom and a wide range of geometries including the Franck-Condon region and the reaction valley along the breaking S–CH_3 bond with the full ranges of the torsion angles. The parameters in the PESs and couplings 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, where the anchor-point force fields are obtained with a locally modified version of the QuickFF package. The PESs and couplings are now being used for coherent-switches-with-decay-of-mixing dynamics calculations of the photodissociation process.

Future Plans

We will complete the fitting of the surfaces and couplings for the OH_3 system, and we will perform semiclassical dynamics simulations of the electronically nonadiabatic processes by the method of coherent switches with decay of mixing. These calculations will include electronically adiabatic and electronically nonadiabatic tunneling by our recently developed army ants tunneling approximation. We will also compare these surfaces and couplings to the work of David Yarkony. We will also provide these surfaces and couplings to Hua Guo for quantum mechanical wave packet calculations. The dynamical results will be compared to each other and used to interpret the experimental data.

We will continue the dynamics calculations on thioanisole photochemistry, interpret them by statistical methods, including distributions of the minimum-energy gaps during trajectories and analysis of product-state translational distributions, and use them to interpret the experimental observations of a resonance in this process.

Grant Numbers and Grant Titles

"Variational Transion State Theory," March 1, 2015–May 31, 2016; PI: Donald G. Truhlar; grant no. DE-FG02-86ER13579

"Nonadiabatic Photochemistry," April 15, 2016–April 14, 2019; PI: Hua Guo, Co-PIs: David Yarkony, Donald G. Truhlar; grant no. DE- SC0015997

Postdoctoral associates, 2016-April 2017: Steven M. Mielke, Yinan Shu, Joanna Kryven

Graduate students, 2016-April 2017: Kelsey A. Parker, Shaohong L. Li, Junwei Lucas Bao

Ten most recent publications acknowledging these two grants

1098. “Benchmark Calculations for Bond Dissociation Enthalpies of Unsaturated Methyl Esters and the Bond Dissociation Enthalpies of Methyl Linolenate,” X. Li, X. Xu, X. You, and D. G. Truhlar, Journal of Physical Chemistry A **120**, 4025-4036 (2016). dx.doi.org/10.1021/acs.jpca.6b02600

1101. “Predicting Pressure-Dependent Unimolecular Rate Constants Using Variational Transition State Theory with Multidimensional Tunneling Combined with System-Specific Quantum RRK Theory: A Definitive Test for Fluoroform Dissociation,” J. L. Bao, X. Zhang, and D. G. Truhlar, Physical Chemistry Chemical Physics **18**, 16659-16670 (2016). dx.doi.org/10.1039/C6CP02765B

1108. “Perspective: Kohn-Sham Density Functional Theory Descending a Staircase,” H. S. Yu, S. L. Li, and D. G. Truhlar, Journal of Chemical Physics **145**, 130901/1-23 (2016). dx.doi.org/10.1063/1.4963168 (invited perspective article)

1109. “Atmospheric Chemistry of Criegee Intermediates. Unimolecular Reactions and Reactions with Water,” B. Long, J. L. Bao, and D. G. Truhlar, Journal of the American Chemical Society **138**, 14409-14422 (2016). dx.doi.org/10.1021/jacs.6b08655

1111. “Barrierless Association of CF_2 and Dissociation of C_2F_4 by Variational Transition State Theory and System-Specific Quantum RRK Theory,” J. L. Bao, X. Zhang, and D. G. Truhlar, Proceedings of the National Academy of Sciences, U.S.A. **113**, 13606-13611 (2016). dx.doi.org/10.1073/pnas.1616208113

1118. “HLE16: A Local Kohn–Sham Gradient Approximation with Good Performance for Semiconductor Band Gaps and Molecular Excitation Energies,” P. Verma and D. G. Truhlar, Journal of Physical Chemistry Letters **8**, 380-387 (2016). dx.doi.org/10.1021/acs.jpclett.6b02757

1123. “Diabatic-At-Construction (DAC) Method for Diabatic and Adiabatic Ground and Excited States Based on Multistate Density Functional Theory," A. Grofe, Z. Qu, D. G. Truhlar, H. Li, and J. Gao, Journal of Chemical Theory and Computation **13**, 1176-1187 (2017). dx.doi.org/10.1021/acs.jctc.6b01176

1124. “Computational Kinetics by Variational Transition State Theory with Semiclassical Multidimensional Tunneling: Direct Dynamics Rate Constants for the Abstraction of H from CH_3OH by Triplet Oxygen Atoms,” H. Ma, R. Meana-Pañeda, X. Xu, and Donald G. Truhlar, Journal of Physical Chemistry A **121**, 1693-1707 (2017). dx.doi.org/10.1021/acs.jpca.6b10600 (published as part of *The Journal of Physical Chemistry* virtual special issue “Mark S. Gordon Festschrift”)

1125. “Reaction of SO_2 with OH in the Atmosphere,” B. Long, J. L. Bao, and D. G. Truhlar, Physical Chemistry Chemical Physics **19**, 8091-8100 (2017). dx.doi.org/10.1039/c7cp00497d.

1126. “HLE17: An Improved Local Exchange–Correlation Functional for Computing Semiconductor Band Gaps and Molecular Excitation Energies,” P. Verma and D. G. Truhlar, Journal of Physical Chemistry C **121**, 7144-7154 (2017). dx.doi.org/10.1021/acs.jpcc.7b01066

Speaker: David R. Yarkony

Nonadiabatic Photochemistry

David R. Yarkony, Chemistry Department, Johns Hopkins University, Baltimore, MD 21218
Multiple PI Grant with: Hua Guo, University of New Mexico
Donald G. Truhlar, University of Minnesota

ABSTRACT

While electronic structure is essential to explain chemical reaction mechanisms, quantification of those results requires nuclear dynamics. However the accuracy of the computational nonadiabatic dynamics is limited by the accuracy of the coupled potential energy surfaces(PESs) needed to describe such reactions, particularly when the nuclear dynamics employs electronic structure data determined on-the-fly.

A. Unique Tool: To circumvent this limitation, in systems currently up to the size of phenol, we have developed an algorithm to construct $\mathbf{H}^d$ a coupled diabatic state representation of adiabatic electronic states coupled by conical intersections by fitting and simultaneously diabatizing, energies, energy gradients and derivative couplings obtained from multireference configuration interaction single and double excitation (MRCISD) wave functions.[1] The algorithm can (in principle) efficiently describe any number of adiabatic states. The method derives its ability to describe disparate regions of nuclear coordinate space through the use of a flexible set of anharmonic distance and angle dependent functions combined with localizing functions that focus the representation to selected regions. Another challenging issue is the selection of nuclear configurations (points) to define the fit. The systems we aim to describe are too large to be described using a grid of points. Instead the electronic structure data is calculated at points determined by quasi classical surface hopping trajectories (QCT) obtained using Truhlar's ANT program.

B. Production: In work citing exclusively DoE and NERSC completed since the beginning of 2016 we have reported and made freely available multistate, full dimensionality, $\mathbf{H}^d$, for the accurate description of

C_6H_5OH photodissociation 4 states 33 internal coordinates 1 channel[2]
https://www.github.com/yarkonygrp/surfaces/phenol/4state

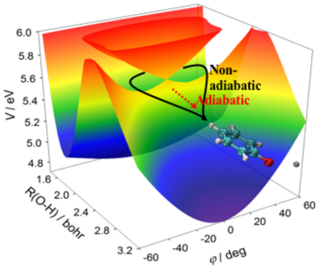
CH_2OH photodissociation 3 states 9 internal coordinates 3 channels[3]
https://www.github.com/yarkonygrp/surfaces/hydroxymethyl/3state.shifted

These representations, derived from accurate *ab initio* data, have enabled, as part of collaboration with Hua Guo of the University of New Mexico, fully quantum mechanical reduced dimensionality studies of lifetimes for photodissociation of phenol in its 2^1A state[4] as well as work in progress on CH_2OH photodissociation.[5] These later studies complement accurate experimental work in Reisler's USC laboratory. The excellent agreement between the computed and measured tunneling lifetimes for phenol photodissociation[4] provides convincing evidence for a proposed dissociation mechanism, nonadiabatic tunneling and attests to the accuracy of the constructed $\mathbf{H}^d$. But there is much more to this story as we now explain.

C. Recent Progress-New Ideas Fully quantum mechanical reduced dimensionality calculations of phenol 2^1A photodissociation, noted above, were performed by Guo in a four diabatic state representation. However in the region determining the lifetimes of the low lying vibrational levels of the 2^1A state, the 2^1A PES is sufficiently isolated that it was expected that standard single state adiabatic dynamics would provide a good approximation to the four diabatic state results. However this turned out not to be the case, as Guo's single adiabatic state dynamics

lifetime was ~100 times shorter than the exact four diabatic state result. The surprising explanation for this result is shown in the following figure which illustrates the topography that produces nonadiabatic tunneling.[4] The black lines illustrate alternative paths on the 2^1A PES around an energetically inaccessible conical intersection. It is this conical intersection and the geometric phase it produces, absent in the standard adiabatic state treatment, that converts constructive to destructive interference therebye increasing the lifetime. The observed effect is an extension of the Molecular Aharonov-Bohm (MAB) effect described by Mead and Truhlar in 1979,[6] to tunneling dynamics.

Figure 1



This finding has the potential to change the way we think about single state tunneling dynamics in particular and even single state dissociative dynamics in general. For example the ground state PES describing CH_2OH high overtone induced dissociation to CH_2O +H has the topography exhibited in Fig.1. However a previous high quality computational study of this process employed the traditional single adiabatic state approximation.[7] We believe technical issues have limited assessment of the prevalence and impact of the MAB effect. The issues are being overcome. Guo is developing techniques to handle the singular terms that occur in the nonadiabatic dynamics. We have shown that our algorithm for describing adiabatic states can, because of its ability to accurately describe derivative couplings, enable treatment of MAB impacted dynamics in general molecular systems.[8] To accomplish this a two diabatic state representation of the adiabatic state in question and the excited state creating the conical intersection seam is required.

In collaboration with Guo, we will undertake a systematic study of this MAB effect in systems we have targeted for the study of photodissociation as part of our DoE research effort including $CH_2OH(X) + h\nu \rightarrow CH_2O + H$ and $H_2O + H \rightarrow OH(X) + H_2$. In this regard we have already produced a two state, $\mathbf{H}^d$ for the ground and first excited state of CH_2OH. This $\mathbf{H}^d$ will be used to study high overtone photodissociation on the ground state and photodissociation on the 2^2A state. A new two state $\mathbf{H}^d$ for phenol is currently being constructed.

References

[1] X. Zhu, and D. R. Yarkony, J. Chem. Phys. **140,** 024112 (2014).
[2] X. Zhu, C. L. Malbon, and D. R. Yarkony, J. Chem. Phys. **144,** 124312 (8 pages)(2016).
[3] C. L. Malbon, and D. R. Yarkony, J. Chem. Phys. **146,(**2017).
[4] C. Xie, J. Ma, X. Zhu, D. R. Yarkony, D. Xie, and H. Guo, J. Am. Chem. Soc. **138,** 7828(2016).
[5] C. Xie, C. Malbon, D. R. Yarkony, and H. Guo, J. Chem Phys. (2017).
[6] C. A. Mead, and D. G. Truhlar, J. Chem. Phys. **70,** 2284(1979).

[7] E. Kamarchik, C. Rodrigo, J. M. Bowman, H. Reisler, and A. I. Krylov, J. Chem. Phys. **136,** 084304(2012).
[8] C. L. Malbon, X. Zhu, H. Guo, and D. R. Yarkony, J. Chem. Phys. **145,** 234111(2016).

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Postdocs:	Xiaolei Zhu
Graduate Students:	Xiaolei Zhu, Christopher Malbon

Publications Acknowledging DoE Support (2015-Present)

1. *Perspective:Accurate Nonadiabatic Dynamics*
   Hua Guo and David R. Yarkony, Phys. Chem. Chem. Phys. *18*, 26335-26352 (2016)

2. Nonadiabaticity: The Importance of Conical Intersections
   Zhu, X.; Yarkony, D. R. *Molec. Phys.* . 114,1983-2013 (**2016)**

3. *On the Electronic Structure of the Ground State of Cyclopentoxy. The Case for a Two Coupled State Description*
   C. L. Malbon, D. R. Yarkony, and X. Zhu, J. Mol. Spec., 311, 36-41 (2015)
4. *On the Nonadiabatic Photodissociation of the Hydroxymethyl Radical from the 2^2A State. Surface Hopping Simulations Based on a Full Nine Dimensional Representation of the $1,2,3^2A$ Potential Energy Surfaces Coupled by Conical Intersections*
   Christopher L. Malbon and David R. Yarkony, J. Phys .Chem. A 119, 7498-7509 (2015)
5. *On the Elimination of the Electronic Structure Bottleneck in On the Fly Nonadiabatic Dynamics for Small to Moderate Sized (10-15 atom) Molecules Using Fit Diabatic Representations Based Solely on ab initio Electronic Structure Data: The Photodissociation of Phenol*
   Zhu, X.; Yarkony, D. R. *J. Chem. Phys 144*, 024105 (2016)
6. *An Improved Quasi-Diabatic Representation of the 1,2,3 ^1A Coupled Adiabatic Potential Energy Surfaces of Phenol in the Full 33 Internal Coordinates.*
   Xiaolei Zhu, Christopher L. Malbon and David R. Yarkony, J. Chem. Phys. 144, 124312 (2016)
7. *Nonadiabatic Tunneling in Photodissociation of Phenol*
   C. Xie, J. Ma, X. Zhu, D. R. Yarkony, D. Xie, and H. Guo, J. Amer. Chem. Soc. 138, 7828-7831 (2016).
8. *Nonadiabatic tunneling via conical intersections and the role of the geometric phase.*
   Xie, C.; Yarkony, D. R.; Guo, H. *Phys. Rev. A 95,* 022104 (2017).
9. *Multistate, Multichannel Coupled Diabatic State Representations of Adiabatic States Coupled by Conical Intersections. CH2OH Photodissociation*
   Christopher Malbon and David Yarkony, J. Chem. Phys.146, 134302 (2017)

The Strange World of Nonadiabatic Tunneling - Geometric Phase and Diagonal Born-Oppenheimer Correction

Hua Guo (hguo@unm.edu)

Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131

Abstract

While the Born-Oppenheimer approximation is considered as a corner stone in treating molecular spectroscopy and dynamics, its failure near electronic degeneracies has been well documented.[1] Such degeneracies are quite common for excited electronic states, and they control many importance processes such as internal conversion, intersystem crossing, charge transfer and energy transfer. A common type of electronic degeneracy is a conical intersection (CI), in which two electronic states become degenerate in the N-2 dimension where N is the number of internal coordinates.

Dynamics through a CI necessitates treatments beyond the Born-Oppenheimer approximation. There are two approaches, via the adiabatic or diabatic representation. The former is based on the assumption that the electronic motion adjusts instantaneously to the change of nuclear motion. When the nonadiabatic couplings between different adiabatic states are neglected, the adiabatic representation is reduced to the familiar Born-Oppenheimer approximation. On the other hand, a diabatic representation can be obtained from the adiabatic representation via an orthogonal transformation which removes the nonadiabatic coupling in the adiabatic representation. This is however only strictly possible in diatomic systems. For polyatomic systems, this adiabatic-to-diabatic transformation can only be established approximately and consequently the diabatic representation is not unique.

One often overlooked problem with the adiabatic representation near a CI is the presence of the geometric phase (GP), which renders a real-valued electronic wavefunction changing its sign when transported along a closed circle around the CI. This phase was first pointed out by Longuet-Higgins,[2] and developed in a broader context by Berry,[3] thus often called the Berry's phase. The double-valued electronic wavefunction needs be compensated by a double-valued nuclear wavefunction to maintain the single valuedness of the total wavefunction. In the late seventies, Mead and Truhlar presented an elegant approach to incorporate the GP into an adiabatic Hamiltonian.[4] In addition, there is also a term in the Hamiltonian that is called the diagonal Born-Oppenheimer correction (DBOC), which becomes infinity at the CI.

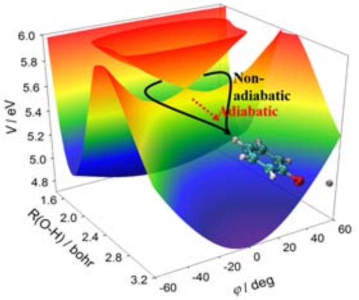


Figure 1. Potential energy surfaces of phenol. The lower S_1 state forms a CI with the higher S_2 state. The nonadiabatic tunneling is subject to interference between tunneling trajectories around the CI on the two sides.

We have recently been interested in the photodissociation dynamics of prototypical molecules, which may present an interesting case of nonadiabatic tunneling.[5-8] As shown in Figure 1, photoexcitation of phenol (C_6H_5OH) to its S_1 state necessitates its dissociation to C_6H_5O + H via tunneling because of insufficient energy to overcome a barrier formed between the S_1 and S_2 states via a CI. Experimental studies of this system have determined the tunneling lifetimes, which show a large isotope effect. Using recently developed full-dimensional coupled quasi-diabatic potential energy surfaces,[9] we have investigated the nonadiabatic tunneling dynamics under the CI with a reduced-dimensional quantum model. While the lifetime for the ground vibrational state of C_6H_5OH (S_1) calculated using

this quasi-diabatic model is in good agreement with experimental data, it was found that the corresponding lifetime of the same state is about two orders of magnitude shorter if the tunneling is treated within the adiabatic representation with only the lowest adiabat included in the calculation (i.e., BO approximation).[5] Furthermore, the dissociation wave function in the two representations is quite different, one with a clear node in the region outside the CI.[5] These observations were quite surprising as the energy of the tunneling state is well below the CI, which suggests that a single state BO approximation should be sufficient.

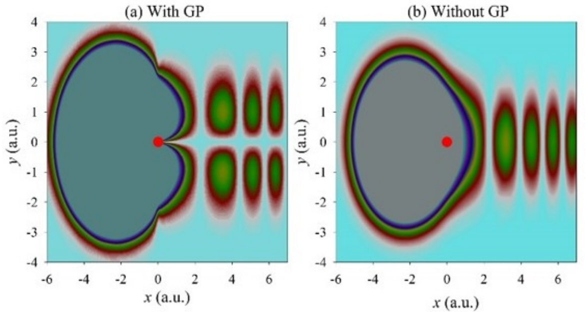


Figure 2. Comparison of adiabatic tunneling wavefunctions with and without the GP. The CI is denoted by a red dot.

To understand the underlying physics, we developed a simple two-dimensional model, in which both the diabatic and adiabatic representations can be uniquely defined.[6] Implicitly including the GP, the diabatic model can be considered as exact. In the adiabatic representation, on the other hand, the GP can be introduced through a vector potential, following Mead and Truhlar.[4] In this simple model, it is possible examine systematically the impact of the GP and DBOC on the tunneling dynamics. Our results clearly demonstrated that the inclusion of the GP in the adiabatic model is decisive in recovering much of the error in the BO treatment of the tunneling for the lowest vibronic state.[6] Indeed, the GP slows down tunneling and forms a node in the dissociating wavefunction at y=0 outside the CI (Figure 2), as found in the diabatic model. The node can be interpreted as the result of destructive interference between tunneling trajectories moving around the CI on the two sides, which carry different phases (Figure 1). The addition of DBOC further improves the result, as this diagonal term provides an additional barrier near the CI for the tunneling trajectories. The remainder of the errors is due to the neglect of the nonadiabatic coupling in a single-state approximation. Similar results have been obtained for bound Jahn-Teller systems as well.[6] More recently, we have demonstrated that nonadiabatic tunneling of excited vibronic states with odd quanta in the coupling (y) mode leads to constructive interference, which enhances tunneling.[8] Differing from the destructive interference for vibronic states with even quanta (including the lowest state discussed above), the constructive interference features a dissociating wavefunction that has no node at y=0.

These new insights raise questions on the conventional wisdom that tunneling can be treated within the BO approximation. This problem is particularly acute on the excited states, as electronic degeneracies are much more prevalent. In the future research, we intend to demonstrate the importance GP in other systems with higher dimensionality.[10]

Grant Number and Grant Title

DE-SC0015997 **Nonadiabatic photochemistry**

PI: Hua Guo, University of New Mexico
Co-PI: Donald G. Truhlar, University of Minnesota; David R. Yarkony, Johns Hopkins University

Postdoc(s): Changjian Xie

References (2016-2017 publications supported by the current DOE grant with *)

*1. Guo, H.; Yarkony, D. R., Accurate nonadiabatic dynamics, *Phys. Chem. Chem. Phys.* **2016,** *18*, 26335-26352.

2. Longuet-Higgins, H. C.; Öpik, U.; Pryce, M. H. L.; Sack, R. A., Studies of the Jahn-Teller effect. II. The dynamical problem, *Proc. Royal Soc. A (London)* **1958,** *244*, 1-16.
3. Berry, M. V., Quantal phase factors accompanying adiabatic changes, *Proc. Royal Soc. A (London)* **1984,** *392*, 45-57.
4. Mead, C. A.; Truhlar, D. G., On the determination of Born–Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei, *J. Chem. Phys.* **1979,** *70*, 2284-2296.
*5. Xie, C.; Ma, J.; Zhu, X.; Yarkony, D. R.; Xie, D.; Guo, H., Nonadiabatic tunneling in photodissociation of phenol, *J. Am. Chem. Soc.* **2016,** *138*, 7828-7831.
*6. Xie, C.; Yarkony, D. R.; Guo, H., Nonadiabatic tunneling via conical intersections and the role of the geometric phase, *Phys. Rev. A* **2017,** *95*, 022104.
*7. Xie, C.; Guo, H., Photodissociation of phenol via nonadiabatic tunneling: Comparison of two ab initio based potential energy surfaces, *Chem. Phys. Lett.* **2017,** *in press, DOI: 10.1016/j.cplett.2017.02.026*.
*8. Xie, C.; Kendrick, B. K.; Yarkony, D. R.; Guo, H., Constructive and destructive Interference in nonadiabatic tunneling via conical intersections, *J. Chem. Theo. Comput.* **2017,** *in press, DOI: 10.1021/acs.jctc.7b00124*.
9. Zhu, X.; Yarkony, D. R., On the elimination of the electronic structure bottleneck in on the fly nonadiabatic dynamics for small to moderate sized (10-15 atom) molecules using fit diabatic representations based solely on ab initio electronic structure data: The photodissociation of phenol, *J. Chem. Phys.* **2016,** *144*, 024105.
*10. Malbon, C. L.; Zhu, X.; Guo, H.; Yarkony, D. R., On the incorporation of the geometric phase in general single potential energy surface dynamics: A removable approximation to ab initio data, *J. Chem. Phys.* **2016,** *145*, 234111.

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

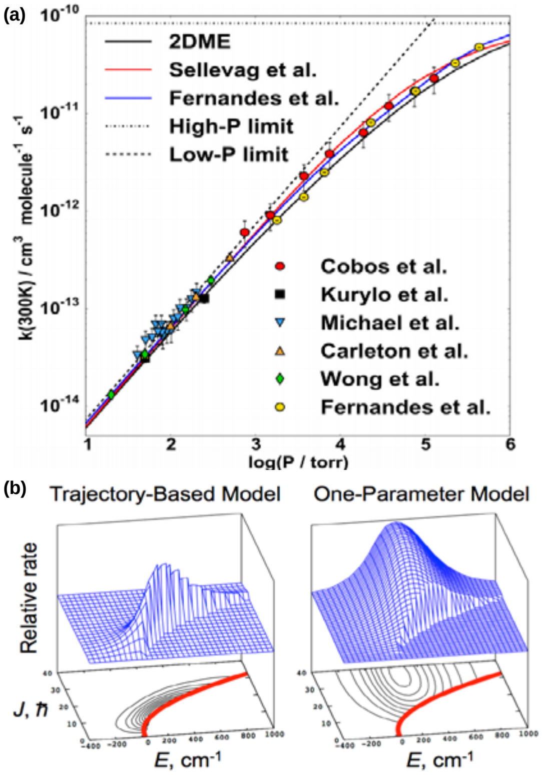
Ahren W. Jasper,[1,a] Judit Zádor,[2,b] and Stephen J. Klippenstein[1,c]

[1]Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave,
Argonne, IL 60439
[2]Combustion Research Facility, Sandia National Laboratories, PO Box 969, Livermore, CA 94551
[a]ajasper@anl.gov, [b]jzador@sandia.gov, [c]sjk@anl.gov

Abstract

The principal goal of this project is the development of accurate, broadly applicable, open-source, and user-friendly codes for predicting gas phase kinetics and dynamics. During the past award period, we made available online the Predictive Automated Phenomenological Rates (PAPR) software package (http://tcg.cse.anl.gov/papr/), which includes source code, documentation, example calculations, and auxiliary scripts for several integrated programs: (1) MESS, a master equation code, (2) VaReCoF, a variable reaction coordinate transition state theory (TST) code, (3) DiNT, a trajectory code, (4) NST, a nonadiabatic statistical theory kinetics code, and (5) OneDMin, a code for predicting Lennard–Jones parameters.

Much of our effort is organized around the master equation code MESS, which implements the ab initio transition-state-theory-based master equation (AITSTME) approach for calculating temperature- and pressure-dependent kinetics from detailed microscopic information. A single AITSTME calculation involves multiple theoretical methods and supporting codes, including: *electronic structure* explorations of the potential energy surface and calculations of molecular geometries and frequencies, *transition state theory* calculations of energy- and angular-momentum-resolved (microcanonical) intramolecular fluxes (for isomerization, bond forming and breaking, etc.), *classical trajectory* calculations of intermolecular collisional energy transfer (via so-called “third-body” collisions), again at the energy- and angular-momentum-resolved level, and *solution of the master equation* describing the competition between the intramolecular and intermolecular processes. The organizing principle of this effort is the coordination of MESS with existing commercial codes, our own research codes, and newly developed distributed codes to allow for high accuracy and flexible applications throughout gas phase chemistry.



Quantitative *a priori* thermal rate coefficients from detailed microcanonical models of collisional energy and angular momentum transfer. (a) Our parameter-free prediction for the pressure-dependent thermal (300 K) rate coefficient for $H + O_2 + Ar \rightarrow HO_2 + Ar$ (black line) is as accurate as existing experimental measurements (symbols) and previous theoretical (red line) and experimental (blue line) empirical fits, with errors of just ~20%. (b) The quantitative accuracy arises in part from the use of a detailed trajectory-based collision model. Microcanonical rates obtained using the detailed model are compared to those from a simple one-parameter model, which typically produces thermal rates with errors of 2-3x.

In recent work supported by this program, several accuracy and efficiency improvements were made to MESS. Efficiency improvements include the implementation of parallel libraries and automatic energy-grid optimization. A typical calculation for a system with 20 intermediate complexes and 30 transition states can now be completed in ~one minute using 16 cores, which is nearly three orders of magnitude faster than the master equation code that preceded MESS. Chemical and physical models with improved accuracy are continually being added to MESS, with recent additions including a flexible treatment of collisional energy transfer and several new methods for computing anharmonic corrections to partition functions and state counts. For example, a new method was implemented for treating multiple coupled internal rotations as adiabatically separable from the remaining spectator modes. Torsional contributions to rovibrational properties can be evaluated using either quantum mechanical (for up to 4 rotors) or semiclassical approaches.

Our other distributed codes can be run independently and are designed to produce information in a format readily usable by MESS. For example, the Nonadiabatic Statistical Theory (NST) code interfaces with quantum chemistry codes, locates crossing seams for electronic surfaces with differing multiplicities, calculates nonadiabatic fluxes for intersystem crossing (ISC) using the Landau-Zener or weak coupling approximations, and writes MESS-readable data files of the nonadiabatic fluxes. In a recent application supported by this effort, product branching in the $^3O + C_2H_4$ reaction was calculated using MESS, NST, and an a priori treatment of ISC. Branching in this reaction is largely determined by the fate of the initial triplet adduct $^3OC_2H_4$, which can either fall apart on the triplet surface or undergo a spin-forbidden transition to the singlet surface. The singlet surface features different bimolecular product pathways than the triplet surface, and so overall branching is sensitive to the ISC rate. Our a priori predictions agreed well with available room temperature measurements. At the elevated temperatures relevant to combustion where no direct experimental thermal measurements are available, however, our branching was found to differ significantly from room temperature branching and from the branching assumed in earlier empirical calculations. Specifically, the a priori calculations predicted much less CH_3 and HCO production than what had been previously assumed at high temperatures; the use of our updated values had a measurable impact on macroscale combustion properties (e.g., shortening ignition delay times by a factor of two in C_2H_4 flames).

Modeling pressure dependence in the master equation requires collision rates and efficiencies for each unimolecular species and bath gas of interest. For many systems and conditions, reaction rates and product branching fractions depend sensitively on the supplied collision parameters, and the lack of a priori collision parameters severely compromises the predictive value of the calculations. To address this deficiency, we developed codes for predicting collision parameters that can be used in MESS calculations. The construction of a full-dimensional potential energy surface (PES) describing collisions is a prerequisite for the a priori prediction of collision parameters. Continuing earlier work, we extended and validated a set of ab initio based PESs for saturated and lightly unsaturated C_xH_y in atomic and diatomic bath gases. In ongoing work, this strategy is being extended to oxygenated fuels and polyatomic baths.

Two methods were developed for calculating collision rates. In the most detailed approach, the collision integral associated with the dilute gas diffusion coefficient (proportional to the collision rate) was calculated for H, H_2, and several normal alkanes + N_2 using full-dimensional trajectories and our distributed code DiNT. The resulting diffusion coefficients were shown to agree with experimental results to better than 2%. These results were then used to test the accuracy of simpler approaches for predicting collision rate parameters, including the "one-dimensional minimization" method developed with support from this award and distributed in the code OneDMin. In the simpler approach (which can treat systems with several heavy atoms using direct PES evaluations via quantum chemistry code calls), the full-dimensional intermolecular potential is orientationally sampled and averaged to obtain an effective one-dimensional potential, from which collision parameters (typically Lennard-Jones parameters) are extracted.

A new model for collisional energy transfer was developed. The model typically used in master equation calculations (the "single exponential down" model) can have errors of up to a factor of three when used with a priori calculations of the collision efficiency. We developed a more detailed model of the energy transfer function, which we showed to have an a priori accuracy of just 20%. Theoretical error bars of this size are comparable to those assigned in many kinetics experiments, such as in the comparison shown for HO_2 decomposition in Ar in Figure (a). The detailed theoretical model has nine parameters, which improves upon the single exponential down model by allowing for the explicit treatment of: angular momentum dependence, the nonseparability of changes in energy and angular momentum, and "long tail" supercollisions. The nine parameters were determined by optimizing them to reproduce low-order moments of the energy transfer function calculated using classical trajectories and the PESs discussed above. As shown in Figure (b), the trajectory-based detailed model predicts significantly different energy- and angular-momentum-dependent collision induced dissociation rates than the simple one-parameter model. The error in these microcanonical details manifests as a factor of 2–3 error in the thermally averaged rate coefficient.

A key element of this new approach was the implementation of the "two-dimensional" master equation (2DME), where the microcanonical collisional and intramolecular rates are resolved as functions of both the total energy E and the total angular momentum J. Although isolated 2D test cases have appeared in the literature, widely used master equation codes are "one-dimensional" and depend only on E. Setting up and solving the 2DME adds significant complexity, and we first implemented the 2DME in a research version of the master equation code VariFlex as part of this project. The extension of the 2DME to multichannel/multiwell systems and the incorporation of 2D corrections into MESS are planned for future work.

We will also develop methods and codes for studying reaction networks coupled via nonthermal intermediates. Specifically, we plan to develop a "global" master equation code that can treat sequences of chemically activated reactions through explicit consideration of energy-resolved population distributions, with collision and chemistry induced state changes. Prior efforts to explore sequences of chemically activated reactions have restricted attention to the coupling of two steps and have made various decoupling assumptions to avoid the need for a joint master equation. The proposed code would allow for quantitative explorations of the full coupling of energy relaxation and chained chemical reactions. At the simplest level, the code would function by directly propagating the time dependent species concentrations, with comparisons to corresponding simulations for presumed rapid thermal relaxation providing an indication of the importance of the coupling. We will also explore the generalization of MESS's chemically significant eigenvector approach to this more complex case, with the goal of obtaining appropriately reduced descriptions of utility in chemical modeling. The proper analysis of the coupling of energy relaxation and chemical dynamics will require the development of our companion codes to predict the microscopic kinetics for microcanonical distributions of reactants colliding with thermal translational energies. We will develop both statistical and trajectory based codes for these rate processes.

Finally, in future work we will continue automating our codes for higher throughput and for sensitivity analysis, with continued improvements to the PES-exploration and kinetics codes KinBot and EStokTP. Our planned software development efforts are designed to advance the utility of theoretical methods for gas phase chemical kinetics and dynamics. The development of a global master equation code and improved treatments of collisional energy and angular momentum transfer will allow for detailed exploration of core scientific problems in combustion and atmospheric chemistry. The coupling of MESS with global sensitivity and uncertainty codes will enhance the value of uncertainty and optimization studies for characterizing complex gas phase systems.

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

Postdoc(s): Xiaohu Li (Sandia)

Student(s): none

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

. S. J. Klippenstein, **From Theoretical Reaction Dynamics to Chemical Modeling of Combustion** *Proc. Combust. Inst.* **36**, 77–111 (2017).

. A. M. Mebel, Y. Georgievskii, A. W. Jasper, and S. J. Klippenstein, **Temperature- and Pressure-Dependent Rate Coefficients for the HACA Pathways from Benzene to Naphthalene**, *Proc. Combust. Inst*. **36**, 919–926 (2017).

. X. Li, A. W. Jasper, J. Zádor, J. A. Miller, and S. J. Klippenstein, **Theoretical Kinetics of O + C_2H_4**, *Proc. Combust. Inst.* **36**, 219–227 (2017).

. A. W. Jasper, **Multidimensional Effects in Nonadiabatic Statistical Theories of Spin-Forbidden Kinetics: A Case Study of $O(^3P) + CO \rightarrow CO_2$**. *J. Phys. Chem. A*, **119**, 7339–7351 (2015).

. A. W. Jasper, C. M. Oana, J. A. Miller, **"Third-Body" Collision Efficiencies for Combustion Modeling: Hydrocarbons in Atomic and Diatomic Baths**, *Proc. Combust. Inst*. **35**, 197–204 (2015).

. A. W. Jasper, K. M. Pelzer, J. A. Miller, E. Kamarchik, L. B. Harding, and S. J. Klippenstein, **Predictive A Priori Pressure Dependent Kinetics**, *Science*, **346**, 1212–1215 (2014).

. A. W. Jasper, E. Kamarchik, J. A. Miller, and S. J. Klippenstein, **First-Principles Binary Diffusion Coefficients for H, H_2, and Four Normal Alkanes + N_2**, *J. Chem. Phys*., **141**, 124313 (2014).

. A. W. Jasper and J. A. Miller, **Lennard–Jones Parameters for Combustion and Chemical Kinetics Modeling from Full-Dimensional Intermolecular Potentials**, *Combust. Flame* **161**, 101–110 (2014).

PI: Barry. D Dunietz

Photo-Induced and Voltage-biased Charge Transfer and Transport Processes: A First Principles Based Perspective.

Kent State University
Department of Chemistry
Kent, OH.
(bdunietz@kent.edu)

Abstract

A computational approach is developed and employed to contribute to the design of materials used in energy conversion applications. In one thrust we investigate photoinduced electron transport and transfer in organic semiconductor materials and interfaces relevant to photovoltaic functionality. In the second thrust we investigate bias-induced electron transport through molecular bridges.

We take part in a collaborative project that brings together groups of complementary expertise: Classical molecular dynamics (MD) simulations of complex condensed phase systems (Cheung, University of Houston), cutting edge theory and simulation techniques for modeling quantum dynamics in the condensed phase (Geva, University of Michigan), and state-of-the-art *ab-initio* electronic structure calculations (Dunietz, Kent State University). For truly facing the associated challenges, a combination of such methods is required.

Our first-principles based approach uses range-separated hybrid (RSH) functionals that provide a quantitative description of key properties including ionization energies and charge transfer state energies. We have used our electronic structure approach to calculate conductance of molecular bridges and rates of charge transfer processes employing a fully quantum mechanical approach. We obtained excellent agreement with available experimental measurements and therefore provide unique insight at the molecular level.

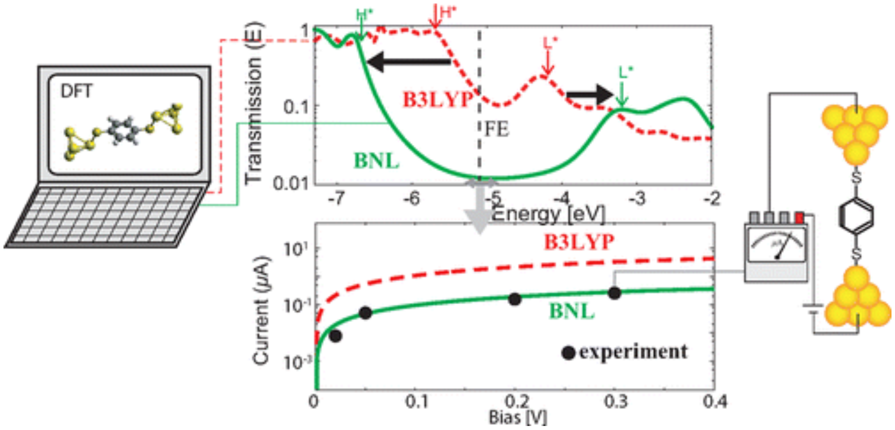
In Figure 1 we represent the recent success of our approach to provide predictive level of calculated conductance. We use a RSH functional, where the increased fundamental orbital gap yields a calculated conductance that agrees well with the measured value for the four types of bridges considered.
In Figure 2 we showcase our study on a molecular triad system, where the nature of the CT process and dependence on molecular conformations are resolved.
In Figure 3 we illustrate the different classes of CT states that can affect photovoltaic efficiencies in typical organic based devices.
In Figure 4 we summarize the success of our electronic structure approach to reproduce measured vibrational and electronic spectra that is associated with a widely studied tri-metal complex. (The complex consists of a central Pt ion bridging Fe ions through cyano ligands). Our interpretation of the solvated complex structure leads to a novel understanding of the complex structure-function

relationships and in-particular the possible CT process in that system.

We are pursuing in collaboration with the groups of Eitan Geva (University of Michigan) and Margaret Cheung (University of Houston), a hierarchy of methodologies that combine molecular dynamics simulations, electronic structure calculations and quantum dynamics methods that is used for modeling charge transfer rates. The triad system will be targeted as a benchmark system in the development of our comprehensive computational scheme.

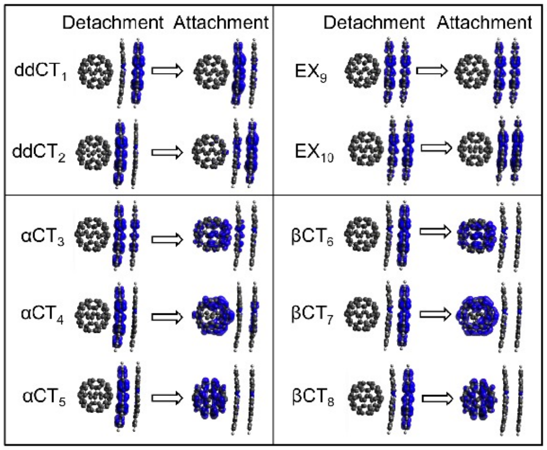
More specifically, interfacial structure and distributions of donor-acceptor geometries will be achieved using reliable and predictive MD simulations. Excited state energies, charge distributions, distortions of equilibrium geometries and electronic coupling coefficients for the different donor-acceptor geometries will be determined using electronic structure techniques. Finally, CT rates will be estimated, as well as its dependence on and sensitivity to donor-acceptor geometry via linearized path-integral semiclassical and mixed-quantum-classical techniques

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



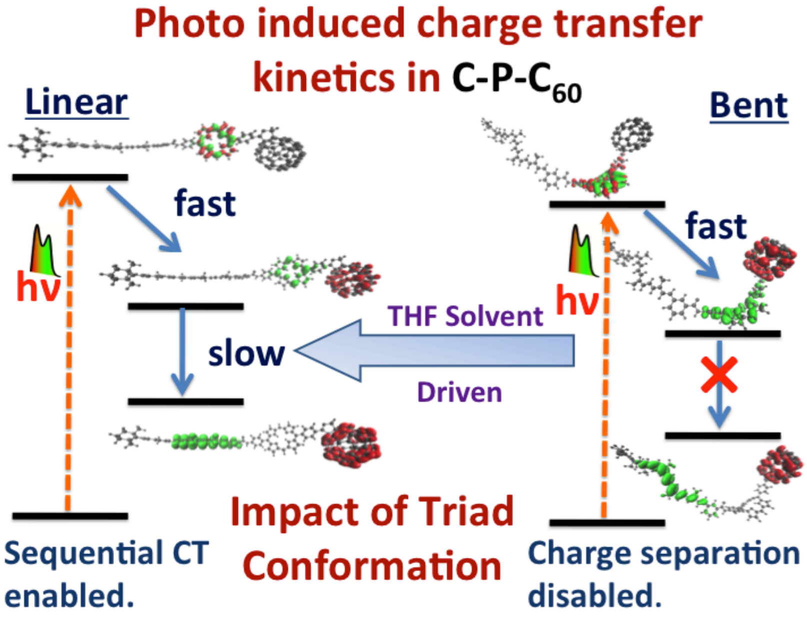
(Yamada et al, Nano.. Lett. 16, 6092, 2016)

Figure 2. Various CT processes can affect charge separation efficiencies



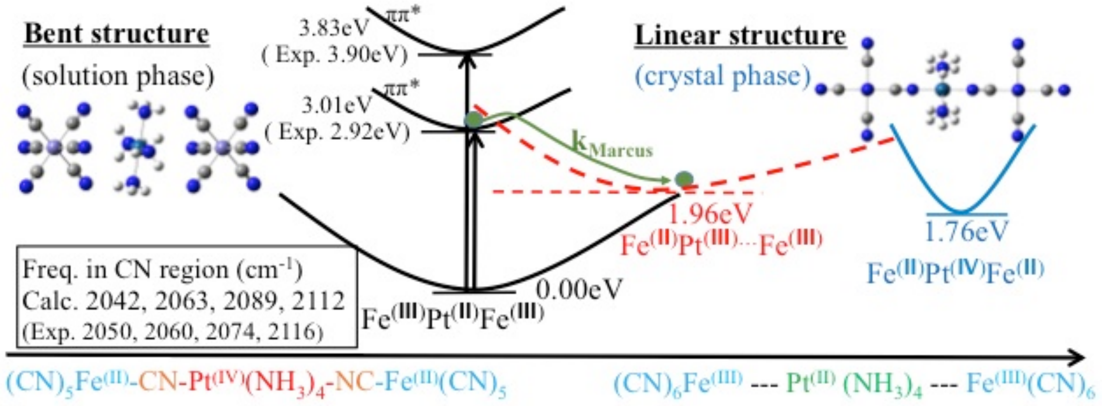
(Yamada et al, Nano.. Lett. 16, 6092, 2016)

Figure 3. CT process in a molecular triad – relating structural flexibility to charge separation



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

Figure 4. Charge polarization and conformation in a trimetal complex



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

Grant Numbers

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- "Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials" Basic Energy Sciences through the Chemical Sciences Geosciences and Biosciences Division: Award number DE-SC0016501 (09/15/2016 - 09/14/2017).

Postdocs: Arun K. Manna, Zilong Zheng, Qinquo Feng, Atushi Yamada, Alex Schubert
Graduate Students: Heidi, Phillips**,** Srijana Bhandari

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

1) Modification of molecular conductance by in-situ deprotection of thiol-based porphyrin, ,Zhou, Q. and Yamada, A. and Feng, Q. and Hoskins, A. and Dunietz, B. D. and Lewis, K. M., ACS Appl. Mater. Interfaces, ASAP 2017.
2) Deleterious effects of exact exchange functionals on predictions of molecular conductance Feng, Q. and Atsushi, Y. and Baer, R. and Dunietz, B. D., J. Chem. Theory Comput., 12, 3431-3435, 2016.
3) 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**,** 6092-6098, 2016.
4) Calculating High Energy Charge Transfer States Using Optimally Tuned Range-Separated Hybrid Functionals; Manna, A. K. and Lee, M. H. and McMahon, K. L. and Dunietz, B. D., J. Chem. Theo. Comp.. 11, 1110−1117, 2015.
5) Unraveling the Mechanism of Photoinduced Charge Transfer in Carotenoid–Porphyrin–C60 Molecular Triad; Manna, A. K. and Balamurugan, D. and Cheung, M. S. and Dunietz, B. D., J. Phys. Chem. Lett. 6, 1231−1237, 2015.
6) The Effect of Interfacial Geometry on Charge-Transfer States in the Phthalocyanine/Fullerene Organic Photovoltaic System, Lee, M. H. and Geva, E. and Dunietz, B. D., J. Phys. Chem. A., 120 2970-2975, 2015.
7) Ultrafast Charge-Transfer Dynamics at the Boron Subphthalocyanine Chloride/C60 Heterojunction: Comparison between Experiment and Theory; Wilcox, D. E. and Lee, M. H. and Sykes, M. E. and Niedringhaus, A. and Geva, E. and Dunietz, B. D. and Shtein, M. and Ogilvie, J. P., *J. Phys. Chem. Lett.*, *6* , 569–575, 2015.
8) Molecular Structure, Spectroscopy, and Photoinduced Kinetics in Trinuclear Cyanide Bridged Complex in Solution: A First-Principles Perspective; Zheng, Z. and Manna, A. K. and Hendrickson, H. P. and Hammer, M. and Song, C. and Geva, E. and Dunietz, B. D., J. Am. Chem. Soc. 136, 16954−16957, 2014.
9) Communication: Charge-transfer Rate Constants in Zinc-Porphyrin-Porphyrin-derived dyads: A Fermi Golden Rule First-Principles-Based Study; Manna, A. K. and Dunietz, B. D., J. Chem. Phys. 141, 121102, 2014.
10) End-Group Influence on Frontier Molecular Orbital Reorganization and Thermoelectric Properties of Molecular Junctions; Balachandran, J. and Reddy, P. and Dunietz, B. D. and Gavini, V., *J. Phys. Chem. Lett.*, *4*, 3825–3833, 2013.

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

Eitan Geva
Department of Chemistry, University of Michigan
930 N. University Ave., Ann Arbor MI 48109-1055
eitan@umich.edu

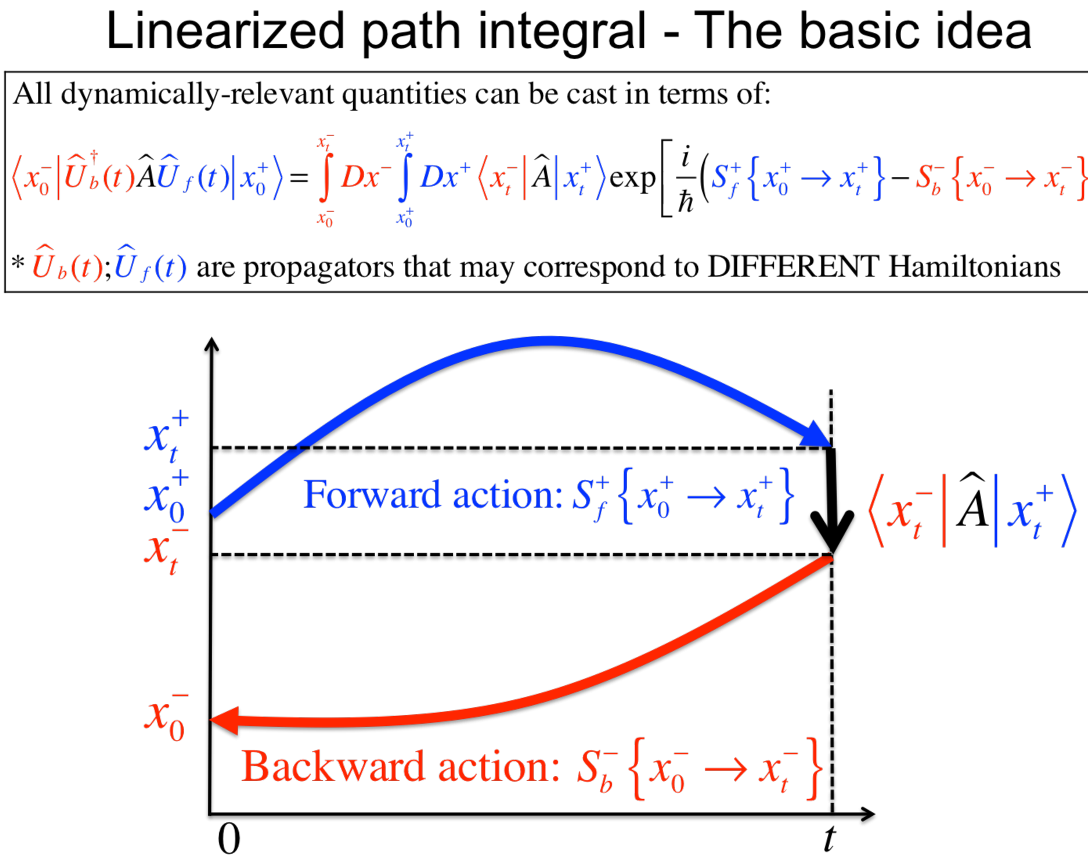
The rates of charge transfer (CT) processes can vary on an extremely wide range and can be very sensitive to the underlying molecular structure and molecular environment. Molecular level understanding of the mechanism underlying CT processes and the factors that determine their rates is key for controlling and improving the efficiency of these reactions, and thereby the technologies based on them.

The work I will present represents one component of a new collaborative project that brings together groups with expertise in classical molecular dynamics (MD) simulations of complex condensed phase systems (Margaret Cheung, University of Houston), state-of-the-art *ab-initio* electronic structure calculations (Barry Dunietz, Kent State University), and recently develped theory and simulation techniques for modeling quantum dynamical effects in the condensed phase (Eitan Geva, University of Michigan). Truly molecular modeling of systems of the level of complexity of organic photovoltaic (OPV) materials requires such a combination of methodologies. More specifically, reliable MD simulations are needed for determining interfacial structure and distributions of donor-acceptor geometries. Electronic structure techniques are needed for determining excited state energies, charge distributions, distortions of equilibrium geometries and electronic coupling coefficients for those donor-acceptor geometries. Finally, feasible, robust and transferable quantum dynamics theory and simulation techniques are necessary for simulating CT dynamics, as well as its dependence on and sensitivity to donor-acceptor geometry and interactions with the environment. The resulting modeling approach is expected to provide unique insight into the dependence of CT rates on the underlying molecular structure, chemical composition, type of photo-excitation, temperature, etc., which could prove critical for improving device performance.

	Marcus	Equilibrium FGR	Nonequilibrium FGR	GQME/TTM
Strong donor-acceptor coupling	-	-	-	+
Nonequilibrium initial state	-	-	+	+
Anharmonic force fields	-	+	+	+
Quantum nuclear effects	-	+	+	+
Dynamical nuclear effects	-	+	+	+
Non-Condon effects	-	+	+	+

Table 1: Hierarchy of post-Marcus methods for calculating electronic transition rates.

In this talk, I will present a recently developed hierarchy of methods for calculating electronic transition rates in molecular systems on the level of complexity of OPV materials (see Table 1). The equilibrium Fermi's golden rule (FGR) represents the simplest level of description, where the electronic transition is given in terms of a rate constant. This is also the level of description within which the classical Marcus expression can be obtained upon imposing additional approximations. The next level corresponds to the nonequilibrium FGR, which goes beyond equilibrium FGR by allowing for nonequilibrium initial nuclear configurations and describing electronic transitions by a rate, as opposed to a single rate constant. The next level in the hierarchy corresponds to the generalized quantum master equation (GQME) and transfer tensor method (TTM), which unlike the nonequilibrium FGR do not require a perturbative treatment of the electronic coupling.



Linearized path integral - The basic idea

All dynamically-relevant quantities can be cast in terms of:

$$\langle x_0^- | \hat{U}_b^\dagger(t) \hat{A} \hat{U}_f(t) | x_0^+ \rangle = \int_{x_0^-}^{x_t^-} Dx^- \int_{x_0^+}^{x_t^+} Dx^+ \langle x_t^- | \hat{A} | x_t^+ \rangle \exp\left[\frac{i}{\hbar} \left(S_f^+\{x_0^+ \to x_t^+\} - S_b^-\{x_0^- \to x_t^-\} \right) \right]$$

* $\hat{U}_b(t); \hat{U}_f(t)$ are propagators that may correspond to DIFFERENT Hamiltonians

Figure 1 the linearized path-integral approximation is based on the assumption that the main contributions to the forward-backward path integral come from forward-backward paths with small forward-back action. The approximation corresponds to linearizing the forward-backward action with respect to the difference between forward and backward paths. This leads to a family of feasible, versatile and surprisingly accurate classical-like methods that can capture quantum effects in complex molecular systems. Different methods correspond to applying the approximation to different quantities and/or different degrees of freedom.

A quantum-mechanically exact implementation of these methods is not feasible for systems as complex as OPV materials. The linearized forward-backward path-integral approximation (see Fig. 1) provides a platform within which all of the above mentioned levels of description could be dealt with in a manner that achieves an effective compromise between accuracy and feasibility necessary for treating OPV materials. Importantly, this approximation is known to reproduce the exact *quantum-mechanical* rates for the canonical Marcus model (i.e. when the Condon approximation is valid and donor and acceptor potential energy surfaces are described by shifted parabolas). Furthermore, the resulting methods are formulated in a manner that allows one to obtain electronic transition rates in complex molecular systems directly from classical MD simulations based on state of the art force fields and *ab-initio* inputs. Recent applications of this approach to benchmark and model dyad and triad OPV systems will be presented (see Fig. 2).

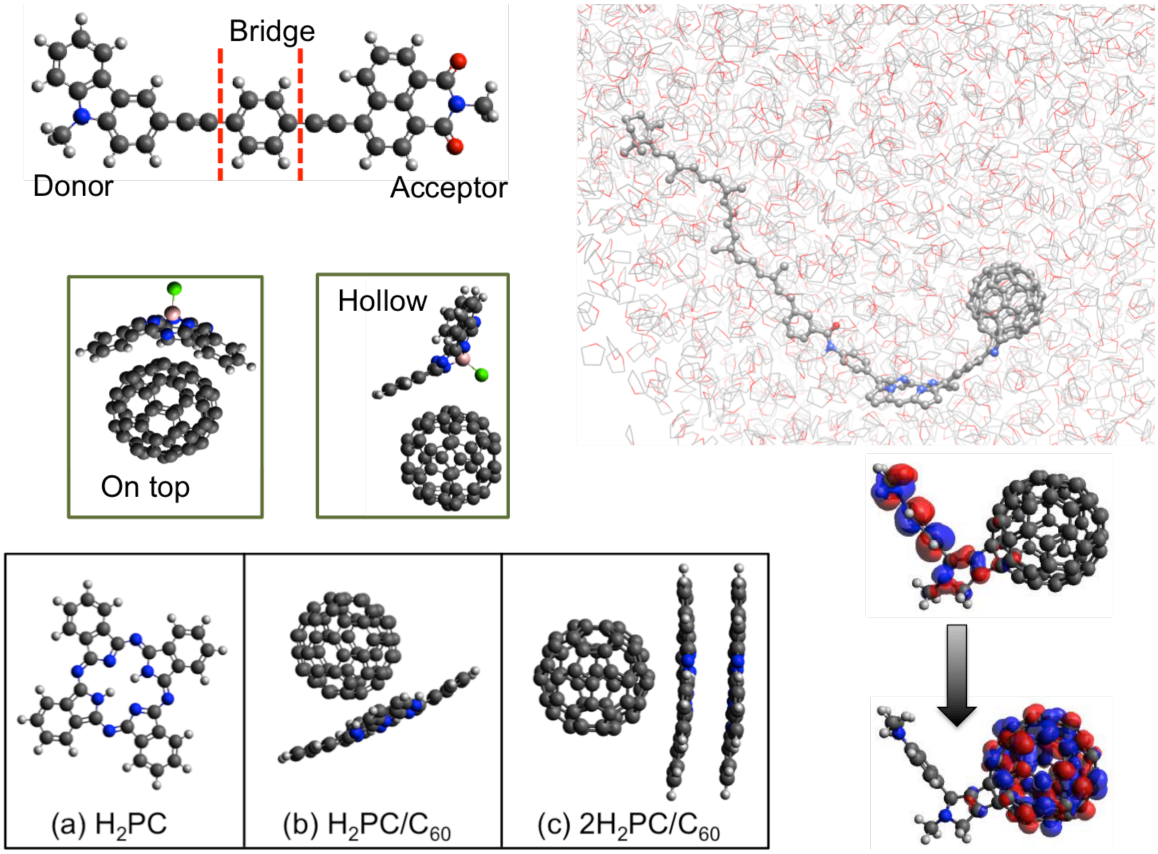


Figure 2: Model systems studied.

Grant Numbers

"Post-Marcus theory and simulation of interfacial charge transfer dynamics in organic semiconducting materials" Basic Energy Sciences through the Chemical Sciences Geosciences and Biosciences Division: Award number DE-SC0016501 (09/15/2016 - 09/14/2017).

Postdocs: Xiang Sun, Alex Schubert.
Graduate Students: Ellen Mulvihill, Kyle Williams.

References:

1. A. A. Kananenka, C-Y Hsieh, J. Cao and E. Geva (2016), "Accurate long-time mixed quantum-classical Liouville dynamics via the transfer tensor method", *J. Phys. Chem. Lett.* **7**, 4809−4814

2. X. Sun and E. Geva (2016) "Non-Condon Nonequilibrium Fermi's Golden Rule Rates from the Linearized Semiclassical Method" *J. Chem. Phys.* **145**, 064109
3. X. Sun and E. Geva (2016) "Non-Condon Equilibrium Fermi's Golden Rule Electronic Transition Rate Constants via the Linearized Semiclassical Method" *J. Chem. Phys.* **144**, 244105
4. X. Sun and E. Geva (2016) "Nonequilibrium Fermi's Golden Rule Charge Transfer Rates via the Linearized Semiclassical Method" *J. Chem. Theory Comput.* **12**, 2926−2941
5. X. Sun and E. Geva (2016) "Equilibrium Fermi's Golden Rule Charge Transfer Rate Constants in the Condensed Phase: The Linearized Semiclassical Method vs. Classical Marcus Theory" *J. Phys. Chem. A* **120**, 2976−2990
6. M. H. Lee, E. Geva and B.D. Dunietz (2016) "The effect of disorder on interfacial charge-transfer states in the phthalocyanine/fullerene organic photovoltaic system" *J. Phys. Chem. A* **120**, 2970−2975
7. Lee M. and Geva E. and Dunietz B. (2014) "Donor-to-donor vs. donor-to-acceptor interfacial charge transfer states in the phthalocyanine-fullerene organic photovoltaic system" *J. Phys. Chem. Lett.* **5** 3810-3816
8. Lee M., Geva E. and Dunietz B. (2014) "Calculation from First Principles of Golden-Rule Rate Constants for Photo-Induced Subphthalocyanine/Fullerene Interfacial Charge Transfer and Recombination in Organic Photovoltaic Cells" *J. Phys. Chem C* **118** 9780-9789

Scalability improvement of electronic structure code for molecular simulations in the presence of environment

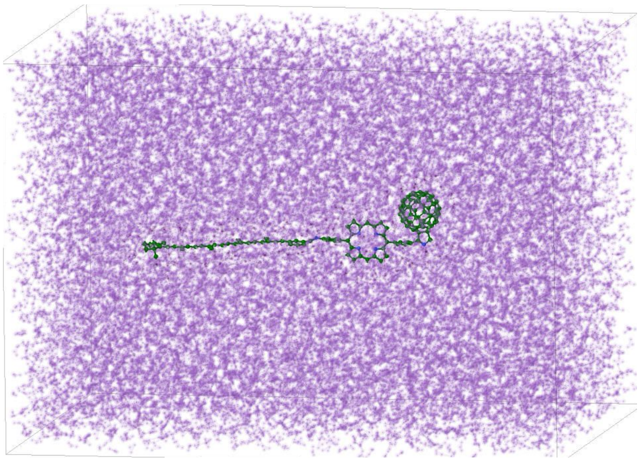
PI: Rajendra Zope, Department of Physics, University of Texas at El Paso.
email: rzope@utep.edu

The project aims to improve the scalability of our electronic structure software for investigation of ground and excited state properties of molecular systems in the presence of an environment. The project began in Sept 2015. A post doc (Luis Basurto) was hired on Jan. 1, 2016. A graduate student (Carlos Diaz) is working on the project from the Fall 2016.

Technical progress- The work is primarily focused on improving the scalability in memory of the NRLMOL electronic structure 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. 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 that 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 meeting, we reported a version of the code in which the Hamiltonian and Overlap matrices were stored using a distributed storage following the block cyclic distribution as employed in the ScaLapack library. In this version, each processor builds parts of the Hamiltonian that it has to store. The storage of the Hamiltonian and Overlap matrices is scalable in memory, since as the system size grows, the memory needed can be kept same by increasing the number MPI cores. However, the numerical grid dependent arrays that store the density and its derivatives as well the various component of the effective potential were replicated in this version which can result in a bottleneck for large system. This problem can be solved by building the Hamiltonian matrix in blocks of mesh. With this version we can simulate systems containing up to 20000-25000 basis functions depending on the grid size. As an application of this version, a calculation on the reaction center in the LH1 complex was presented in the last CTC PI meeting (May 2016).

During the last year we focused on the developments of two alternative approaches. In first approach, for each atom in the system we determine a cluster consisting of its neighbors by including all the atoms in a sphere whose radius depends on the most diffuse basis function (the basis function with the smallest exponent) of that atom. Thus the total system is broken down into subsystems. At this point we must note that this is not a fragment based or divide-and-conquer type methodology. Rather it is a parallelization approach to reduce the memory bottlenecks. The Kohn-Sham problem is still solved for the full system. Once the cluster for each atom is defined, we determine the variational mesh for that cluster and all the potentials and the Hamiltonian matrix elements corresponding to the atom under consideration are computed. Once the Hamiltonian matrix is computed, it is mixed with previous iterations using Johnson-Broyden scheme and redistributed for diagonalization. The resultant code is essentially linear scaling in memory. A serial version of this code has been developed and tested. A preliminary parallel version of the code wherein each processor works on an atom is also developed and tested. A significant speed up can be obtained if instead of a single processor, a group of processors works on each cluster. This would require two levels of parallelization wherein the main communicator is split into groups, so that a group of processors works on each clusters. We plan to complete this during the forthcoming year.

The second approach is an alternative to the cluster based approach. While the algorithm described in previous paragraph can lead to a code that is essentially linear scaling in memory, it does result in somewhat redundant computation of potentials as the grids of various clusters overlap. This isn't a problem if computational budget is not an issue. The redundant computation is eliminated in the second approach at the expense of storage of the Hamiltonian matrix in sparse format on each node. This is accomplished by dividing the mesh into blocks wherein a group of processors work on building the Hamiltonian for each block of mesh. The Hamiltonian matrix is stored on a node in a compressed sparse row format using the shared memory features of MPI. The total Hamiltonian is obtained by reducing the Hamiltonians of each block of mesh. This implementation also leads to a scalable code. This version is almost ready. We are still working on checkpoints for restart purposes. We have used this version to simulate a 2076 atom water cluster with 6-311G** basis by utilizing all the cores on Edison.



Applications- Using the developed software, 3 systems are being simulated. The first application consist of computation of ionization potential, electron affinity and the excited states of a carotene-porphyrin-fullerene triad in the presence of environment (explicit solvent) (See fig. 1). The systems consists of a triad surrounded by about 150 water molecules and approximately 17000-18000 basis functions were used to describe the system. The second simulated system is a multichromophoric heptad molecule that consists of BODIPY, Zn-tetraphenyl porphyrin, bis-phenyl anthracene, and fullerene. The solvent effects on the electronic properties are studied using the snapshots from the classical molecular dynamics simulations and the point charge model. These results were presented in the 2017 March meeting of the American Physical Society (Abstract: L25.00002). Finally we have also studied charge-transfer excitations in the concentric carbon onion $C_{60}@C_{240}$. The results of these simulations are being written up for submission to journals.

Grant number and grant title

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

Postdoc - Luis Basurto
Student - Carlos Diaz

Publications acknowledging this grant:

1. *Electronic and Optical Properties of VSc2N@C68 Fullerene,* S. Bhusal, S. Bhatta, R. R. Zope and T. Baruah , J. Phys. Chem. C. (2016).
2. Electronic and Structural Properties of C60 and Sc3N@C80 Supported on Graphene Nanoflakes, J. Ulises Reveles, N. N. Karle, T. Baruah, and R. R. Zope J. Phys. Chem. C, 120, 26083 (2016).
3. *Density functional study of the electronic structure of dye-functionalized fullerenes and their model donor-acceptor complexes containing P3HT,* T. Baruah, A. Garnica, M. Paggen, L. Basurto and R. R. Zope J. Chem. Phys. 144, 144304 (2016).
4. *Density functional investigation of the electronic structure and charge transfer excited states of a multichromophoric antenna,* L. Basurto, R. R. Zope, and T. Baruah Chemical Physics 469, 1 (2016).

5. *Ti4- and Ni4-Doped Defective Graphene Nanoplatelets as Efficient Materials for Hydrogen Storage,* RC. M. Ramos-Castillo, J. U. Reveles, M. E. Cifuentes-Quintal, R. R. Zope, and R. de Coss, J. Phys. Chem. C 120, 5001 (2016).

6. *Site specific atomic polarizabilities in endohedral fullerenes and carbon onions,* Rajendra R. Zope, S. Bhusal, L. Basurto, Tunna Baruah, and Koblar Jackson, J. Chem. Phys. 143, 084306 (2015).

7. *Crystalline Alloys of Organic Donors and Acceptors Based on TIPS-Pentacene,* Monica Kai Jes, Tunna Baruah, Parking Guan, Sean Parkin, Balaji Purushothaman, Rajendra Zope, and Michael Chabinyc, J. Phys. Chem. C, 2015, 119 (36), pp 20823–20832.

Probing Large Complex Systems with DFTB: GPU Enhancements and Self-Interaction Corrections

Bryan M. Wong
Department of Chemical & Environmental Engineering and Materials Science & Engineering Program, University of California-Riverside, Riverside, CA 92521

1. Abstract

This project is comprised of two complementary (but parallel) thrusts: (1) implementing massively-parallelized 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 mesoscale 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 GPU enhancements implemented in this project will enable accurate *and* computationally efficient approaches to directly probe quantum dynamics in these large, complex systems.

2. Recent Progress

The start date of this project was 08/15/2016, and during the past eight months we have devoted half of our initial efforts to GPU parallelization of electron dynamics and the other half of our focus to an in-house (i.e., from scratch) implementation of self-interaction corrections (SICs) in an all-electron DFT code. Both of these efforts and our progress in each of these initiatives are described further below.

The specific material systems we have chosen for GPU parallelization are large metallic nanoclusters systems and arrays. In particular, we are harnessing GPUs and implementing new computational routines to understand plasmonic interactions and collective many-body excitations in these metallic nanoparticles on an atomistic scale with DFTB. We have chosen metallic nanoparticles as an ideal system for GPU parallelization since our understanding of the detailed quantum-mechanical mechanisms in these collective excitations is severely limited due to the sheer size and complexity of plasmonic nanostructure-molecule interfaces. Specifically, while classical electrodynamics methods can handle metallic nanostructures at a continuum level, they cannot provide a first-principles based description of plasmonic systems at the quantum level, which is *absolutely crucial for describing electron tunneling processes at sub-nanometer gaps*. While conventional linear-response time-dependent methods can probe the quantum-mechanical dynamics of chemical systems, these (frequency-domain) methods cannot tackle the large sizes relevant to *collective excitations* in plasmonic materials. Recently, using real-time time-dependent

DFTB (TDDFTB), we have shown that collective plasmonic excitations produce large electric fields on metallic surfaces, leading to dramatic enhancements in the optical response. In particular, the largest electric field enhancements occur on regions of highest local curvature (i.e., at the corners of the structure), yielding "hot spots" on the surface of the metal nanoparticle (cf. **Figure 1**). As such, the development of GPU-enhanced electron dynamics methods that can resolve these features for large systems plays an important step in predicting and understanding the dynamics in these complex plasmonic systems.

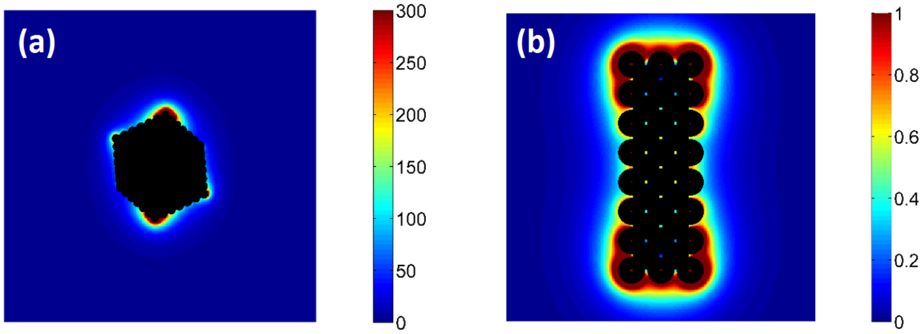


Figure 1. Electric field enhancement obtained from RT-TDDFTB for (a) an icosahedral-shaped sodium nanoparticle and (b) a rod-shaped sodium nanoparticle.

To probe the dynamics of these large systems using massively-parallelized GPUs, we calculate the time evolution of the density matrix from a numerical integration of the Liouville-Von Neumann equation of motion. For extremely large systems, the memory requirements for storing the DFTB density matrices exceeds the GPU global memory, which severely limits the types of systems that can be studied. Currently, we are implementing and evaluating three custom algorithms for out-of-core matrix-matrix multiplication designed to address this problem for larger systems. Within these three different algorithms, we split the multiplicands into block matrices and perform the multiplication as follows:

$$[A][B] = \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} \begin{bmatrix} B_1 & B_2 \end{bmatrix} = \begin{bmatrix} A_1B_1 & A_1B_2 \\ A_2B_1 & A_2B_2 \end{bmatrix}. \tag{1}$$

In **Algorithm 1**, memory is allocated for one submatrix of the first multiplicand and one submatrix of the second. The single multiply is performed, and memory is copied back to the product matrix before moving on to the next computation. Of the three algorithms tested, this uses the least memory of the algorithms, but generates the most memory transfer operations as we split the matrix into more submatrices. In **Algorithm 2**, memory is allocated for one submatrix of the first multiplicand and the entire second multiplicand. Using this additional memory, we are able to launch all of the kernels for one row group at once. This allows for better performance at the cost of additional memory requirements. Finally, for **Algorithm 3**, we modified the first algorithm and pipelined it with CUDA streams, with each thread in the operation having a corresponding CUDA stream. This increases the performance of the first algorithm in most cases when the number of threads and streams is optimal for the number of submatrices and the size of the problem. A downside of this approach is that this algorithm uses more memory than the first on both the host and the GPU, because each thread or stream needs a context to work in.

Using these custom GPU algorithms, we have calculated the absorption spectrum of extremely large gold nanoparticles obtained from the Fourier transform of the time-dependent dipole moment after deconvolution of the applied electric field (cf. **Figure 2**). It is worth mentioning that it is computationally prohibitive to obtain these results with conventional Casida-type TDDFT methods due to the immense size of these systems, whereas the entire spectrum can be directly obtained with the RT-TDDFTB approach. Most importantly, as opposed to frequency-domain calculations common in linear-response TD-DFT, it is relatively straightforward to parallelize the time-propagation steps on GPUs. We are still evaluating the efficiencies in each of the three different algorithms, and our preliminary assessment is as follows: Algorithm 3 serves as a pipelined version of Algorithm 1 which puts the amount of memory it uses on a sliding measure between algorithm 1 and 2. Accordingly, it exhibits the best performance of all three algorithms for all matrix sizes tested in this project. At the recent 2017 American Chemical Society (ACS) meeting in San Francisco, *the PI received an ACS COMP Open Eye Outstanding Junior Faculty Award for this DOE-acknowledged work on GPU parallelization.*

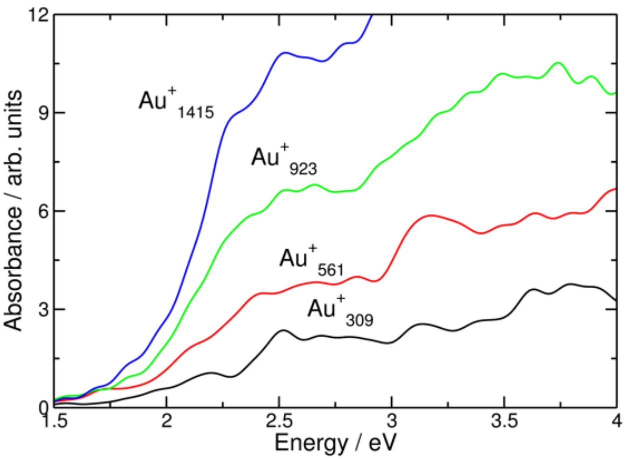


Figure 2. Absorption spectra of gold nanoparticles obtained from the GPU-enhanced RT-TDDFTB approach.

Within the second thrust of this project, we have focused on implementing unitarily-invariant self-interaction corrections (SICs) using Fermi Orbitals (FOs) as described by Pederson and coworkers (Pederson, M.R.; Ruzsinszky, A.; Perdew, J. P. *J. Chem. Phys.* **2014,** *140*, 121103). During the past eight months, we have concentrated our efforts on developing an in-house (i.e., from scratch) implementation of FO-SIC in NWChem. We have chosen to implement this first in an all-electron DFT code to both verify and understand all the subtle intricacies of the FO-SIC approach before proceeding to the more difficult task of modifying this new formalism for DFTB. The specific procedure for implementing the FO-SIC approach in our NWChem implementation is summarized in **Figure 3** and given as follows: (1) For a set of DFT orbitals, $\{\psi_\alpha\}$, N centroid positions $\{\mathbf{a}_1, \mathbf{a}_1, \cdots, \mathbf{a}_N\}$ 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-DFTB energy from the set of FOs; (3) the SIC-DFTB energy is minimized as a function of the DFTB 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 addition, 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 should be instrumental when this approach is implemented in DFTB. 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

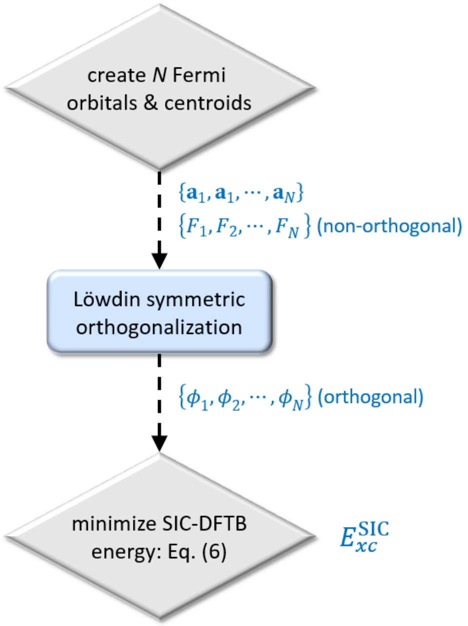


Figure 3. Simplified algorithmic flowchart for our NWChem implementation of FO-SIC. The computed outputs of each block are listed next to the dotted arrows, which are later used in subsequent blocks.

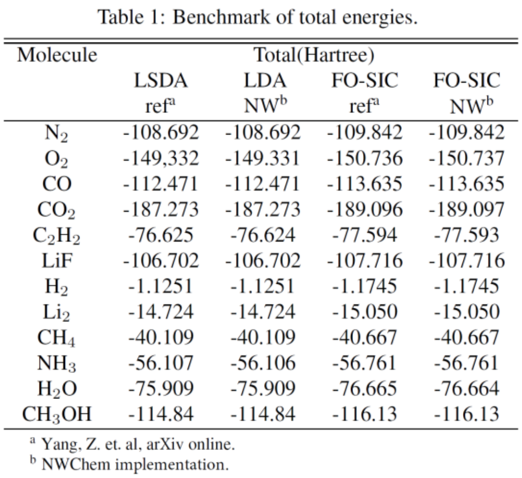


Table 1: Benchmark of total energies.

Molecule	Total(Hartree)			
	LSDA ref[a]	LDA NW[b]	FO-SIC ref[a]	FO-SIC NW[b]
N_2	-108.692	-108.692	-109.842	-109.842
O_2	-149,332	-149.331	-150.736	-150.737
CO	-112.471	-112.471	-113.635	-113.635
CO_2	-187.273	-187.273	-189.096	-189.097
C_2H_2	-76.625	-76.624	-77.594	-77.593
LiF	-106.702	-106.702	-107.716	-107.716
H_2	-1.1251	-1.1251	-1.1745	-1.1745
Li_2	-14.724	-14.724	-15.050	-15.050
CH_4	-40.109	-40.109	-40.667	-40.667
NH_3	-56.107	-56.106	-56.761	-56.761
H_2O	-75.909	-75.909	-76.665	-76.664
CH_3OH	-114.84	-114.84	-116.13	-116.13

[a] Yang, Z. et. al, arXiv online.
[b] NWChem implementation.

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]) as shown in Table 1. After several extensive benchmark comparisons between centroid positions, electronic energies atomization 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 the DFTB FO-SIC approach properly benchmarked, we intend to couple this approach with the GPU enhancements mentioned previously to probe the electronic structure and dynamics of large systems within DFTB.

3. Future Plans

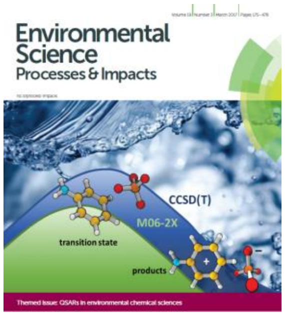
With the FO-SIC all-electron DFT code fully-working and functional, we intend to focus all our effort into modifying this formalism in both the DFTB and a real-time DFTB dynamics approach. Two manuscripts detailing our GPU enhancements in real-time DFTB dynamics are also in progress. This DOE Grant has partially supported 1 Postdoctoral Associate, 1 PhD student, and 2 MS students. The 2 MS theses will be completed by the summer of 2017, and two additional manuscripts by these MS students have been published (see below).

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 8 months:

1. Alejandro Alvarez Barragan, Niranjan V. Ilawe, Lanlan Zhong, Bryan M. Wong, and Lorenzo Mangolini, *“A Non-Thermal Plasma Route to Plasmonic TiN Nanoparticles.”* *Journal of Physical Chemistry C*, **121**, 2316 (2017).
2. Sangavi Pari, Inger A. Wang, Haizhou Liu, and Bryan 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)



3. Lindsey N. Anderson, M. Belén Oviedo, and Bryan 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).

Next generation first principles molecular dynamics

PI Anders M.N. Niklasson

Theoretical Division T-1, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, amn@lanl.gov

Abstract

Molecular dynamics simulation is one of the most general and widely used methods for obtaining a broad variety of properties in computational chemistry, materials science and molecular biology, such as phase transitions, molecular structures, and chemical reactions. Most molecular dynamics simulations depend on a parameterization of a simplified classical model of the atomic interaction potential. These simulations are often not very reliable because of limited transferability between the unknown systems of interest and the original set of parameterized structures. First principles molecular dynamics derived from self-consistent field theory such as density functional theory (DFT) offers a more rigorous and reliable alternative. DFT based molecular dynamics simulations within the Born-Oppenheimer approximation of uncoupled electronic and nuclear motion is regarded as one of the most reliable standards for atomistic simulations. Unfortunately, first principles Born-Oppenheimer molecular dynamics is often limited by some fundamental shortcomings, such as a very high computational cost or unbalanced phase-space trajectories, numerical instabilities and a systematic long-term energy drift. The overreaching goal of this proposal is to go beyond conventional Born-Oppenheimer molecular dynamics and create a framework for a next generation of first principles MD schemes that overcome 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.

One important step to achieve our goal is provided by reduced complexity algorithms that have a computational cost that scales only linearly with the system size instead of cubically as with regular methods. However, the immense promise of linear scaling electronic structure theory to enable computational studies of complex materials directly from the fundamental principles of quantum mechanics has never been fully realized because of a number of

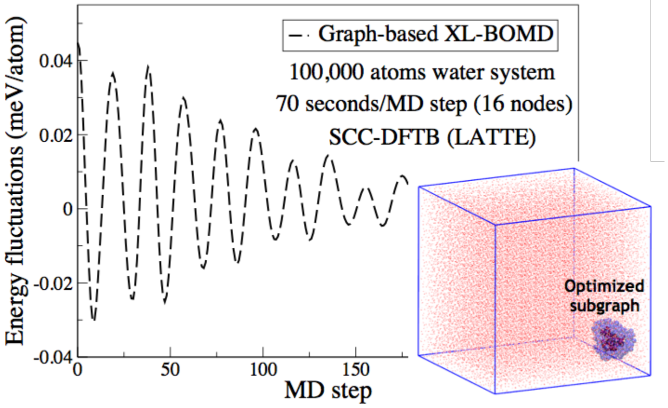


Figure 1 +100,000 atoms water simulation using self-consistent charge density functional based tight-binding theory (SCC-DFTB) as implemented in the electronic structure package LATTE. The molecular dynamics simulation was performed on a 16-node platform using graph-based electronic structure theory and next generation extended Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD).

shortcomings, in particular, (a) the accuracy is reduced to a level that is often difficult, if not impossible, to control; (b) the computational pre-factor is high and the linear scaling benefit occurs only for very large systems that in practice often are beyond acceptable time limits or available computer resources; and (c) the parallel performance is generally challenged by a significant overhead and the wall-clock time remains high even with massive parallelism. All these specific linear-scaling obstacles are particularly limiting in quantum-based molecular dynamics simulations. In one of our more recent and possibly most significant progress, we showed how graph theory could be combined with quantum theory to overcome major bottlenecks and be used to calculate the electronic structure of large complex systems with well-controlled accuracy and natural low-communication parallelism. Off-the-shelf graph-partitioning tools can be used to optimize the performance for a variety of computational platforms. In combination with the next generation extended Lagrangian Born-Oppenheimer molecular dynamics, developed under this program, quantum mechanical, nanosecond-duration molecular dynamics simulations of large complex systems are within practical reach. A recent +100,000 atoms Born-Oppenheimer molecular dynamics simulation is illustrated in Figure1. The work was presented in the Journal of Chemical Physics that was selected as an Editor's choice article of 2016.

Our future plans involve practical implementations and extensions of extended Lagrangian Born-Oppenheimer molecular dynamics, including excited state dynamics, constrained density functional theory, molecular-dynamics based sampling techniques, exploring the possibility of new spin and spin-lattice dynamics formulations, alternative shadow potential formulations and generalized kernel expressions for the extended Lagrangian including finite electronic temperature ensembles, as well as applications beyond regular density functional based theory, e.g. applications to classical force field models.

LANL2014E8AN, "Next generation first principles molecular dynamics"

Postdoc (now staff scientist): Christian F.A. Negre

1) *"First principles molecular dynamics without self-consistent field optimization"*, P. Souvatzis and A.M.N. Niklasson, The Journal of Chemical Physics 140, 044117 (2014)

2) *"Interior eigenvalues from density matrix expansions in quantum mechanical molecular dynamics"*, E.H. Rubensson, A.M.N. Niklasson, SIAM Journal on Scientific Computing 36 (2), B147-B170 (2014)

3) *"Generalized extended Lagrangian Born-Oppenheimer molecular dynamics"*, A.M.N. Niklasson and M.J. Cawkwell, The Journal of Chemical Physics 141, 164123 (2014).

4) *"Thermostating extended Lagrangian Born-Oppenheimer molecular dynamics"*, E. Martinez, M.J. Cawkwell, A.F. Voter, A.M.N. Niklasson, The Journal of chemical physics 142 (15), 154120 (2015)

5) *"Extended Lagrangian Formulation of Charge-Constrained Tight-Binding Molecular Dynamics"*, M.J. Cawkwell, J.D. Coe, S.K. Yadav, X.Y. Liu, A.M.N. Niklasson, Journal of chemical theory and computation 11 (6), 2697-2704 (2015)

6) *"Extended Lagrangian density functional tight-binding molecular dynamics for molecules and solids"*, B. Aradi, A.M.N. Niklasson, T. Frauenheim, Journal of chemical theory and computation 11 (7), 3357-3363 (2015)

7) *"Graph-based linear scaling electronic structure theory"*, A.M.N. Niklasson, S.M. Mniszewski, C.F.A. Negre, M.J. Cawkwell, P.J. Swart, J. Mohd-Yusof, T.C. Germann, M.E. Wall, N. Bock, E.H. Rubensson, H. Djidjev, The Journal of Chemical Physics 144 (23), 234101 (2016) [Editor's choice 2016 article]

8) *"Recursive Factorization of the Inverse Overlap Matrix in Linear-Scaling Quantum Molecular Dynamics Simulations"*, C.F.A. Negre, S.M. Mniszewski, M.J. Cawkwell, N. Bock, M.E. Wall, A.M.N. Niklasson, The Journal of chemical theory and computation 12 (7), 3063-3073 (2016)

9) *"Performance of extended Lagrangian schemes for molecular dynamics simulations with classical polarizable force fields and density functional theory"*, V. Vitale, J. Dziedzic, A. Albaugh, A.M.N. Niklasson, T. Head-Gordon, and C-K

Skylaris, The Journal of Chemical Physics, 146, 124115 (2017)

10) *"Accurate Classical Polarization Solution with No Self-Consistent Field Iterations",* A. Albaugh, A.M.N. Niklasson, and T. Head-Gordon, The Journal of Physical Chemistry Letters, 8, 1714 (2017)

Sampling Rare Events In Aqueous Systems Using Molecular Simulations

Ryan DeFever[1], Walter Hanger[2], Amy Apon[3], Linh Ngo[4], and Sapna Sarupria[1]
[1]Chemical and Biomolecular Engineering
[2]Electrical and Computer Engineering
[3]School of Computing
[4]Cyberinfrastructure Technology Integration
Clemson University, Clemson SC

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

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

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

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

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

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

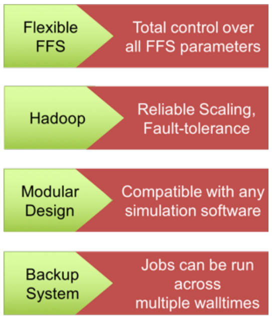


Figure 1:User friendly features of ScaFFS

Specific goals of proposed research:

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

Recent Progress:

- We have developed a new version of ScaFFS that is more user-friendly and also has updated back end for easier modifications. This will help us change the code as needed for nDFFS. We refer to this version of ScaFFS as SAFFIRE.
- We have developed a framework to perform 2DFFS on simple systems. Our model test case systems include an analytical two well 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 are able to reduce this bias when we use 2DFFS, however, the methodology has other limitations. We are currently addressing these challenges.
- We have developed the framework to perform largescale FFS simulations of Lennard Jones liquid-to-solid transition. This work is being done by an undergraduate student under the supervision of the graduate student. The preliminary analysis and set up has been completed and we currently largescale FFS for the same are in progress. We will then use the framework developed by the studies of the model system to evaluate 1D vs 2DFFS for Lennard Jones liquid.
- We have performed largescale 1DFFS of ice nucleation on silver iodide surfaces. We are currently investigating various order parameters that best correlate to committor probability (and therefore, are closest to the reaction coordinate). Interestingly, we have not yet

identified any one or two best order parameters. We are analyzing the results to further probe and understand these outcomes.

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

Grant Number and Title:
DE-SC0015448 Sampling Rare Events In Aqueous Systems Using Molecular Simulations

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

Seogjoo Jang

Quantum Dynamics and Coarse-Grained Modeling of Delocalized Excitons in Natural Light Harvesting Complexes and Conjugated Oligomers

PI: Seogjoo Jang

Department of Chemistry and Biochemistry, Queens College, City University of New York, 65-30
Kissena Boulevard, Queens, New York 11367; Email:SJang@qc.cuny.edu

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. During the past three years, significant progress has been made in computational modeling of the light harvesting 2 (LH2) complex of purple bacteria and its mutants [3,8], and in quantum simulation of long range exciton dynamics involving these complexes [10]. Important advances have also been made in developing/improving quantum dynamics [1,2,5,7] and in computational modeling of conjugated oligomer systems [9]. This talk will be focused mainly on LH2 and its synthetic/natural mutants, and will offer brief overview of new results on quantum dynamics theory development and the modeling of conjugated oligomers.

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. At present, structural and spectroscopic data of individual LH2 complexes are fairly well established. However, how the aggregates of LH2 complexes function as reliable and effective functional units of exciton migration are not clearly understood yet. There have been important spectroscopic and computational studies offering some insights, but key molecular-level mechanisms endowing such remarkable functionality are not clearly established yet. The PI's group has combined classical all-atomistic simulation, electronic structure calculation, and coarse-grained quantum dynamics study to understand these issues. One interesting question that has been addressed in this context is why natural LH2 complexes have only 8-10 fold symmetries [3]. The PI's group has found that stable and consistent hydrogen bonding (HB) can be formed only for such natural sizes. Comparative electronic structure calculations have identified significant solvatochromic red shift (~ 0.06 eV) of the Q_y excitation energy of BChl due to HB. In relation to this, it was found that consistent and stable formation of HB leads to minimum amount of energetic disorder. Application of a coarse-grained quantum master equation approach [2] has also shown that larger disorder for complexes with non-natural symmetry numbers results in significantly smaller inter-LH2 exciton transfer rates, diminishing the efficiency of inter-LH2 exciton migration.

Most recently, the PI's group has made effort to construct more complete and satisfactory coarse-grained exciton-bath models for both LH2 and LH3 complexes [8]. In LH3 complex, the lower energy exciton band occurs at about 820 nm region as opposed to 850 nm observed for LH2. MD simulation results for LH3 confirm that parts of BChls constituting LH3 are missing HB as suggested from the X-ray crystallography structural data. However, the shift due to the absence of HB accounts for only half of the blue shift observed from LH3. It has long been speculated that torsional rotation of the carbonyl group in BChls might account

for the other half of the blue shift. However, combined MD and electronic structure calculation study suggests that it is not the case. Although computational investigation into the source of the spectral shift of LH3 by the PI's group is not complete as of now, results obtained so far offer fairly comprehensive information that helps constructing a nearly complete coarse-grained model common for both LH2 and LH3 complexes. Future incorporation of this model with additional spectroscopic and high level electronic structure calculation can help understand how different structural and energetic features of light harvesting complexes are related to different exciton harvesting capability.

The PI has also made extensive simulation of exciton dynamics [10] for a model of LH2 representing only the 850 nm exciton band, employing the coarse-grained quantum master equation approach [2]. The dependence of inter-LH2 exciton transfer rates on the inter-LH2 distance reveals that natural distances found in the PSU of purple bacteria are in the range where there is significant enhancement of the exciton transfer rate due to quantum delocalization of excitons (see Fig. 1). Dependence of rates on the disorder and the relative energy bias of two LH2 complexes also demonstrate that the exciton dynamics is unusually robust against the perturbation due to possible energetic and structural disorder.

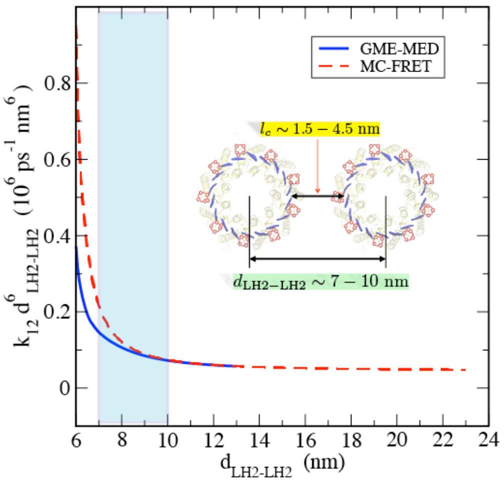


Figure 1. Dependence of inter-LH2 rate (multiplied by the sixth power of the distance) on distance, which shows enhancement over the Förster rate. Inset and blue shade show typical range of natural inter-LH2 distances. Comparison of both GME-MED and multichromophoric FRET (MC-FRET) shows the contribution of non-Markovian effects.

For general description of exciton and charge transport dynamics in complex and condensed molecular environments, further progress is needed for development of reliable and efficient quantum dynamics calculation approach. The PI has recently formulated a new quantum Fokker-Planck equation [6] that can be applied to the cases of non-Markovian bath and moderate system-bath couplings, and has also led an analysis of a newly developed path integral based quantum transition state theory [1,7].

The PI's group has completed comparative semiempirical and time dependent density functional study calculation of small oligothiophenes and charged species [9]. Comparison of these results with available experimental data suggests relative good performance of M06-2X functional and its utility for larger oligomers. Analyses of computational results also suggest the possibility of developing simple coarse-grained models to represent singlet excitons in such systems. Similar approaches will be performed for other oligophenylene-vinylene type molecules.

Overall, outcomes of the PI's research projects for the past three years have elucidated new information on microscopic details of photosynthetic light harvesting complexes endowing their efficient and robust exciton transferring capability, have helped improve quantum dynamics calculation methods, and have laid foundation for the long term effort of the PI's group for computational modeling of conjugated polymers. Future effort will be dedicated to the advancement of these efforts to a new level, and 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): Daniel Montemayor, Eva Rivera, and Marta Kowalczyk (part time)

Student(s): Ning Chen and Taner Ture

Publications Acknowledging this Grant in the last 3-4 years

1. S. Jang, A. V. Sinitskiy, and G. A. Voth, "Can the ring polymer molecular dynamics method be interpreted as real time quantum dynamics?," *J. Chem. Phys.* **140**, 154103 (2014).
2. S. Jang, S. Hoyer, G. R. Fleming, and K. B. Whaley, "Generalized master equation with non-Markovian multichromophoric Förster resonance energy transfer for modular exciton densities," *Phys. Rev. Lett.* **113**, 188102 (2014).
3. S. Jang, E. Rivera, and D. Montemayor, "Molecular level design principle behind optimal sizes of photosynthetic LH2 complex: Taming disorder through cooperation of hydrogen bonding and quantum delocalization," *J. Phys. Chem. Lett.* **6**, 928 (2015).
4. S. Jang and A. M. Castillo, "Charge hopping dynamics along a disordered chain in quantum environments: Comparative study of different rate kernels," *J. Phys. Chem. B* **119**, 7659 (2015).
5. S. Jang and G. A. Voth, "Can quantum transition state theory be defined as an exact t=0+ limit?" *J. Chem. Phys.* **144**, 084110 (2016)
6. S. Jang, "Generalized quantum Fokker-Planck equation for photoinduced nonequilibrium processes with positive definiteness condition," *J. Chem. Phys.* **144**, 214102 (2016)
7. S. Jang and G. A. Voth, "Non-uniqueness of quantum transition state theory and general dividing surfaces," *J. Chem. Phys.*, Accepted for Publication (2017)
8. D. Montemayor, E. Rivera, and S. Jang, "Constructing coarse-grained exciton-bath models for LH2 and LH3 complexes of purple photosynthetic bacteria at room temperature," Manuscript in Preparation (2017).
9. M. Kowalczyk and S. Jang, "Comparative semiempirical and time dependent density functional study of singlet electronic excitations of small oligothiophenes and their charged species," Manuscript in Preparation (2017)
10. S. Jang, "Dependences of inter-LH2 exciton dynamics on distance and energy bias reveal robust and cost-effective long range energy transferring capability," Manuscript in Preparation (2017)

Program Title: **EARLY CAREER RESEARCH PROGRAM:** ***Modeling of Photoexcited Process at the Interfaces of Functionalized Quantum Dots*** **(grant DE-SC008446)**
Principal Investigator: **Svetlana Kilina**
Address: 1355, Elm Circ. N, Fargo, ND 58102; e-mail: Svetlana.kilina@ndsu.edu

Effect of Interactions between Quantum Dots and Their Passivating Shells on Radiative and Non-Radiative Processes

Svetlana Kilina
Chemistry and Biochemistry Department, North Dakota State University, ND

Colloidal nanocrystals, also called quantum dots (QDs), are near-ideal materials for solar energy conversion and lighting technologies. However, high sensitivity of their properties to the surface chemistry is the main roadblock for their practical usage. Optically forbidden nature of surface-associated states makes their direct measurements challenging. Our computational research aims to fill the gap in understanding the role of the QD surface in light-driven processes. Here we report several cases, where calculations based on density functional theory (DFT) and time dependent DFT (TDDFT) succeed in resolving this challenge, allowing for explanations of experimental trends and observables sensitive to defects and passivating ligands at the QD surface.

In particular, our recent calculations have identified conditions for the most preferential binding of ionic ligands, such as carboxylates, thiolates, and hydrides, to the CdSe QDs. We found that the most stable ligated conformations are those where a carboxylate group is attached to extra Cd^{2+} forming a $[Cd^{2+}(CH_3COO^-)]$ cation at the surface, while also accompanied by an carboxylate anion attached nearby at the surface balancing the overall neutral charge of the system [1]. This results in 2:1 ratio between carboxylate and extra Cd ions agreeing with experimental findings. Also our calculations reveal much more complicated exchange mechanism of the native surface ligands of CdSe QDs with phenyldithiocarbamates (PTCs) as it was thought before [2]. PTCs decompose during exchange with native ligands, while only a small portion of deprotonated PTCs covalently bounds to the Cd-enriched QD's surface. These predictions well agree with NMR data on PTC-ligated QDs [2]. Overall, we found that ionic ligands are mainly bound to non-stoichiometric $Cd_{n\neq m}Se_m$ QDs, eliminating surface-driven optically inactive midgap states [1]. This explains enhanced emission in metal-enriched compared to nonmetal-enriched QDs in a presence of ionic ligands that is observed experimentally. These results are essential in understanding the role of acidic ligands during synthesis and ligand exchange, as well as in manipulating the QD's photophysical properties.

However, photophysical properties of QD-based materials are governed not only by the surface defects and QD-ligand interactions, but also by the interactions between neighboring QDs in nanoassemblies. Thus, our simulations of QD-QD interactions have provided an explanation of experimentally detected enhancement of 'on'-blinking times in closely packed Si QDs [3]. Calculated energy transfer rates from transition density matrixes obtained from TDDFT, suggest that ultrafast energy transfer from an excited QD to the nearest one provides an additional channel for occupation of long-living optically forbidden trap states in neighboring QDs, forcing the emission to happen from higher-energy optically active states. This pathway increases 'on' blinking time and photo-luminescent quantum yield in aggregates of strongly interacting Si QDs, as experimentally observed. There is another open question on interactions between QDs with the p- and n-type impurities (doping): does the interface between p- and n-doped QDs govern formation of charge transfer states when QDs are separated from each other at 0.5-1 nm distances? We have analyzed the charge density distribution at p-n nanointerface using model systems of dimers of doped silicon QDs interacting through bonds and through space.

Spatial distributions of transition densities between the ground and excited states show a redistribution of electronic density from n-impurities to p-impurities. Although impurities contribute very few orbitals to the total density, changes in the ground state charge distribution and polarization both facilitate formation of a large number of charge transfer excitatons (with hole localized on p-doped QD and electrons on n-doped QD) involving solely delocalized silicon orbitals, beyond doping sites [4].

For simulating the light driven processes in QDs, the electron-vibrational couplings are important and have to be incorporated into calculations. For this, we are implementing time-domain non-adiabatic dynamics (NAMD) based on DFT and Surface Hopping Technique (SHT). This method allows us to determine conditions that govern exciton relaxation in QDs passivated by organic or inorganic shells and in other nanostructures with complicated interfaces, such as TiO_2 nanowires at aqueous environment [5]. Our approach treats phonons semi-classically, which allows us to explicitly incorporate quantum decoherence effects within the electronic subsystem. Both elastic and inelastic electron-phonon interactions play key roles in solar energy harvesting. Coherence of these processes is very important, since quantum transitions can occur only through buildup of coherence. Our simulations provide fundamental insights into the origin of the pure-dephasing process in the bare and passivated QDs. Thus, we found that phonon-induced pure-dephasing processes determined by elastic electron-phonon scattering in CdSe QD capped with ligands are much longer than that in bare CdSe QDs [6]. The difference is rationalized by the fact that ligands have no direct contributions to the electronic densities of the lower-energy states involved in the superpositions, while they indirectly reduce mobility and fluctuations of the surface atoms. In contrast, the higher-energy electronic states involved in the relaxation are delocalized over ligands and the QD, and therefore, ligands increase the electron-phonon coupling in the case of inelastic processes.

Our current investigations are focused on PbSe QDs having efficient absorption and emission in near IR range, which is optimal for solar cells. Additionally, engineering of interfaces in PbSe-based nanostructures, including core/shell QDs and 2-D nanoplates (NPLs) allows for altering unique carrier cooling dynamics, reduce Auger recombination (AR) rates, raise carrier multiplication (CM), and low amplified spontaneous emission thresholds – all properties are beneficial for optoelectronics and photovoltaics. Here, we will present our very recent work on studying **(i)** the role of surface ligands on the formation of 2-D (100) face-oriented PbSe NPL and, in particular, the effect of the Pb-Cl-Pb bridging defects on light-driven dynamics and **(ii)** the impact of the core and shell compositions on exciton relaxation rates in core/shell QDs, with the core made from PbX and the shell of CdX, where X=S, Se, Te. Our joined experimental and computational studies [7] show that halide passivation of PbSe QDs is critical to the growth of the (100) face-dominated NPLs. DFT predicts that $PbCl_2$ precursors are attached to the Pb-enriched (111) and (110) facets blocking these surfaces from interactions, while creating Pb-Cl-Pb bridging network with neighboring QDs along (100) facet. We found that a 2D bridging network is energetically favored over a 3D network, driving the formation of NPLs of 2 nm in thickness. Presence of local defects in NPL associated with Pb-Cl-Pb bridging may alter charge carrier recombination and cooling processes, substantially impacting the efficiency of CM. Our future studies will be focused on modeling of these processes using NAMD.

Recent experimental studies of CM in core/shell PbSe/CdSe QDs indicate a dramatic increase in the multi-exciton yield accompanied by the development of a shell-related emission band consistent with slowed cooling of shell-localized holes. Surprisingly, PbS/CdS show much less increase in CM than PbSe/CdSe. Our NAMD simulations demonstrate that despite very similar electronic structure and phonon spectra of PbSe/CdSe and PbS/CdS QDs, electron cooling is happening much faster in PbS/CdS than in PbSe/CdSe due to twice stronger electron coupling to ‘softer’ phonons in structures of lighter elements. Our data imply that slower electron cooling in PbSe/CdSe QDs allows for CM being the first in this competition and, thus, improving its efficiency – the process that can boost the efficiency of IR QD-based solar cells by producing additional current from high-energy photons. However, further studies, including improving NAMD accuracy, have to be conducted to confirm these predictions. Thus, inclusion of many-electron interactions into NAMD is needed for studying the competition between exciton cooling, AR, and CM. The DFT-based many-body perturbation theory (MBPT) allows for accurate treatment of bound excitons and will be incorporated into NAMD in future.

Overall, our calculations provide insights into the surface chemistry of QDs and offer the guidance for controlling an optical response of nanostructures by means of core-shell, QD-QD and QD-ligand engineering. Our resent review articles [8,9] describe in detail how theory, modeling, and simulation can complement experiments in order to fully understand and exploit electronic, optical, and structural properties of QDs sensitive to defects and passivating organic or inorganic shells at their surfaces.

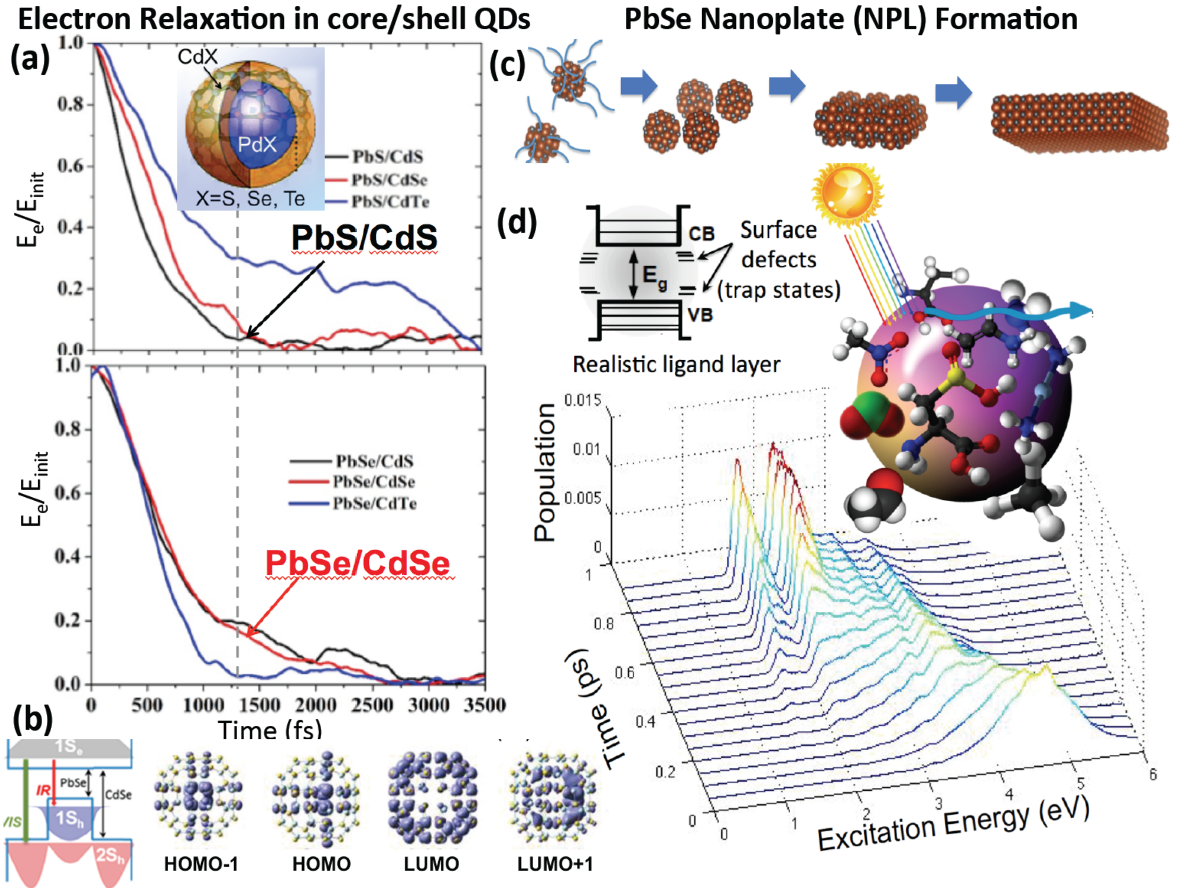


Figure 1: *Effect of surface defects and passivating organic or inorganic shells on the electronic structure and energy dissipation in QDs.* ***(a)*** *NAMD results of electron cooling in core/shell PbX/CdX (X=S, Se, Te) QDs showing faster energy relaxation in PbS/CdS than in PbSe/CdSe.* ***(b)*** *Illustration of the quasi-type II electronic structure of PbX/CdX QDs, where band-edge electrons are delocalized over the entire QD (LUMOs), while band-edge holes have higher localization in the core (HOMOs).* ***(c)*** *Illustration of the formation of 2-D (100) face-oriented NPL from PbSe and* ***(d)*** *effect of surface ligands on the electronic structure and exciton relaxation in QDs.*

EARLY CAREER RESEARCH PROGRAM: *Modeling of Photoexcited Process at the Interfaces of Functionalized Quantum Dots* (grant DE-SC008446)

Postdoc(s): Patrick Tamukong (9/2014-12/2016)

Student(s):

1. Peng Cui (Summer 2012-2016), PhD obtained in November 20, 2016
2. Naveen Dandu (Summer 2013-2016), PhD obtained in November 20, 2016
3. Levy Lystrom (Fall 2015 – current)
4. Jabed Mohammed (Summer 2016 – current)

References (Publications Acknowledging these Grant in 2015-2017)

1. P. K. Tamukong, W. D. N. Peiris, and S. Kilina. *Computational Insights into CdSe Quantum Dots' Interactions with Acetate Ligands.* **Phys. Chem. Chem. Phys. 2016**, *18,* 20499-20510
2. A. Munro, C. Chandler, M. Garling, D. Chai, V. Popovich, L. Lystrom, and S. Kilina. *Phenyldithiocarbamate Ligands Decompose During Nanocrystal Ligand Exchange.* **J. Phys. Chem. C 2016**, *120*, 29455-29462
3. B. Miller, N. Dandu, R. J. Anthony, U. R. Kortshagen, D. M. Kroll, K. Velizhanin, S. Kilina, and E. K. Hobbie. *Silicon Nanocrystal Interactions and Enhanced Ensemble Luminescence;* **ACS Nano 2015**, *9*, 9772–9782
4. N. Dandu, S. Tretiak, S. Kilina, and D. Kilin. *Through space and through bridge channels of charge transfer at p-n nano-junctions: A DFT study.* **Chem. Phys. 2016,** *481*, 144-156
5. S. Huang, C. Balasanthiran, J. D. Hoefelmeyer, S. Kilina, and D. S. Kilin, *Dynamics of Charge at Water-to-Semiconductor Interface: Case Study of Wet [001] Anatase TiO_2 Nanowire.* **Chem. Phys. 2016,** *481*, 184-190
6. J. Liu, S. Kilina, S. Tretiak, and O. Prezhdo. *Ligands Slow Down Pure-Dephasing in Semiconductor Quantum Dots;* **ACS Nano 2015**; *9*, 9106-9116
7. W-K. Koh, N. Dandu, A. Fidler, V. Klimov, J. Pietryga, and S. Kilina. *Thickness-controlled quasi-two dimensional colloidal PbSe nanoplatelets.* **J. Am. Chem. Soc. 2017**, *139*, 2152–2155
8. S. Kilina, D. Kilin, and S. Tretiak. *Light-Driven and Phonon-Assisted Dynamics in Organic and Semiconductor Nanostructures.* **Chem. Rev. 2015,** *15*, 5929–5978
9. S. Kilina, P. Tamukong, D. Kilin. *Surface Chemistry of Semiconducting Quantum Dots: Theoretical Perspectives.* **Acc. Chem. Res. 2016,** *49*, 2127-2135

Excited States with Real-Time TDDFT: Excited State Absorption and Spin-Orbit Effects

Niri Govind[1], David N. Bowman[2], Jason C. Asher[2], Amity Andersen[1], Kenneth A. Lopata[3], Sean A. Fischer[1],
Christopher J. Cramer[2]

[1] Pacific Northwest National Laboratory, Richland, WA 99352
[2] Department of Chemistry, University of Minnesota, Minneapolis, MN 55455
[3] Department of Chemistry, Lousiana State University, Baton Rouge, LA 70803

niri.govind@pnnl.gov

Project Title: Charge Transfer and Charge Transport in Photoactivated Systems

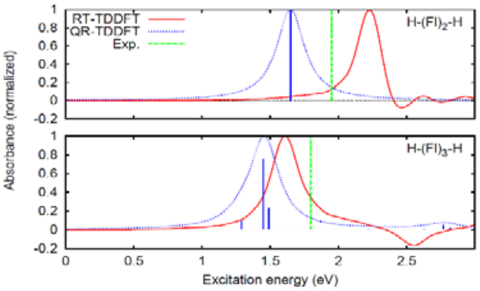
Investigators: Christopher Cramer (Project Director, University of Minnesota, cramer@unm.edu), Niri Govind (PNNL), Esmond Ng (LBNL), Laura Gagliardi (University of Minnesota), Don Truhlar (University of Minnesota), Ilja Siepmann (University of Minnesota), Wibe A. de Jong (LBNL), Chao Yang (LBNL), Leonid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

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

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

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

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

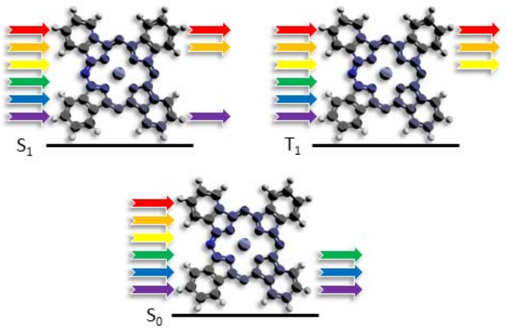


Excited state absorption spectra of oligofluorenes calculated with RT-TDDFT (solid curve) and QR-TDDFT (broken curve/sticks)

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

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

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



Optical Limiting in Zinc Phthalocyanine

Excited-State Absorption in Tetrapyridyl Porphyrins: Comparing Real-Time and Quadratic- Response Time-Dependent Density Functional Theory

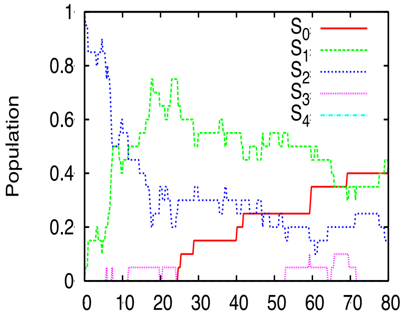
As part of ongoing work, we are performing a benchmark study comparing our excited-state absorption (ESA) approach against quadratic response TDDFT (QR-TDDFT). Ongoing work also includes transient absorption studies. Three meso-substituted tetrapyridyl porphyrins (free base, Ni(II), and Cu(II)) were investigated for their optical limiting (OL) capabilities using real-time (RT-), linear-response (LR-), and quadratic-response (QR-) time-dependent density functional theory (TDDFT) methods. These species are experimentally known to display a prominent reverse saturable absorption feature between the Q and B bands of the ground state absorption (GSA), which has been attributed to increased excited-state absorption (ESA) relative to GSA. We used the recently developed RT-TDDFT method described above for calculating ESA from a LR-TDDFT density with seven exchange-correlation functionals (BLYP, PBE, B3LYP, PBE0, M06, BHLYP, and BHandH), and contrasted to calculations of ESA using QR-TDDFT with four exchange-correlation functionals (BLYP, B3LYP, BHLYP, BHandH). This allowed for comparison between functionals with varying amount of exact exchange (0-50%) as well as between the ability of RT-TDDFT and QR-TDDFT to reproduce OL behavior in porphyrin systems. The absorption peak positions and intensities for GSA and ESA are significantly impacted by the choice of DFT functional, with the most critical factor identified as the amount of exact exchange in the functional form. Calculating ESA with QR-TDDFT is found to be significantly more sensitive to the amount of exact exchange than GSA and ESA with RT-TDDFT, as well as GSA with LR-TDDFT. This is problematic when using the same approximate functional for calculation of both GSA and ESA, as the LR- and QR-TDDFT excitation energies will not have similar errors. Overall the RT-TDDFT method reproduces the OL features for the systems studied here and is a viable computational approach for efficient screening of molecular complexes for OL properties.

Real-Time TDDFT Including Spin-Orbit Effects

Probing electron dynamics in the sub-femtosecond time regime offers unparalleled insight into the underlying mechanisms charge transfer and optical absorption to name a few. As part of this SciDAC project we have extended our RT-TDDFT implementation developed earlier as part of this project to include spin-orbit effects. This is achieved via a two-component formalism. Both effective core potential including spin-orbit effects as well as all-electron calculations including relativistic effects can be performed. We apply the approach to several heavy element atoms as well as compounds with heavy elements to describe spin-forbidden transitions. Plans to tackle larger systems and efficient propagation schemes will be discussed.

Non-Adiabatic Molecular Dynamics

As part of developing a non-adiabatic molecular dynamics (NAMD) framework within NWChem, we have implemented Tully's fewest switches surface hopping algorithm[1] for non-adiabatic dynamics. The non-adiabatic couplings are calculated numerically using the pseudo-wavefunction approach via the recent approach of Ryabinkin and co-workers, which is significantly faster than the traditional numerical approach. Both TDDFT and TDDFT/TDA versions have been implemented. The electronic density matrix is propagated via fourth order Runge-Kutta and interpolation and extrapolation are used to obtain values for the elements of the electronic Hamiltonian and non-adiabatic couplings at times between nuclear time steps. We have implemented the decoherence correction due to Truhlar and Persico and co-workers. As part of our prototyping we have performed surface hopping molecular dynamics on the well-studied $CH_2NH_2^+$ (Protonated Schiff Base 1) system. Our results are in good agreement with the published results of Tapavicza and co-workers. We are currently studying larger molecular complexes in solvation environments to study non-radiative relaxation.



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

Relevant publications in the past 3 years

1. D. N. Bowman, J. C. Asher, S. A. Fischer, C. J. Cramer, N. Govind, "Excited-State Absorption in Tetrapyridyl Porphyrins: Comparing Real-Time and Quadratic Response Time-Dependent Density Functional Theory", (in review, 2017)
2. E. Vecharynski, J. Brabec, M. Shao, N. Govind, C. Yang, "Efficient Block Preconditioned Eigensolvers for Linear Response Time-Dependent Density Functional Theory, *Computer Physics Communications*, *submitted,* (in review, 2017)
3. S. A. Fischer, E. Aprà, N. Govind, W.P. Hess, P. Z. El-Khoury, "Nonequiibrium Chemical Effects in Single-Molecule SERS Revealed by *ab initio* Molecular Dynamics Simulations", *J. Phys. Chem. A* **121**, pp 1344-1350 (2017)
4. I. H. Nayyar, S. E. Chamberlin, T. C. Kasper, N. Govind, S. A. Chambers, P. V. Sushko, "Effect of Doping and Chemical Ordering on the Optoelectronic Properties of Complex Oxides: Fe_2O_3-V_2O_3 Solid Solutions and Hetero-Structures", *Phys. Chem. Chem. Phys*, **19**, 1097-1107 (2017)
5. S. A. Fischer, C. J. Cramer, N. Govind, "Excited State Absorption from Real-Time Time-Dependent Density Functional Theory: Optical Limiting in Zinc Phthalocyanine", *J. Phys. Chem. Lett,* **7**, pp 1387-1391 (2016)
6. T.W. Ueltschi, S. A. Fischer, E. Aprà, A. N. Tarnovsky, N. Govind, P. Z. El-Khoury, W.P. Hess, "Time-Domain Simulations of Transient Species in Experimentally Relevant Environments", *J. Phys. Chem. A*, **120**, pp 556–561 (2016)
7. S. A. Fischer, C. J. Cramer, N. Govind, "Excited State Absorption from Real-Time Time-Dependent Density Functional Theory", *J. Chem. Theory Comput,* **11** (9), pp 4294-4303 (2015)

8. S. A. Fischer, T. W. Ueltschi, P. Z. El-Khoury, A. L. Mifflin, W. P. Hess, H-F. Wang, C. J. Cramer, N. Govind, "Infrared and Raman Spectroscopy from *ab initio* Molecular Dynamics and Static Normal Model Analysis: The C-H Region of DMSO as a Case Study", *J. Phys. Chem. B*, **120**, pp 1429–1436 (2016)
9. G. Li, N. Govind, M. A. Ratner, C. J. Cramer, L. Gagliardi, "Influence of Coherent Tunneling and Incoherent Hopping on the Charge Transfer Mechanism in Linear Donor-Bridge-Acceptor Systems", *J. Phys. Chem. Lett,* **6**, pp 4889-4897 (2015)
10. B. Moore, H. Sun, N. Govind, K. Kowalski, J. Autschbach, "Charge-Transfer Versus Charge-Transfer-Like Excitations Revisited", *J. Chem. Theory Comput.*, **11**, pp 3305–3320 (2015)
11. J. Brabec, L. Lin, M. Shao, N. Govind, C. Yang, Y. Saad, E. G. Ng, "Efficient Algorithms for Estimating the Absorption Spectrum within Linear Response TDDFT", *J. Chem. Theory Comput,* **11** (11), pp 5197-5208 (2015)
12. S. Tussupbayev, N. Govind, K. Lopata, C. J. Cramer, "Comparison of Real-Time and Linear-Response Time-Dependent Density Functional Theories for Molecular Chromophores Ranging from Sparse to High Densities of States", *J. Chem. Theory Comput*, **11** (3), pp 1102-1109 (2015)
13. Y. Wang, K. Lopata, S.A. Chambers, N. Govind, P.V. Sushko, "Optical Absorption and Band Gap Reduction in (Fe1–xCrx)2O3 Solid Solutions: A First-Principles Study" *J. Phys Chem. C.*, **117** (48), pp 25504-25512 DOI: 10.1021/jp407496w (2013)
14. S. E Chamberlin, Y. Wang, K. Lopata, T.C. Kaspar, A. W. Cohn, D. R. Gamelin, N. Govind, P. V. Sushko, S. A Chambers, "Optical absorption and spectral photoconductivity in α-$(Fe_{1-x}Cr_x)_2O_3$solid-solution thin films", *J. Phys.: Condens. Matter* 25 392002 (2013)
15. K. Lopata, N. Govind, "Near and Above Ionization Electronic Excitations with Non-Hermitian Real-Time Time-Dependent Density Functional Theory", *J. Chem. Theory Comput*, 2013**,** 9 (11), pp 4939-4946 DOI: 10.1021/ct400569s
16. D. W. Silverstein, N. Govind, H. J. J. van Dam, L. Jensen, "Simulating One-Photon Absorption and Resonance Raman Scattering Spectra Using Analytical Excited State Energy Gradients within Time-Dependent Density Functional Theory", *J. Chem. Theory. Comput*, 9 (12), 5490-5503 (2013)

Grant Numbers and Grant Titles

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Postdoc(s): Sean A. Fischer (PNNL), David N. Bowman (Minnesota)
Undergraduate Student: Jason C. Asher (Minnesota)

J. Ilja Siepmann

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

Laura Gagliardi,[1] Nandini Ananth,[2] Kit Bowen,[3] Aurora E. Clark,[4] Christopher J. Cramer,[1]
Michael W. Deem,[5] Omar K. Farha,[6] Jason D. Goodpaster,[1] Maciej Haranczyk,[7] Martin Head-Gordon,[7]
Joseph T. Hupp,[6] Jeffrey R. Long,[8] David S. Sholl,[9] Randall Q. Snurr,[6] Donald G. Truhlar,[1]
Michael Tsapatsis,[1] and J. Ilja Siepmann[1]

[1]University of Minnesota, [2]Cornell University, [3]Johns Hopkins University, [4]Washington State University, [5]Rice University, [6]Northwestern University, [7]Lawrence Berkeley National Laboratory, [8]University of California–Berkeley, [9]Georgia Institute of Technology

Abstract

The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including **metal-organic frameworks** (MOFs), **zeolites**, and **porous polymer networks** (PPNs). These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. Towards that end, the NMGC (i) develops state-of-the-art predictive theories (from high-level electronic structure methods to validated molecular mechanics force fields), hierarchical screening approaches, data-driven discovery tools, applets, databases, and web-based repositories, and (ii) employs them to increase the pace of materials discovery and to understand the fundamentals of interactions and mechanisms that govern performance of nanoporous materials. The goals of the NMGC are advanced by a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups with experience in Monte Carlo and molecular dynamics simulations, electronic structure calculations, data-driven science, scientific computation, and applied mathematics. The majority of the completed and on-going projects benefit from iterative feedback where computational modeling and large-scale data generation/analysis is instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis, characterization, and validation.

The NMGC research efforts have already led to more than 100 publications. In this short presentation, we will highlight key achievements of selected projects leading to the discovery/design of nanoporous materials for separation and catalysis applications and providing improved understanding of the fundamental interactions governing performance of nanoporous materials (see **Figure 1** and **Figure 2**). In addition, we will introduce a first principles Monte Carlo framework that allows for the calculation of adsorption isotherms and reaction equilibria in nanoporous confinements with all interactions described using Kohn-Sham density functional theory. In particular, we will present (i) the adsorption isotherms of CO_2 and N_2 on Mg-MOF-74 where strong interactions of CO_2 with the open-metal site lead to large separation factors and (ii) the chemical equilibria of H_2S and CO_2 in a sodium-exchanged zeolite where favorable interactions with the cations shift the equilibrium toward the production of H_2O and OCS.

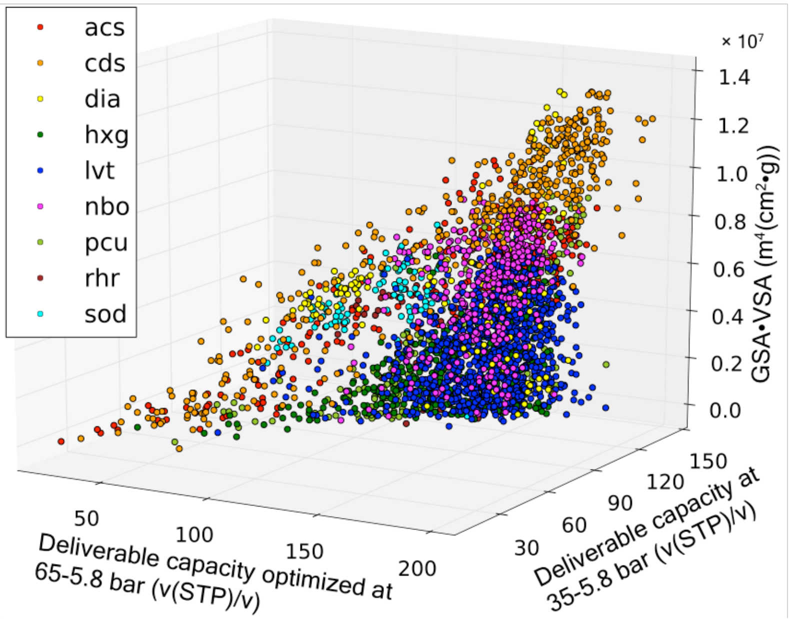


Figure 1: Relationship between optimized deliverable capacity at the 65 bar condition, deliverable capacity at the 35 bar condition, and surface area for MOFs discovered using a genetic algorithm.

Figure 2: Electronic structure calculations aid the design of catechol-ligated transition metals as MOF-linkers for gas separations.

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

Conventional approaches aimed at discovery and development of nanoporous materials for storage, separation, and catalysis applications are hampered by the large number of already synthesized zeolites and MOFs, the much larger number of hypothetical zeolite and MOF structures, and the large number of potential applications, i.e., it would be impossible to synthesize a significant fraction of these materials and to characterize their performance for a variety of applications. The materials genome approach, including genetic algorithms and machine learning tools, developed and employed by the NMGC allows one to explore thousands of materials for a plethora of applications in a relatively short time frame. NMGC research has led to the discovery of zeolites for extraction of ethanol from aqueous solution (Patent Application PCT/US2015/41566), for hydrocarbon dewaxing (Patent Application PCT/US2015/41544), and for sweetening of highly sour natural gas mixtures (Patent Application PCT/US2016/054624), and of MOFs for Kr/Xe and CO_2/H_2 separation and for ethane-to-ethanol conversion.

Over the next year, the NMGC team will continue its collaborative endeavors to discover nanoporous materials with optimal gas storage, separation, and catalytic abilities and to use an integrated computational/experimental approach for unraveling structure/chemistry/function relationships.

Grant Number and Grant Title

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

Postdoc(s): Peng Bai, Pallavi Bhattacharyya, Jeffrey Camp, Dhabih Chulhai, Yongchul Chung, Hakan Demir, Bahman Elyassi, Laura Fernandez, Emmanuel Haldoupis, Mustafa Kucukkal, Rachel Klet, Aaron League, Kyuho Lee, Wei-Guang Liu, Andreas Mavrantonakis, Remi Maurice, Per Miro, Liang R. Niestemski, Manuel Ortuno, Samuel Odoh, Abdullah Ozkanlar, Nora Planas, Payal Parmar, Shuanglin Qu, Dai Tang, Raghuram Thyagarajan, Jeffrey Van Humbeck, Konstantinos Vogiatzis, Jian Wu, Xuefei Xu

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

Ten Publications Acknowledging this Grant (selected from 105 publications)

[102] M. Y. Jeon, D. Kim, P. Kumar, P. S. Lee, N. Rangnekar, P. Bai, M. Shete, B. Elyassi, H. S. Lee, K. Narasimharao, S. N. Basahel, S. Al-Thabaiti, W. Xu, H. J. Cho, E. O. Fetisov, R. Thyagarajan, R. F. DeJaco, W. Fan, K. A. Mkhoyan, **J. I. Siepmann**, and **M. Tsapatsis**, Ultra-Selective High-Flux Membranes from Directly Synthesized Zeolite Nanosheets, *Nature* **543**, 690–694 (2017).

[93] Y. G. Chung, D. A. Gómez-Gualdrón, P. Li, K. T. Leperi, P. Deria, H. Zhang, N. A. Vermeulen, F. Stoddart, F. You, J **. T. Hupp, O. K. Farha**, and **R. Q. Snurr**, In Silico Discovery of Metal–Organic Frameworks for Precombustion CO_2 Capture Using a Genetic Algorithm, *Sci. Adv.* **2**, e1600909 (2016).

[91] K. D. Vogiatzis, E. Haldoupis, D. J. Xiao, **J. R. Long, J. I. Siepmann**, and **L. Gagliardi**, Accelerated Computational Analysis of Metal−Organic Frameworks for Oxidation Catalysis, *J. Phys. Chem. C* **120**, 18707–18712 (2016).

[84] M. S. Shah, **M. Tsapatsis**, and **J. I. Siepmann**, Identifying Optimal Zeolitic Sorbents for Sweetening of Highly Sour Natural Gas, *Angew. Chem. Int. Ed.* **55**, 5938–5942 (2016).

[77] C.M. Simon**, B. Smit**, and **M.Haranczyk**, pyIAST: Ideal Adsorbed Solution Theory (IAST) Python Package, CPC. **200**, 364–380 (2016).

[45] J. E. Mondloch, M. J. Katz, W. C. Isley III, P. Ghosh, P. Liao, W. Bury, M. Hall, J. B. DeCoste, G. Peterson, **R. Q. Snurr**, **C. J. Cramer**, **J. T. Hupp**, and **O. K. Farha**, Destruction of Chemical Warfare Agents Using Metal–Organic Frameworks, *Nat. Mater.* **14**, 512–516 (2015).

[44] T. M. McDonald, J. A. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocellà, F. Giordano, S. Odoh, W. Drisdell, B. Vlaisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, L. Kyuho, T. Pascal, D. Prendergast, **J. B. Neaton**, **B. Smit**, J. B. Kortright, **L. Gagliardi**, S. Bordiga, J. A. Reimer, and **J. R. Long**, Cooperative Insertion of CO_2 in Diamine-Appended Metal–Organic Frameworks, *Nature* **519**, 303–308 (2015).

[42] P. Bai, M.-Y. Jeon, L. Ren, C. Knight, **M. W. Deem**, **M. Tsapatsis**, and **J. I. Siepmann**, Discovery of Optimal Zeolites for Challenging Separations and Chemical Transformations Using Predictive Materials Modeling, *Nat. Commun.* **6**, 5912 (2015).

[36] Y. G. Chung, J. Camp, **M. Haranczyk**, B. J. Sikora, W. Bury, V. Krungleviciute, T. Yilidrim, **O. K. Farha**, **D. S. Sholl**, and **R. Q. Snurr**, Computation-Ready, Experimental Metal–Organic Frameworks: A Tool to Enable High-Throughput Screening of Nanoporous Crystals, *Chem. Mater.* **26**, 6185–6192 (2014).

[24] D. J. Xiao, E. D. Bloch, J. A. Mason, **W. L. Queen**, M. R. Hudson, N. Planas, J. Borycz, A. L. Dzubak, P. Verma**,** K. Lee, F. Bonino, V. Crocellà, J. Yano, S. Bordiga, **D. G. Truhlar**, **L. Gagliardi**, C. M. Brown, and **J. R. Long**, Oxidation of Ethane to Ethanol by N_2O in a Metal–Organic Framework with Coordinatively Unsaturated Iron(II) Sites, *Nat. Chem.* **6**, 590–595 (2014).

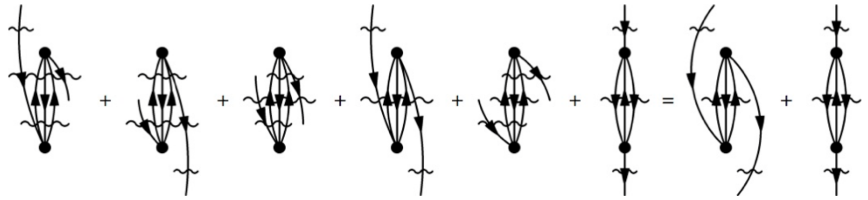
One-Particle Many-Body Green's Function Theory: Algebraic Recursions, Linked-Diagram Theorem, Irreducible-Diagram Theorem, and General-Order Algorithms

So Hirata[1], Alexander E. Doran[1], Peter J. Knowles[2], and J. V. Ortiz[3]
[1] Department of Chemistry, University of Illinois at Urbana-Champaign
[2] School of Chemistry, Cardiff University
[3] Department of Chemistry and Biochemistry, Auburn University

Abstract

One-particle many-body Green's function theory (MBGF) furnishes a systematically converging series of approximations for the direct calculations of correlated electron-detachment and attachment energies for molecules and quasiparticle energy bands for solids, which are the key properties of much of chemistry and materials science. We conduct a thorough analytical and numerical characterization of the whole Feynman-Dyson perturbation series of MBGF. It

- introduces 3 distinct, but mathematically equivalent algebraic (first-quantized) recursive definitions of the Green's function in the style of the recursion of the Rayleigh–Schrödinger perturbation theory;
- 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**);



- shows the equivalence of ΔMPn [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 ΔMPn 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 ΔMPn 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).

DE-FG02-11ER16211

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. C. M. Johnson, S. Hirata, and S. Ten-no,
Chemical Physics Letters (published online, 2017) [Ahmed Zewail Commemoration Issue],
"Explicit correlation factors."

2. 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."

3. A. E. Doran and S. Hirata,
Journal of Chemical Theory and Computation **12**, 4821-4832 (2016),
"Monte Carlo MP2 on many graphical processing units."

4. 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."

5. J. A. Faucheaux and S. Hirata,
The Journal of Chemical Physics **143**, 134105 (2015) (21 pages),
"Higher-order diagrammatic vibrational coupled-cluster theory."

6. T. Yamada and S. Hirata,
The Journal of Chemical Physics **143**, 114112 (2015) (7 pages),
"Singlet and triplet instability theorems."

7. M. R. Hermes and S. Hirata,
The Journal of Chemical Physics **143**, 102818 (2015) (11 pages) [Special Topic Issue on "Advanced Electronic Structure Methods for Solids and Surfaces"],
"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."

8. 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."

9. S. Y. Willow, K. S. Kim, and S. Hirata,
Physical Review B (Rapid Communications) **90**, 201110(R) (2014) (5 pages),
"Brueckner-Goldstone quantum Monte Carlo for correlation energies and quasiparticle energy bands of one-dimensional solids."

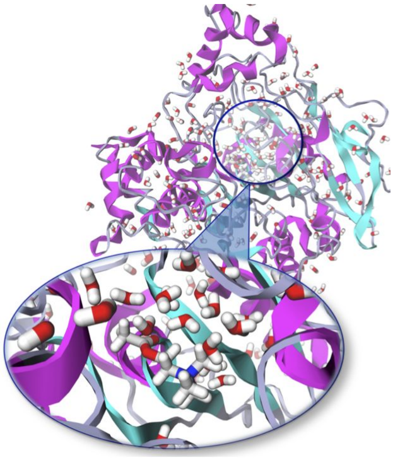
10. S. Hirata and M. R. Hermes,
The Journal of Chemical Physics **141**, 184111 (2014) (7 pages),
"Normal-ordered second-quantized Hamlitonian for molecular vibrations."

CHARMMing: A Flexible Web-User Interface For Molecular Simulation, Multiscale Modeling, and Workforce Development

Yihan Shao[1] and Lee Woodcock[2]

[1]Q-Chem, Inc. 6601 Owens Drive, Suite 105, Pleasanton, CA 94588
[2]Department of Chemistry, University of South Florida,
4202 E. Flower Ave CH 205, Tampa, FL 33620
E-mail: hlw@usf.edu

Abstract



Molecular simulation techniques have been universally accepted as a key tool in chemical and biological research; however, most simulation programs can be very intimidating for the non-expert. Further, advanced methodologies (e.g., novel simulation methodologies) are often inaccessible to anyone outside of the academic laboratories where they are developed.

To assist in overcoming these barriers, we have developed a Web-user interface, initially for the CHARMM simulation package but now greatly extended, CHARMMing (CHARMM interface and graphics, charmming.org). This tool provides a user-friendly interface for the preparation, submission, monitoring, and visualization of molecular simulations. Our recent progresses include:

- Web-based graphical capabilities have been overhauled using a Javascript framework called React (http://facebook.github.io/react), which is fully compatible with modern mobile Web browsers (e.g., phones and tablets), allowing easy integration of advanced simulation techniques. In addition, most of the server architecture and infrastructure has been migrated to the Django 1.9 framework and Python 3, with some additional custom framework level code to make application development simpler. Finally, CHARMMing has been overhauled and integrated, at the task level, via Docker containers. This greatly enhances scalability and facilitates deployment on cloud resources such as AWS and GCP.
- A python library is being built for visualizing key QM results directly from QM calculation checkpoint files, which will facilitate the support of a multitude of QM packages beyond Q-Chem. Additionally, the recently developed ability to natively write macromolecular topology information makes integration of additional classical simulation packages (e.g., AMBER, GROMACS, etc.) seamless.
- Advanced multiscale modeling techniques are being implemented into CHARMMing. This includes an ongoing effort to support the interoperability of various classical and quantum mechanical software packages. Initially, these efforts have focused on developing interfaced and advanced functionality between Q-Chem and both CHARMM and NAMD [1-3].

- Web-based “lessons” (i.e, interactive step-by-step instructions for performing common molecular simulation tasks) have been developed and implemented into CHARMMing. This functionality has two primary goals: (1) the creation of workflows to facilitate the distribution of complicated workflows, and (2) the general enhancement of computational education - be that students in K12 or university or experimental researchers that may be new to simulation.
- A freely available tutorial (www.charmmtutorial.org) to bridge the gap between graphical simulation set-up and the technical knowledge necessary to perform simulations without user interface assistance.
- Development and integration of an array of tools to facilitate molecular docking calculations. These new features include implementation of free fragment-based docking and QSAR protocols, API development to interact with web services for structural bioinformatics, and development of novel flexible molecular docking procedures. [4-X]

[1] Alexander J. Sodt, Ye Mei, Gerhard König, Peng Tao, Ryan P. Steele, Bernard R. Brooks, and Yihan Shao, "Multiple Environment Single System Quantum Mechanical/molecular Mechanical (MESS-QM/MM) Calculations. I. Estimation of Polarization Energies", J. Phys. Chem. A 119, 1511 (2015). DOI: 10.1021/jp5072296

[2] Gerhard König,Ye Mei,Frank C. Pickard IV, Andrew C. Simmonett, Benjamin T. Miller, John M. Herbert, H. Lee Woodcock, Bernard R. Brooks and Yihan Shao, "Computation of Hydration Free Energies Using the Multiple Environment Single System Quantum Mechanical / Molecular Mechanical Method", J. Chem. Theory Comput., 12, 332 (2016). DOI: 10.1021/acs.jctc.5b00874

[3] Jing Huang, Ye Mei, Gerhard Koenig, Andrew C. Simmonett, Frank C Pickard, Qin Wu, Lee-Ping Wang, Alexander D. MacKerell, Bernard R. Brooks, and Yihan Shao, "An Estimation of Hybrid Quantum Mechanical Molecular Mechanical (QM/MM) Polarization Energies for Small Molecules Using Polarizable Force-Field Approaches", J. Chem. Theory Comput., 13, 679 (2017). DOI: 10.1021/acs.jctc.6b01125

[4] Janez Konc, Benjamin T. Miller, Tanja Štular, Samo Lešnik, H. Lee Woodcock, Bernard R. Brooks, and Dlušanka Janežič, "ProBiS-CHARMMing: Web Interface for Prediction and Optimization of Ligands in Protein Binding Sites", J. Chem. Info. Model. 55, 2308 (2015). DOI:10.1021/acs.jcim.5b00534

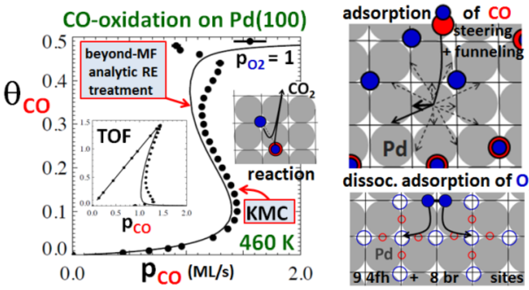
Jim W. Evans

Statistical mechanical and energetic analysis of chemisorption and catalysis on metals

Da-Jiang Liu, F. Zahariev, M.S. Gordon, T.L. Windus, and Jim Evans
Ames Laboratory – USDOE, Division of Chemical & Biological Sciences

Abstract

We describe development of predictive molecular-level models for chemisorption and catalytic reaction-diffusion processes (determining, e.g., reaction yield or TOF) on surfaces. Traditional mean-field (MF) chemicals kinetics can fail due to strong spatial correlations between adsorbed reactants (either of thermodynamic or kinetic origin). Thus, we utilize stochastic multi-site lattice gas models (accounting for distinct adsorption sites), behavior of which is analyzed by KMC simulation. Such modeling must precisely describe (e.g., with ab-initio energetics) adlayer thermodynamics, well as local-environment-dependent kinetics of adsorption, desorption, diffusion, and reaction. Model validation comes from extensive comparison with experiment, e.g., for CO-oxidation on metal(100) surfaces at low pressure (P) recovering and elucidating observed steady-state bifurcations and TPR kinetics. For deeper insight, we have developed beyond-MF rate equations accounting for subtle equilibrium adlayer ordering to describe these systems. In other work, we successfully analyze non-MF CO-oxidation kinetics at high P producing strong non-equilibrium correlations. We also explore the role of chemisorbed species (e.g., catalytic promoters and poisons) such as S which induce dynamic rearrangement of the catalytic surface and possible metal-S complex formation.



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

Personnel associated with the above projects: PIs: J.W. Evans, M.S. Gordon; T.L. Windus
Staff Scientists: D.-J. Liu, F. Zahariev; Students: Andres Garcia, Jeff Boschen, Jiyoung Lee

PROGRAM SCOPE

The theoretical Chemical Physics project at Ames Laboratory pursues molecular-level and coarse-grained modeling of **heterogeneous catalysis and other complex reaction phenomena** at surfaces and in mesoporous materials. The effort incorporates: *electronic structure analysis and non-equilibrium statistical mechanical and multi-scale modeling*. The former includes quantum chemistry studies for large systems, and for homogeneous & heterogeneous catalysis. The latter (by Liu & Evans) described in part below explores molecular-level descriptions of: (i) the interplay between anomalous transport and catalytic reaction in functionalized mesoporous materials; (ii) chemisorption and heterogeneous catalysis on metal surfaces and nanoclusters. These studies also connect molecular-level treatments to mesoscale spatiotemporal mesoscale behavior, and analysis of fundamental non-equilibrium behavior in reaction-diffusion systems.

RECENT PROGRESS

Chemisorption and Catalysis on Extended Surfaces (and Nanoclusters)

Detailed and predictive multisite lattice-gas (msLG) models and efficient KMC simulation algorithms were developed to describe CO-oxidation on unreconstructed metal(100) surfaces under lower-pressure (P) conditions.[1] The msLG models account for multiple stable adsorption sites of some reactant species, and thus allow more accurate treatment of adlayer ordering and reaction configurations. Reactive steady-states are controlled by kinetics as well as adlayer thermodynamics. Thus, guided by DFT, we developed realistic models for dissociative adsorption of oxygen on mixed reactant adlayers on metal(100) surfaces addressing the shortcomings of Langmuir and Brundle-Behm-Barker pictures,[2] and also for CO-adsorption including "steering". Extensive DFT analysis has been performed to determine adspecies adsorption energies and interactions, with higher-level theory (by Zahariev, Gordon) assessing DFT limitations.[3] Model predictions for bifurcations of reactive steady-states, titration, TPD and TPR kinetics were compared extensively with experiment.[1] For deeper insight into behavior controlling reactivity, and for practical utility, we have also developed an analytic beyond-MF rate equation treatment for a slightly simplified msLG model of CO-oxidation on Pd(100), which still accounts for the complex equilibrium adlayer superlattice ordering.[3]

Another effort explored CO-oxidation at high-P on $RuO_2(110)$, an oxidized surface of Ru. Reuter *et al.* noted a dramatic failure of MF-rate equation treatment of kinetics due to strong spatial correlations induced by a combination of reaction and limited mobility. We develop a formalism to precisely describe these correlations and also the sluggish dynamics in this system.[4] We also pursued the BESAC scientific grand challenge to develop a fundamental understanding of non-equilibrium phase transitions (e.g., nucleation/metastability in catalytic poisoning).[5]

Detailed characterization of chemisorption is key to describe reactant ordering in catalysis, but also possible chemisorption-induced restructuring and dynamics of metal surfaces by reactants or impurities (promoters or poisons). We recently focused on the effect of sulfur (S) which can induce reconstruction on terraces and at steps, and metal-S complex formation on Au, Ag, and Cu coinage metal surfaces. Liu has performed extensive DFT analysis is closely integrated with high-resolution low-T STM studies from Japanese and US collaborators for a comprehensive exploration of low-energy structures, sometimes combined with statistical mechanical analysis.[6] For S/Cu, experimental data suggests a preference for motifs both in reconstruction and complex formation suggest a preference for 4-fold (over 3-fold) hollow sites and for S-M-S motifs. With Windus et al., we explore this trend for nanoclusters as well as extended surfaces with both plane-wave and localized atomic orbital bases finding strong quantum size effects with increasing size but emergence of 4fh preference.[7] Separate analysis with Windus explored the stability of X-Au-X "staple" motifs on Au(111) where X = S, CH_3S,..[8]

Catalytic Reactions in Functionalized Nanoporous Materials

Recent efforts have considered catalytic conversion reactions occurring inside linear nanopores of zeolites, functionalized mesoporous silica (by the Ames Lab catalysis group), etc.. Previous analyses had produced limited characterization of low reactivity due to inhibited transport into pores. We showed that mean-field reaction-diffusion equation (RDE) treatments fail to describe such behavior, instead developing a successful "generalized hydrodynamic" treatment. A key parameter is the propensity for reactants and products to pass each other in the pore, a quantity which can be assessed by suitable Langevin simulations or equivalent Fokker-Planck equation analysis.[9] Our recent efforts extended our modeling to treat: concentration-dependent (stereo-) selectivity (with Windus), the effect of interactions between reactant and product species and the porous material, and developed new strategies to determine the generalized tracer diffusivity (the key input to our generalized hydrodynamic formulation).[10]

FUTURE PLANS

Future research efforts will include the following: **(i)** Development of more detailed system-specific models for catalysis in nano- and meso-porous materials. These studies should account for different mobilities of reactants and products, the details of rotational-translational diffusion in controlling passing propensities of molecules in pores, solvent-mediated interactions, etc. In collaboration with the *Gordon group,* we aim to apply EFP-MD analysis to assess both the solvent-mediated diffusivity and interactions of reactant and product species. This key information will provide input to our coarse-grained modeling, in particular for our Langevin simulations of passing propensities. **(ii)** Development of realistic and predictive models for catalytic reactions on metal surfaces addressing limitations of DFT predictions for energetics, and incorporating the local environment dependence of barriers for reactions and of the dynamics of dissociative adsorption, etc. Here, we will collaborate further with *Zahariev and Gordon* comparing predictions of high-level methods including QMC with DFT predictions. **(iii)** Development of appropriate theoretical framework to reliably describe strong correlations due to inhibited mobility in surface reactions at high-pressures. Related more general studies will attempt to provide a fundamental understanding of non-equilibrium poisoning transitions and related phenomena in catalytic reaction systems. **(iv)** Further analysis of the interaction of metal surfaces and nanoclusters with chemisorbed species, particularly S which can act as a promoter or poison. This work involves a collaboration with the *Windus group* to elucidate the nature of the metal-S interaction and the stability of various surface motifs.

Selected Publications Acknowledging this Grant from 2014-present

1. Liu, D.-J.; Garcia, A.; Wang, J.; Ackerman, D.; Wang, C.-J.; Evans, J.W. KMC simulation of statistical mechanical models and coarse-grained mesoscale descriptions of catalytic reaction-diffusion processes: 1D nanoporous and 2D surface systems, *Chemical Reviews*, 2015, *115*, 5979-6050.
2. Liu, D.-J.; Evans, J.W. Dissociative adsorption of O_2 on unreconstructed metal(100) surfaces: Pathways, energetics, and sticking kinetics, *Phys. Rev. B* 2014, *89*, 205406; Also: Statistical mechanical models…with blocking, steering, and funneling, *J. Chem. Phys.* 2014, *140*, 194704.
3. Liu, D.-J.; Zahariev, F.; Gordon, M.S.; Evans, J.W. Predictive Beyond-Mean-Field Rate Equations for… Catalytic Surface Reactions: CO-Oxidation on Pd(100), *J. Phys. Chem. C*, 2016, *120*, 28639-28653.
4. Liu, D.-J.; Evans, J.W. Transitions between strongly correlated and random steady-states for catalytic CO-oxidation on surfaces at high-pressure, *J. Chem. Phys.* 2015, *142*, 134703.
5. Wang, C.-J.; Liu, D.-J.; Evans, J.W. Generic two-phase coexistence and metastability in a threshold version of Schloegl's model for autocatalysis, *J. Chem. Phys.* 2015, *142*, 164105.
6. Walen, H.; Liu, D.-J.; Oh, J.; Lim, H.; Evans, J.W.; Aikens, C.; Kim, Y.; Thiel, P.A. Cu_2S_3 complex on Cu(111) as a candidate for mass transport enhancement, *Phys. Rev. B*, 2015, *91*, 045426.
7. Boschen, J.; Lee, J.; Windus, T.L.; Evans, J.W.; Thiel, P.A.; Liu, D.-J. S-adsorption on (111) & (100) facets of Cu nanoclusters, J. Chem. Phys. 2016, 145, 164312. Also: *J. Phys. Chem. C* 2016, *120*, 10268.
8. Lee, J.; Boschen, J.; Windus, T.; Thiel, P.; Liu, D.-J. Stabilization of X-Au-X complexes on Au(111): a theoretical investigation and comparison of X = S, Cl, CH_3S,.. *J. Phys. Chem. C* 2017, *212*, 3870.
9. Wang, C.-J.; Ackerman, D.M.; Slowing, I.I.; Evans, J.W. Langevin and Fokker-Planck analyses of inhibited molecular passing processes… in nanoporous materials, *Phys. Rev. Lett.* 2014, *113*, 038301.
10. Garcia, A.; Evans, J.W. Catalytic Conversion in Nanoporous Materials: Concentration Oscillations and Spatial Correlations due to Inhibited Transport and Intermolecular Interactions, *J. Chem. Phys.* 2016 *145*, 174705.

Henry F. Schaefer

Theoretical Studies of Elementary Hydrocarbon Species and their Reactions

Henry F. Schaefer and Wesley D. Allen

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

Abstract

1. Recent Progress

In this abstract, we first describe research completed in two rather different areas.

A. Large Molecules

The high computational cost of molecular electronic structure methods can be reduced by approximating the two-electron integral tensor

$$g_{\mu\nu,\lambda\sigma} \equiv (\mu\nu|\lambda\sigma) = \int \chi_\mu(\vec{r}_1)\, \chi_\nu(\vec{r}_1) \frac{1}{r_{12}}\, \chi_\lambda(\vec{r}_2)\chi_\sigma(\vec{r}_2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{1}$$

where μ, ν, λ, σ, . . . indicate atomic orbital indices. The $O(N^4)$ scaling with basis set size (and, consequently, with molecular system size) makes the full computation of this tensor prohibitive for very large molecules. In particular, the evaluation of this tensor is the limiting step for conventional Hartree–Fock (HF) and density functional theory (DFT) methods. The number of significant entries in this tensor that need to be computed can be reduced (almost) to $O(N^4)$ using a priori screening based on the Schwarz inequality

$$|(\mu\nu|\lambda\sigma)| \leq (\mu\nu|\mu\nu)^{1/2}(\lambda\sigma|\lambda\sigma)^{1/2} \tag{2}$$

However, for sufficiently large systems even this reduced cost is prohibitive, since the prefactor to the quadratic scaling is large. Furthermore, this prefactor grows rapidly with the quality of the one-electron basis set. Since realistic correlated computations usually require a basis set of at least triple-zeta quality, the usefulness of Schwarz-based screening can deteriorate quite rapidly in practical applications. Substantial effort has been invested in more aggressive screening techniques, but the inverse linear decay of the integration kernel in the general case severely limits the efficacy of such methods.

We have developed a local density fitting scheme in which atomic orbital (AO) products are approximated using only auxiliary AOs located on one of the nuclei in that product. The possibility of variational collapse to an unphysical “attractive electron” state (that can affect such density fitting) was alleviated by including atom-wise semi-diagonal integrals exactly. Our approach leads to a significant decrease in the computational cost of density fitting for Hartree–Fock theory, while still producing results with errors 2–5 times smaller than standard, nonlocal density fitting. Our method allows large Hartree–Fock and density functional theory computations with exact exchange to be carried out efficiently. This was demonstrated by benchmarking our method on 200 large molecules, including up to 140 atoms. Our new fitting scheme leads to smooth and artifact-free potential energy surfaces and the possibility of relatively simple analytic gradients.

The electron repulsion integral (ERI) may equally well be defined as

$$g_{AB} \equiv (A|B) = \int \Omega_A(\vec{r}_1)\frac{1}{r_{12}}\Omega_B(\vec{r}_2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{3}$$

where Ω_A and Ω_B are the (Mulliken notation) *bra* and *ket* charge distributions. For large molecules, the numerous (by far) contributors to the ERI tensor are the four-center cases, in which both Ω_A and Ω_B are product densities, composed of either atom-center basis functions in HF/DFT or molecular orbitals in correlated methods such as second-order perturbation theory. To reduce the computational cost of the four-center ERIs, Ω_A and Ω_B can be approximately expanded in terms of an auxiliary basis set; the result density-fitting (DF, also known as the resolution-of-an-identity, RI) approximation involves three- and two-center ERIs in which either or both of the *bra* and *ket* densities are single, atom-centered functions.

We have introduced a new estimator for three-center two-particle Coulomb integrals. Our estimator is exact for some classes of integrals and is much more efficient than the standard Schwartz counterpart due to the proper account of distance decay. Although it is not a rigorous upper bound, the maximum degree of underestimation can be controlled by two adjustable parameters. We also give numerical evidence of the excellent tightness of the estimator. The use of the estimator will lead to increased efficiency in reduced-scaling one- and many-body electronic structure theories. The above methodological advances would not have been possible (even with our relatively strong local computing situation) without major access to the DOE supported National Energy Research Scientific Computer Center (NERSC) at the Lawrence Berkeley Laboratory.

B. Sigma Bond Activation Through Tunneling

With DOE support, we have previously uncovered and examined several reaction mechanisms that are dominated by tunneling (see, for example: *Science* **2011**, 332, 1300; *J. Am. Chem. Soc.* **2010**, 132, 7273; and *Nature* **2008**, 453, 906). While the tunneling of both light and heavy atoms has been widely discussed in the literature – often to explain anomalous results observed during experiments – theory provides a unique tool for quantifying tunneling probabilities. Indeed, for small, archetypal systems, high-accuracy computations allow for near perfect agreement with experiment in such cases. Recently, we investigated the activation of H_2 by boron-hydrides, another case where tunneling was predicted to be a primary component of the mechanism. Prior experimental work had established a forward reaction barrier for $B(H_2)_3^+ \rightarrow HBH(H_2)_2^+$ of 0.5 kcal mol^{-1} from mass spectrometry experiments (*J. Am. Chem. Soc.* **1998**, 120, 7577), but theoretical studies placed the barrier much higher at 5.4 kcal mol^{-1} (*J. Am. Chem. Soc*. **1998**, 120, 7585).

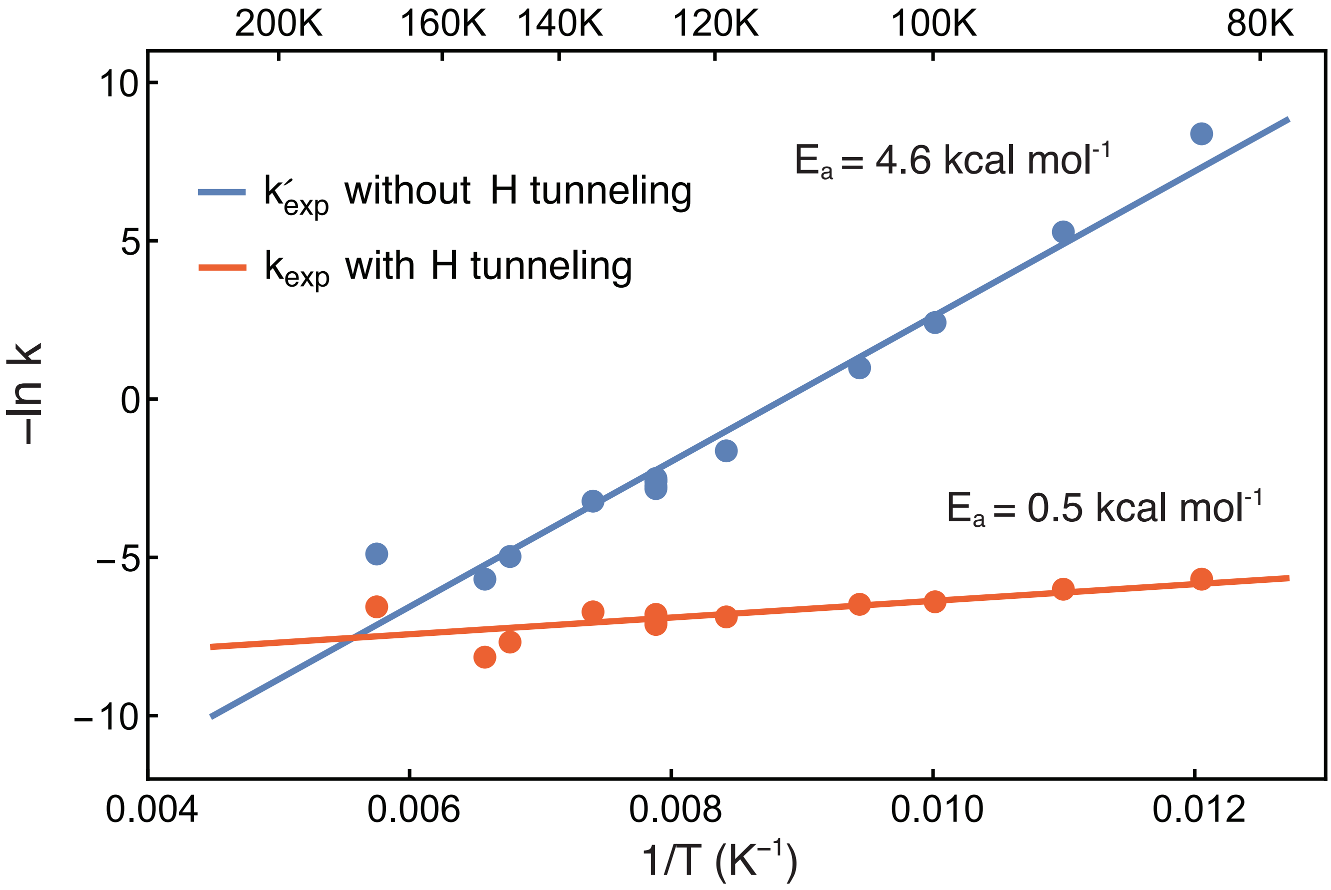


Figure 1. Experimental Arrhenius plots for the insertion reaction $B(H_2)_3^+ \rightarrow HBH(H_2)_2^+$. The red line represents a linear fit of the original experimental data, while the blue line is a linear fit to classical rate constants corrected for tunneling effects.

To resolve this disparity, we rigorously determined the barriers for a series of boron-hydride insertion reactions [$B(H_2)_n^+ \rightarrow HBH(H_2)_{n-1}^+$] using high-level single- and multi-reference coupled cluster theory [up to CCSDTQ and Mk-MRCCSD(T)], with energies extrapolated to the complete basis set (CBS) limit. After removing the tunneling effects from the experimental rate constants using this theoretical data (see Figure 1 for $n = 3$), new Arrhenius fits yielded an activation barrier of 4.6(3) kcal mol^{-1} for the BH_6^+ insertion reaction, which is in excellent agreement with the converged theoretical value (4.6 kcal mol^{-1}). These findings clearly demonstrate that earlier Arrhenius fits grossly underestimated these barriers, and that quantum tunneling dominates the σ-bond activation mechanism witnessed in experiments; moreover, such effects may be present in a variety of H_2 activation processes, such as for hydrogen storage using boron-containing materials.

2. Future Plans

The main challenge of high-level multireference electronic structure theory is the difficulty of avoiding redundant parameters in the wavefunction expansion. Currently the most popular approach is internal contraction, where one generates the wavefunction by applying excitation operators directly on a multi-determinant reference. This produces a non-orthogonal, highly redundant set of excitations, which is compressed into a linearly independent set by a trimmed singular value decomposition (SVD) of the overlap matrix. For linear expansions like configuration-interaction, this approach rigorously eliminates redundancies in the wavefunction expansion. The coupled-cluster expansion, however, is non-linear and includes products of excitations, which are not accounted for by the SVD procedure. This inconsistency produces artifacts unless one severely limits the excitation space with a very coarse-grained compression.

Quasiparticle multireference methods circumvent the redundancy problem through a unitary Fock-space isomorphism that takes the reference function into a pure state of k particles.

$$\left|\Psi_0\right\rangle = \tilde{a}_1^\dagger \cdots \tilde{a}_k^\dagger |\widetilde{\mathrm{vac}}\rangle \qquad \tilde{a}_p^\dagger \equiv U a_p^\dagger \Psi_0 \qquad |\widetilde{\mathrm{vac}}\rangle \equiv U|\widetilde{\mathrm{vac}}\rangle$$

Excitations of the reference function with respect to these transformed operators are automatically orthonormal, which makes non-redundant parametrization of the wavefunction trivial for both linear and non-linear Ansätze. The price paid for this simplification is a more complicated Hamiltonian, whose quasiparticle expansion involves higher-than-two-body interactions. Conceptually this is somewhat analogous to equation-of-motion coupled-cluster theory, which "folds" dynamic correlation into the Hamiltonian by a non-unitary Fock-space isomorphism. Quasiparticle methods fold static correlation into the Hamiltonian.

The main degree of freedom in quasiparticle theories is choosing which state the reference function should map to under the transformation. The following four possibilities are particularly attractive.

1. $|\Psi_0\rangle = \widetilde{\mathrm{vac}}\rangle$

2. $|\Psi_0\rangle = \tilde{a}_1^\dagger \cdots \tilde{a}_{n_\mathrm{o}}^\dagger |\widetilde{\mathrm{vac}}\rangle$

3. $|\Psi_0\rangle = \tilde{a}_1^\dagger \cdots \tilde{a}_{n_\mathrm{o}}^\dagger \cdots \tilde{a}_n^\dagger |\widetilde{\mathrm{vac}}\rangle$

4. $|\Psi_0\rangle = \tilde{a}_{n_\mathrm{o}}^\dagger \cdots \tilde{a}_n^\dagger \cdots \tilde{a}_{n_\mathrm{o}+n_\mathrm{a}}^\dagger |\widetilde{\mathrm{vac}}\rangle$

Option 1 maps the reference function to the physical vacuum. A simple approximation based on this approach was recently developed by Sokolov and Chan (2015). Rolik and Kállay (2015) have developed several methods with Option 3, which employs a particle-number-conserving map onto a privileged *n*-particle state, such as the Brueckner or Hartree-Fock determinant. Options 2 and 4 have yet to be considered. Option 2 maps to an ionized determinant containing only the strictly occupied orbitals, and Option 4 maps to an electron-attached determinant in which all of the occupied and active orbitals are filled. The quasiparticle approach presents an attractive starting point for the development of multireference correlation theories. Our group proposes to advance this area of research by developing and benchmarking new methods within this framework. We are actively developing a method which builds on the work of Sokolov and Chan. With further support, we plan to initiate completely new approaches, such as Options 2 and 4 above.

3. Ten Recent DOE Sponsored Publications

1. C. Li, J. Agarwal, C.-H. Wu, W. D. Allen, and H. F. Schaefer, "The Intricate Internal Rotation Surface and Fundamental Infrared Transitions of the n-Propyl Radical", *William L. Jorgensen Special Issue, J. Phys. Chem. B* **119**, 728 (2015).
2. D. S. Hollman, H. F. Schaefer, and E. F. Valeev, "A Tight Distance-Dependent Estimator for Screening Three-Center Coulomb Integrals Over Gaussian Basis Functions", *J. Chem. Phys.* **142**, 154106 (2015).
3. C.-H. Chang, J. Agarwal, W. D. Allen, and D. J. Nesbitt, "Sub-Doppler Infrared Spectroscopy and Formation Dynamics of Triacetylene in a Slit Supersonic Expansion," *J. Chem. Phys*. **144**, 074301 (2016).
4. Y. Qiu, C.-H. Wu, H. F. Schaefer, W. D. Allen, and J. Agarwal, "σ Bond Activation Through Tunneling: Formation of the Boron Hydride Cations (n = 2, 4, 6)," *Phys. Chem. Chem. Phys*. **18**, 4063 (2016).
5. G. Li, Y. Xie, and H. F. Schaefer, "From Gas-Phase to Liquid Water Chemical Reactions: the F + $(H_2O)_n$ n = 1-4 Systems," *Invited Frontiers Article*, *Chem. Phys. Lett.* **648**, 1 (2016).
6. A. Gao, G. Li, B. Peng, Y. Xie, and H. F. Schaefer, "The Symmetric Exchange Reaction $OH + H_2O \rightarrow H_2O + OH$: Convergent Quantum Mechanical Predictions," *Mark Gordon Special Issue, J. Phys. Chem. A* **120**, 10223 (2016).
7. P. R. Franke, D. P. Tabor, C. P. Moradi, G. E. Douberly, J. Agarwal, and H. F. Schaefer, "Infrared Laser Spectroscopy of the n-Propyl and i-Propyl Radicals: Stretch-Bend Fermi Coupling in the Alkyl CH Stretch Region," *J. Chem. Phys.* **145**, 224304 (2016).
8. A. W. Ray, J. Agarwal, B. B. Shen, H. F. Schaefer, and R. E. Continetti, "Energetics and Transition State Dynamics of the $F + HOCH_3 \rightarrow HF + OCH_3$ Reaction," *Phys. Chem. Chem. Phys.* **18**, 30612 (2016).
9. K. V. Murphy, W. J. Morgan, Z. Sun, H. F. Schaefer, and J. Agarwal, "Thioformaldehyde *S*-Sulfide. Sulfur Analog of the Criegee Intermediate: Structures, Energetics, and Rovibrational Analysis," *J. Phys. Chem. A* **121**, 998 (2017).
10. H. I. Rivera-Arrieta, J. M. Turney, and H. F. Schaefer, "Structural Distortions Accompanying Non-Covalent Interactions: Methane—Water, the Simplest C—H Hydrogen Bond," *J. Chem. Theory Computation* **13**, 1478 (2017).

Papers 3, 7, and 8 are collaborations with other PIs in the DOE Fundamental Interactions Branch.

Modeling photoionization and photodetachment phenomena in the gas and condensed phase

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

Summary of recent major accomplishments

During the past year, we conducted several computational studies of open-shell and electronically excited species. The common theme in these studies is interactions between states of different character and intersections between the corresponding potential energy surfaces. We also continued to develop and benchmark computational methods for modeling electronic structure and spectroscopy of open-shell species. Particular emphasis was placed on determining spectroscopic signatures of transient species, to facilitate comparisons with experimental data. The following representative publications supported by DOE highlight selected recent results.[1–10]

Highlight: Dyson orbitals and absolute cross sections for photoionization

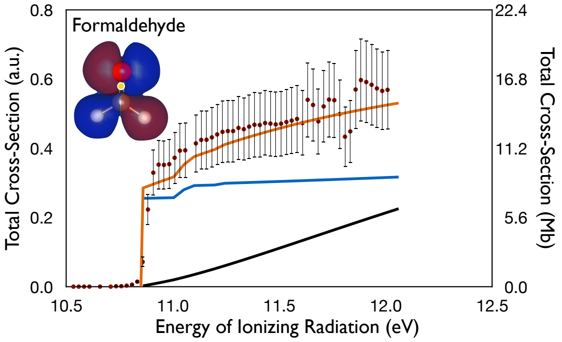


Figure 1: Absolute photoionization cross-section (in atomic units) for formaldehyde. Red dots show the experimental values. Blue and black lines correspond to the cross-sections computed using the Coulomb (Z=1) and plane (Z=0) waves, respectively. Orange line denotes cross-sections computed using the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

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

$$\phi^d(1) = \sqrt{N} \int \Psi^I(1,2,\ldots,N)\Psi^F(2,\ldots,N)d2\ldots dNy \tag{1}$$

We employed correlated Dyson orbitals and tested approximate treatments of the photoelectron wave function, that is, plane and Coulomb waves, by comparing computed and experimental photoionization/photodetachment spectra.[2] Using this simple description of the ejected electron, we were able to reproduce experimental cross-sections for a large set of molecules. This model is implemented in the *ezDyson* code, which is a free software available for download from the *iOpenShell* website; it provides a convenient tool for quick evaluations of the electronic cross-sections. We have applied this approach to aid the interpretation of experiments conducted in Prof. Kaiser group[6] and to study electronic structure of solvated electrons.[7]

Highlight: Photoionization of amino-acids in the gas and condensed phase

In collaboration with Dr. M. Ahmed from LBNL, we are investigating VUV and X-ray photoionization of amino-acids in the gas and condensed phases. Our calculations have shown that VUV photoionization of arginine leads to prompt and extensive fragmentation, explaining low observed yield of the parent ion. Our calculations of arginine in aqueous solution quantified the spectroscopic signatures of different protonation states.

We have also developed new coupled-cluster based approach for core-ionized states. Our benchmark calculations of core-ionized glycine in aqueous solutions have shown that our approach is capable of describing chemical shifts with quantitative accuracy. The results highlight the importance of specific solvent interactions.

Research highlight: Current developments and future plans

In the near future, we plan to complete the following:
(i) finalize the paper on modeling core-ionized states of glycine for publication;
(ii) finalize the paper on modeling arginine photoionization in the gas and condensed phase for publication;
(iii) finalize the implementation of non-adiabatic couplings (NACs) within EOM-CC framework;
(iv) benchmark EOM-CC NACs against MRCI;
(v) continue investigations of spin-forbidden channels in combustion (Cvetanovic diradicals).

Grant numbers and grant titles

Theoretical modeling of spin-forbidden channels in combustion reactions, DE-FG02-05ER15685.
Simulating the Generation, Evolution and Fate of Electronic Excitations in Molecular and Nanoscale Materials with First Principles Methods, coPI, joint with M. Head-Gordon *et al.*
Postdocs: Dr. Samer Gozem, Dr. Ilya Kaliman.
Students: Anastasia Gunina, Arman Sadybekov, Natalie Orms, Xintian Feng.

References

[1] E. Epifanovsky, K. Klein, S. Stopkowicz, J. Gauss, and A.I. Krylov, Spin-orbit couplings within the equation-of-motion coupled-cluster framework: Theory, implementation, and benchmark calculations, J. Chem. Phys. **143**, 064102 (2015).

[2] S. Gozem, A.O. Gunina, T. Ichino, D.L. Osborn, J.F. Stanton, and A.I. Krylov, Photoelectron wave function in photoionization: Plane wave or Coulomb wave?, J. Phys. Chem. Lett. **6**, 4532 (2015).

[3] N.V. Korovina, S. Das, Z. Nett, X. Feng, J. Joy, A.I. Krylov, S.E. Bradforth, and M.E. Thompson, Singlet fission in a covalently linked cofacial alkynyltetracene dimer, J. Am. Chem. Soc. **138**, 617 (2016).

[4] X. Feng and A.I. Krylov, On couplings and excimers: Lessons from studies of singlet fission in covalently linked tetracene dimers, Phys. Chem. Chem. Phys. **18**, 7751 (2016).

[5] X. Feng, D. Casanova, and A.I. Krylov, Intra- and inter-molecular singlet fission in covalently linked dimers, J. Phys. Chem. C **120**, 19070 (2016).

[6] M.J. Abplanalp, S. Gozem, A.I. Krylov, C.N. Shingledecker, E. Herbst, and R.I. Kaiser, Formation of interstellar aldehydes and enols - tracers of a cosmic-ray driven non-equilibrium synthesis of complex organic molecules, Proc. Nat. Acad. Sci. **113**, 7727 (2016).

[7] A.O. Gunina and A.I. Krylov, Probing electronic wave functions of sodium-doped clusters: Dyson orbitals, anisotropy parameters, and ionization cross-sections, J. Phys. Chem. A **120**, 9841 (2016).

[8] I. Kaliman and A.I. Krylov, New algorithm for tensor contractions on multi-core CPUs, GPUs, and accelerators enables CCSD and EOM-CCSD calculations with over 1000 basis functions on a single compute node, J. Comput. Chem. **38**, 842 (2017).

[9] S. Manzer, E. Epifanovsky, A.I. Krylov, and M. Head-Gordon, A general sparse tensor framework for electronic structure theory, J. Chem. Theory Comput. **13**, 1108 (2017).

[10] E.S. Subramaniam Iyer, A. Sadybekov, O. Lioubashevski, A.I. Krylov, and S. Ruhman, Rewriting the story of excimer formation in liquid benzene, J. Phys. Chem. A **121**, 1962 (2017).

Surface Plasmon Enhanced Chemistry

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

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

Recent Progress: Our primary activity during the last year has involved the development of semiempirical electronic structure methods to describe the properties of silver clusters that show plasmon excitations[1-3]. Such clusters have been known for several years based on TDDFT calculations, and they are useful in many different ways for modeling optical properties such as extinction and Raman scattering processes that are influenced by plasmon excitation, and for describing plasmon induced photochemistry. However a serious limitation of TDDFT calculations for describing silver (or gold) clusters with ligands is that charge transfer excited state energies are seriously underestimated (often by several eV) due to self-interaction errors. This has limited what could be done with these clusters, as often the charge transfer states are below the plasmon excitations, leading to physical results. However there is a way around this, which involves using a Hartree-Fock-based method such as INDO, where there is no self-interaction error. This idea has been around for a long time, however it was never implemented as the standard parameters available in INDO to describe silver excited states produced excited state energies of poor quality. What we found is that there is a systematic way to adjust these parameters to give plasmon excited states for bare clusters that match both experiment and results from TDDFT,[2] and once these parameters have been defined for one cluster, the agreement of INDO with TDDFT is good for all clusters. In addition, the INDO code that we are developing is capable of doing both singles and doubles CI calculations (i.e., INDO/S and INDO/SD) which enabled us to determine (for the first time) if doubles excitations make an important contribution to plasmon excited states. But we found that doubles are unimportant, which is very useful for doing further work as the singles-only calculation is much more efficient. With these capabilities we have been able to systematically explore plasmon excitation for a wide variety of silver clusters, and in the process of doing this, we discovered that there can be quadrupole plasmon excited states[2] in addition to the standard dipole excited states. Fig. 1 shows the transition density associated with the quadrupole plasmon of a Ag_{55}^+ nanorod, and contrasts this transition density with the corresponding results for two dipole plasmons modes, and with other nonplasmonic quadrupole states. This is the first example of a "dark" plasmon based on electronic structure calculations, and knowing this

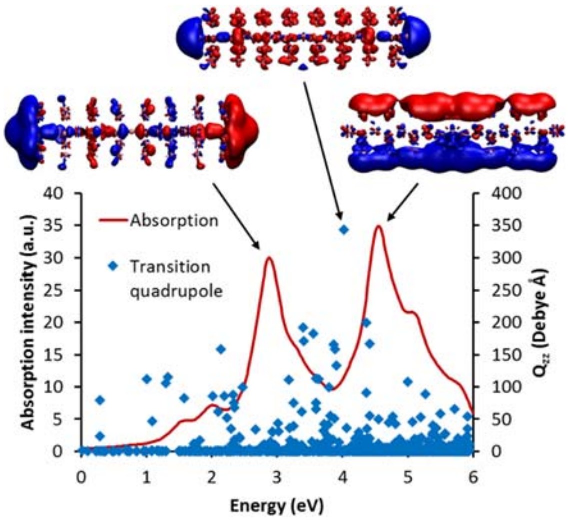


Figure 1. Top: transition densities for three plasmonic excitations (two dipolar and one quadrupolar) associated with a pentagonal Ag$_{55}^{+}$ nanorod. Bottom: Absorption spectrum of the nanorod (red curve), and transition quadrupole intensity for each electronic state in the nanorod. Note that the plasmonic transition quadrupole is much more intense that any of the others, and the two dipole modes have only small transition quadrupoles.

result will enable us to model the role of dark mode excitation in plasmonic properties. Our initial calculations were for clusters in vacuum, but we have since modified our semiempirical code to incorporate continuum solvation [3] at the COSMO level for both ground and excited states. In that work, we demonstrated for a series of prototypical π-conjugated molecules, that our newly implemented INDO/SCI/COSMO model yields more accurate absorption energies and comparably accurate solvatochromic shifts to those computed using TD-ωB97XD and CIS with COSMO solvation at a substantially lower computational cost. These studies are just the beginning of a series of projects that we can do with INDO-based methods, as further described below in our future plans.

Another cluster-based electronic structure study involved a TDDFT study of the impact of ligand passivation on plasmon excitation in silver clusters.[4] There has been confusion for some time as to the relation between the absorption spectra of ligand-protected clusters and the corresponding spectra of bare cores associated with the same clusters. In this study we discovered that the plasmonic excitations in ligand-protected silver clusters (considering both amine and thiolate ligands) are mostly associated with silver cores that are perturbed by the ligands, with essentially no contribution coming from excitations associated with the shell around the core where there are staple bonds and other structures that mix together the metal and ligand atoms. This study further shows that the ligands lead to two effects on plasmon excitation of the bare core: (1) dielectric screening that reduces excitation energies and (2) ligand field splitting that reduces plasmonic character. The dielectric screening can be thought of as a simple dielectric effect, and this lowers the silver plasmon excitation energy from 3.75 eV to 1.8 eV. The ligand field splitting leads to a breakup of the plasmon into groups of plasmons, each of which is less coherent.

We also have used metal clusters to study the coupling of acoustic mode excitation and plasmon excitation.[5] Experiments related to this topic have been done many times over the last 10 years, and in all cases it has been found that ultrafast laser excitation leads to acoustic mode excitation (when the initial electronic excitation gets converted to phonons),and this results in oscillating plasmon wavelengths (on the ps timescale) that are easily detected. These experiments have been interpreted using a combination of continuum mechanics and electrodynamics, but these theories are not capable of describing the coupling of these effects to chemistry in molecules on the surfaces of the nanoparticles. However our TDDFT-based work with bare silver clusters has now been extended to describe the oscillating plasmon experiments from first principles. We generally find good agreement with the continuum theories after correction for quantum size effects in the small clusters, but more information is provided by the quantum calculations, such the atom motions during oscillations, and the coupling of plasmons to modes other than acoustic modes. This methodology now gives us the capability to expand our work to the effect of plasmon-induced coupling of acoustic motions to molecules adsorbed onto the clusters.

In a different direction, we developed a Landauer-Büttiker-based theory for plasmonic hot-carrier solar cells (HCSCs)[6] that has provided important insights into fundamental limitations on solar cell efficiency for this type of solar cell. Fig. 2 shows the structural model used for this work, in which is assumed that plasmon excitation produces carriers that transfer through a Schottky barrier to a semiconductor, and then the built-in potential separates electrons and holes for transfer to the external current. The calculation assumes a simple free electron model for the metal, an oscillator model for the plasmon, and a two-state model for the semiconductor. Other important parameters include the electron/plasmon coupling, the electron/semiconductor interaction, hot electron relaxation times, and coupling of the semiconductor to the leads. These parameters are generally known from earlier work and from comparisons with experiment for other device applications. Note that an advantage of this formalism is that the plasmon, electron, and semiconductor degrees of freedom are treated on an equal footing. The results of this application show that HCSC photocurrent rises at energies below the bandgap, as the only significant constraint to the generation of carriers in the semiconductor is that the electrons need surmount the Schottky barrier, and this barrier is below the bandgap. This leads to a low threshold which is good for photovoltaic performance, but plasmon excitation produces a broad range of electron energies and as a result the IQE (internal quantum efficiency) is less than 50% even for photon energies well above the bandgap. We have used extensions of this model to study the efficiency of a solar cell developed by a Japanese group that consisted of gold nanoparticles interacting with TiO_2 electrodes, showing that the ~1% external quantum efficiency that they observed is consistent with the low IQE that we predict. Our analysis also shows us what parameters to change in order to improve this result.

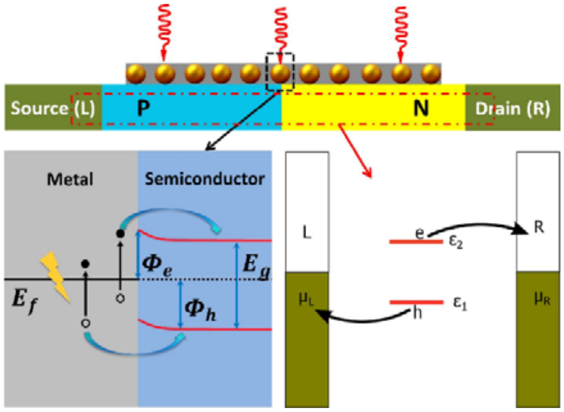


Figure 2. Schematic of hot-carrier solar cell that was studied using Landauer-Buttiker theory. Upper panel: geometry of HCSC. Arrays of spherical nanoparticles are deposited on the top of a pn junction semiconductor. Left bottom panel: Schematic of hot carrier generation and injection over a Schottky barrier to a semiconductor; Right bottom panel: A two-level system is used to model the conduction and valence band of semiconductor. The collected hot-carriers in the semiconductor are driven in different directions by the built-in potential, resulting in photocurrent generation.

Additional studies have involved electrodynamics calculations for a variety of nanoparticle structures and compositions, often involving collaborations with experimentalists [7-8]. We also worked on the development of a new functional (LDA0) that we now use routinely for TDDFT calculations [9] that combines local density functionals with long range corrected functionals, thereby avoiding unnecessary work to include gradient-corrected contributions at short range. We have applied this functional to determine excited state energies for a variety of benchmark molecules, giving results that are in quantitative agreement with calculations that include gradient effects. Finally we wrote a review article concerned with plasmon-induced hot electron effects, and related SERS studies[10]

Future Plans: Our semiempirical calculations are now at the point where there are a myriad of opportunities available to us for addressing fundamental issues in the plasmonics field. This will begin with a detailed study of the chemical effect in SERS where we properly include for the role of resonant charge transfer effects for the first time, thus addressing a nagging question in the SERS community. Another capability that we will consider is the ability to vary the Fermi energy in INDO by simply shifting the atomic orbital energies of the metal atoms while not changing the corresponding energies of the adsorbates. This capability can be used to study SERS enhancements for electrochemical experiments, which is an important first step for eventually studying hot electron effects for experiments under potential control. Such experiments are perhaps the best class of experiments relevant to hot electron effects. And this further gives us the capability of distinguishing electron transfer that occurs when the Fermi energy of the metal matches the LUMO of the molecule, compared to "hot" electron transfer that occurs for electrons that are produced by plasmon excitation well above the Fermi energy. And a key activity of the INDO work will be to determine the "action spectrum" associated with hot electrons, meaning the population of negative ion states of an adsorbate molecule that are produced following plasmon excitation.

Grant Numbers and Grant Titles

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

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

1. Postdocs: Rebecca Gieseking (12), Yu Zhang (6), Martin Mosquera (1), Clotilde Lethiec (1)
2. Students: Lindsey Madison (12,p), Adam Ashwell (12), Mike Ross (12,p)

Up to Ten Publications Acknowledging the Grant (all in the last year)

[1]Semiempirical Modeling of Ag Nanoclusters: New Parameters for Optical Property Studies Enable Determination of Double Excitation Contributions to Plasmonic Excitation, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, J. Phys. Chem. A 120, 4542-49 (2016). DOI:10.1021/acs.jpca.6b04520

[2]Quantum mechanical identification of quadrupolar plasmonic excited states in silver nanorods, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, J. Phys. Chem. A, 120, 9324-29 (2016). DOI:10.1021/acs.jpca.6b09649

[3]Implementation of INDO/SCI with COSMO implicit solvation and benchmarking for solvatochromic shifts, Rebecca L. Gieseking, Mark A. Ratner, George DC. Schatz, J. Phys. Chem. A, 120, 9878-85 (2016) DOI:10.1021/acs.jpca.6b10487

[4]A time-dependent density functional theory study of the impact of ligand passivation on the plasmonic behavior of Ag nanoclusters, Adam P. Ashwell, Mark A. Ratner and George C. Schatz, Adv. Quantum. Chem. 1-29 (2017) DOI: 10.1016/bs.aiq.2017.01.011

[5]Dependence of plasmon energies on acoustic normal modes of Ag_n (n=20,84,120) clusters. Clotilde M. Lethiec, Lindsey R. Madison, George C. Schatz, JPC C, 120, 20572-78 (2016). DOI:10.1021/acs.jpcc.5b12497

[6]Fundamental limitations to plasmonic hot-carrier solar cells, Yu Zhang, ChiYung Yam, George C. Schatz, J. Phys. Chem. Lett. 7, 1852-58 (2016) DOI: 10.1021/acs/jpclett.6b00879

[7]In solution SERS sensing using mesoporous silica-coated gold nanorods, Zhe Gao, Nathan D. Burrows, Nicholas A. Valley, George C. Schatz, Catherine J. Murphy, Christy L. Haynes, Analyst 141, 5088-95 (2016) DOI:10.1039/C6AN01159D; E DOI:10.1039/c6an90098d E:141, 6604.

[8]Plasmonic metallurgy enabled by DNA, M. B. Ross, J. C. Ku, B. Lee, C. A. Mirkin, G. C. Schatz, Adv. Mat. 28, 2790–2794 (2016) DOI:10.1002/adma.201505806

[9]Connection between Hybrid Functionals and Importance of the Local Density Approximation, M. A. Mosquera, C. H. Borca, M. A. Ratner and G. C. Schatz, J. Phys. Chem. A, 120, 1605-1612 (2016) DOI: 10.1021/acs.jpca.5b10864

[10]Review of plasmon-induced hot-electron dynamics and related SERS-chemical effects, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, in **Frontiers of Plasmon Enhanced Spectroscopy**, Volume 1, Ed. Y. Ozaki, G. C. Schatz, D. Graham and T. Itoh, ACS Symposium Series Vols. 1245, American Chemical Society, Washington, D. C., 2016, pp 1-22. DOI: 10.1021/bk-2016-1245.ch001

Discontinuous methods for large-scale quantum molecular dynamics: application to the anode-electrolyte interface in Li-ion batteries

John E. Pask[1*], Vincenzo Lordi[1], Lin Lin[2,3], Chao Yang[3], Erik W. Draeger[4], Peer-Timo Bremer[4], Attila G. Gyulassy[5], and Valerio Pascucci[5]

[1]*Physics Division, Lawrence Livermore National Laboratory*
[2]*Department of Mathematics, University of California, Berkeley*
[3]*Computational Research Division, Lawrence Berkeley National Laboratory*
[4]*Center for Applied Scientific Computing, Lawrence Livermore National Laboratory*
[5]*Scientific Computing and Imaging Institute, University of Utah*
* pask1@llnl.gov, DGDFT Collaboration, http://www.dgdft-scidac.org

Abstract

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

In this work, we seek to understand for the first time the detailed chemistry and dynamics at this critical interface by performing quantum molecular dynamics simulations of anode/SEI/electrolyte systems at unprecedented scale; and in so doing, enable fundamental advances in device performance, lifetime, and safety. To reach the necessary length and time scales, we have developed new electronic structure methodologies in collaboration with the SciDAC FASTMath Institute: the Discontinuous Galerkin (DG), Pole Expansion and Selected Inversion (PEXSI), and Complementary Subspace (CS) methods. In addition, to better understand and potentially accelerate the simulations, we have developed new analysis and visualization tools in collaboration with the SciDAC SDAV Institute. The PEXSI code has now been released. Upon completion, the DG, CS, and analysis codes will be released as well.

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

In this work, we have proceeded from pure-electrolyte systems to larger mixed-electrolyte systems to still larger anode-electrolyte interfaces. In studies of Li solvation and diffusion in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and mixed EC/EMC electrolytes [1], we find that Li prefers tetrahedral coordination in all electrolytes considered. Furthermore, we find that the stronger and more enduring the solvation structure, the lower the diffusivity; so that Li diffusion coefficients are significantly smaller than those of more weakly solvated PF_6 counter-ions. In collaboration with the SciDAC SDAV Institute, we carried out relative angle analysis of ion trajectories in EC, EMC, and EC/EMC electrolytes [2,3]. We find complex, non-Brownian dynamics over a range of time scales, with more strongly solvated Li ions manifesting more complex dynamics and more weakly solvated counter-

ions showing more diffusive behavior. At time scales on the order of 2 ps, we find peaks in the relative angle distribution consistent with caging of Li, while at much shorter and longer time scales, we find transitions to ballistic and Brownian motion, respectively [2,3].

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

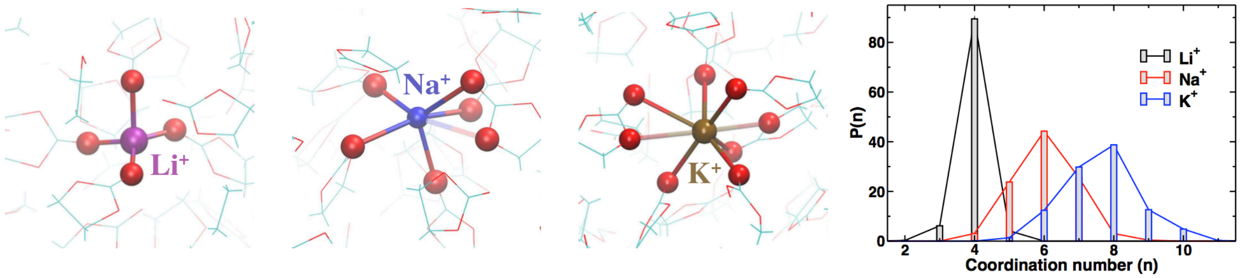


Figure 1: The differing solvation structures of Li^+, Na^+, and K^+ in ethylene carbonate (EC) are illustrated by highlighting the EC oxygen atoms (red spheres) in the first solvation shells from representative snapshots from first-principles molecular dynamics simulations. The histograms at the right show the increased coordination number (CN) and broader distribution of CN with increasing ion size. The first solvation shells of Na^+ and K^+ also involve occasional ether oxygens of EC, as seen in the snapshot for K^+, while Li^+ is always solvated by carbonyl oxygens.

Most recently, we have begun to explore the chemistry and dynamics of Na^+ and K^+ ions (**Figure 1**). In studies of Na^+ and K^+ in EC, we find significant differences in the solvation structure and dynamical properties of Na^+ and K^+ compared to Li^+. In contrast to Li^+, which exhibits a well-defined first solvation shell with a tetrahedral arrangement of carbonyl oxygen atoms of EC molecules, we find that the larger Na^+ and K^+ ions have more disordered solvation structures. We find, furthermore, that these more disordered structures correspond to weaker solvation energies, which in turn correspond to significantly enhanced diffusion, with coefficients 2–3 times larger than Li^+. Such differences have significant implications for battery performance, if realizable in full battery systems.

Going forward, as the new DG based electronic structure methodologies allow, we plan to scale up to larger, more complex interfaces, including model SEI layers in order to understand the intercalation of Li^+ from electrolyte into SEI and SEI into anode, with different edge orientations and external potentials. Indeed, we have initiated smaller-scale investigations of edge-orientation and external potential already. A detailed understanding of the chemistry and dynamics at both interfaces stands to open the way for fundamental advances in device performance, lifetime, and safety.

In collaboration with the SciDAC FASTMath Institute, we have developed and employed new DG, PEXSI, and CS electronic structure methodologies to reach the length and time scales required to understand complex anode-electrolyte systems, and have advanced accuracy beyond conventional LDA and GGA approximations as well [4].

We have developed and implemented accurate, systematically improvable energy and force expressions in the DG basis [5,6], and have carried out static and dynamic calculations on a range of systems. Since the DG basis attains chemical accuracy with tens of basis functions per atom, the size of discrete eigenproblem to be solved is dramatically reduced relative to standard planewave and finite-difference representations, allowing significant reductions in time to solution. However, when problem sizes exceed a few thousand atoms, the cost of subspace diagonalization in Davidson and other such state-of-the-art solvers begins to dominate. To address this, we developed the Projected Preconditioned Conjugate Gradient (PPCG) eigensolver [7], which significantly reduces the number of subspace diagonalizations needed. The new solver has shown 2x speedups in planewave based calculations relative to current state-of-the-art Davidson solvers.

To reach the largest system sizes, the PEXSI methodology [8] has been developed and employed to eliminate the need for diagonalization entirely. The DG and PEXSI codes have now scaled to over 10,000 atoms and 100,000 processors on leadership class supercomputers at LLNL and LBL. However, while PEXSI has provided a breakthrough for low-dimensional systems (quasi-1D and quasi-2D), it has proven less efficient for 3D systems, such as the solid-liquid interfaces studied in the present work.

In order to treat 3D interface systems of 1,000–5,000 atoms efficiently, we implemented Chebyshev filtered subspace iteration (CheFSI) to compute the occupied subspace of the DG Hamiltonian [9]. This has proven particularly effective by virtue of the small size and limited spectral width of the DG Hamiltonian. For a 2D graphene system containing 11,520 atoms and a 3D Li-ion electrolyte system containing 8,586 atoms, the solution times are shown in **Table 1**. For such systems, the advantage of CheFSI is substantial, and all the more so in 3D.

System	ScaLAPACK	PEXSI	CheFSI
Graphene2D	2473	426	80
Li3D	3323	3784	105

Table 1: Wall clock times (in seconds) for 2D graphene system containing 11,520 atoms (Graphene2D) and bulk 3D Li-ion electrolyte system containing 8,586 atoms (Li3D) using DG method with ScaLAPACK, PEXSI, and CheFSI solvers on 13,824 processors on LBL Edison.

Beyond 5,000 atoms, however, even the smaller subspace diagonalization required within CheFSI becomes a bottleneck. To overcome this critical barrier, we have developed a Complementary Subspace (CS) approach, which exploits the fact that the vast majority of states at ambient temperature are either fully occupied or unoccupied, in order to reduce the subspace diagonalization problem to just the few partially occupied states around the Fermi level. In so doing, the cost of subspace diagonalization has now been reduced 1000-fold, essentially to the vanishing point.

Grant Numbers and Grant Titles

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

Postdocs: Mitchell Ong, Anh Pham, Kyoung Kweon, Mathias Jacquelin, Wei Hu, Amartya Banerjee, Harsh Bhatia

Selected Publications Acknowledging these Grants in the last 3-4 years

[1] M. T. Ong, O. Verners, E. W. Draeger, A. C. T. van Duin, Vincenzo Lordi, and John E. Pask, Lithium Ion Solvation and Diffusion in Bulk Organic Electrolytes from First Principles and Classical Reactive Molecular Dynamics, *J Phys. Chem. B* **119**, 1535–1545, 2015.

[2] M. T. Ong, H. Bhatia, A. G. Gyulassy, E. W. Draeger, V. Pascucci, P.-T. Bremer, V. Lordi, and J. E. Pask, Complex Ion Dynamics in Carbonate Lithium-Ion Battery Electrolytes, *J. Phys. Chem. C.* **121**, 6589–6595, 2017.

[3] H. Bhatia, A. G. Gyulassy, V. Pascucci, M. Bremer, M. T. Ong, V. Lordi, E. W. Draeger, J. E. Pask, and P.-T. Bremer, Interactive Exploration of Atomic Trajectories Through Relative-Angle Distribution and Associated Uncertainties, *Proceedings of the 9th IEEE Pacific Visualization Symposium*, pp. 120–127, Taipei, Taiwan. Apr 19–22, 2016.

[4] W. Hu, L. Lin, A. Banerjee, E. Vecharynski and C. Yang, Adaptively compressed exchange operator for large scale hybrid density functional calculations with applications to the adsorption of water on silicene, *J. Chem. Theory Comput.* **13**, 1188, 2017.

[5] G. Zhang, L. Lin, W. Hu, C. Yang, and J.E. Pask, Adaptive local basis set for Kohn-Sham density functional theory in a discontinuous Galerkin framework II: Force, vibration, and molecular dynamics calculations, *J. Comput. Phys*. **335**, 426 2017.

[6] W. Hu, L. Lin, and C. Yang, DGDFT: A massively parallel method for large scale density functional theory calculations, *J. Chem. Phys.* **143**, 124110, 2015.

[7] E. Vecharynski, C. Yang, and J.E. Pask, A projected preconditioned conjugate gradient algorithm for computing many extreme eigenpairs of a Hermitian matrix, *J. Comput. Phys*. **290**, 73–89, 2015.

[8] M. Jacquelin, L. Lin, and C. Yang, PSelInv – A distributed memory parallel algorithm for selected inversion: the symmetric case, *ACM Trans. Math. Software* **43**, 21, 2016.

[9] A. Banerjee, L. Lin, W. Hu, C. Yang, and J. E. Pask, Chebyshev polynomial filtered subspace iteration in the Discontinuous Galerkin method for large-scale electronic structure calculations, *J. Chem. Phys.* **145**, 154101, 2016.

[10] R. Li, Y. Xi, E. Vecharynski, C. Yang, and Y. Saad, A Thick-Restart Lanczos algorithm with polynomial filtering for Hermitian eigenvalue problems, *SIAM Journal on Scientific Computing* **38**, A2512–A2534, 2016.

Polarizability trends in clusters plus new results for self-interaction corrections

Koblar A. Jackson

Physics Department and Science of Advanced Materials Ph.D. Program
Central Michigan University, Mt. Pleasant, MI 48859

Abstract

Our program's research is focused on the properties of atomic clusters, small bits of matter containing up to a few hundred atoms. Clusters are the small-size limit of bulk matter and their properties are of interest for both fundamental reasons and for applications. On the fundamental side, we are interested in how the behavior of matter changes as the size scale is shrunk down to sub-nanometer range. What happens to the physical and chemical attributes of a material in samples containing handfuls of atoms? A particular interest has been in the electrical properties of clusters. Because of their small size, the electronic energy levels in clusters are discrete, so that a characterization of electrical properties based on energy band concepts is inappropriate. Instead, we study the dipole polarizability as a guide to a cluster's response to applied electric fields. Using techniques developed in our group, we analyze the total polarizability into site-specific contributions and further into components that can be linked to charge transfer between atoms or to changes in how the charge density in the vicinity of each atom is arranged. This analysis gives a more detailed view of the response of clusters than can be obtained experimentally. We recently published a study of the trends in silicon cluster polarizabilities which indicates metallic behavior in clusters up to sizes of around 150 atoms. There is also the suggestion of a transition to non-metallic behavior for slightly larger clusters. In addition, we are currently analyzing data from calculations on several metal cluster systems, as well as a series of alkali-halide clusters. Taken together, these calculations will give new insight into the evolution of electronic behavior in metal, semiconductor, and insulator clusters into the bulk.

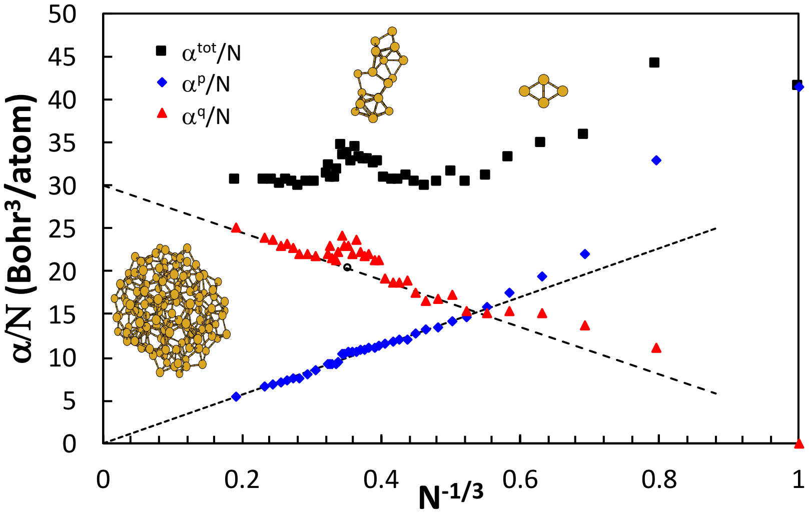


Fig. 1 Per-atom values of α, α^p, and α^q for Si_N. The dashed lines are included as guides to the eye. Representative cluster structures are shown for various sizes.

On the more applied side, we have been interested in the promise of cluster-based heterogeneous catalysis. The atoms in a cluster reside almost exclusively on the surface, where each can participate directly in chemical reactions. This makes clusters very atom-efficient as catalysts in comparison to larger particles where an overwhelming majority of the atoms are buried in the particle's interior and are

therefore not accessible for reactions. A particular interest has been the interaction of H_2 with clusters containing Pd atoms.

A new effort in our group is aimed at removing self-interaction errors from density functional theory (DFT) calculations using the Fermi-orbital-based approach introduced recently by Pederson, Perdew, and Ruzsinszky.[1] In conventional DFT, the treatment of the interactions between the electrons results in a residual, unphysical self-interaction that is responsible for a number of problems in DFT calculations. For example, DFT electron energy levels are invariably too high, making them poor approximations of electron removal energies. The new FLO-SIC method implements the well-known Perdew-Zunger self-interaction correction[2] (SIC), while avoiding a computational bottleneck that has kept prior implementations from more widespread use. Our group has recently obtained FLO-SIC solutions for atoms from Li-Kr. Our SIC total energies for the atoms agree with the results of previous SIC calculations[3] and we find that the energy level of the highest occupied electronic state (HOMO) is a good approximation of the first ionization energy in all the FLO-SIC atomic calculations. We plan to turn our attention next to transition metal-containing molecules. The solutions for the atoms are expected to provide good starting points for these calculations.

References:

[1] M. R. Pederson, A. Ruzsinszky, and J. P. Perdew, “Communication: Self-interaction correction with unitary invariance in density functional theory”, J. Chem. Phys. **140**, 121103 (2014).
[2] M. R. Pederson, “Fermi orbital derivatives in self-interaction corrected density functional theory: Applications to closed-shell atoms”, J. Chem. Phys. **142**, 064112 (2015).
[3] O. A. Vydrov and G. E. Scuseria, “Effect of the Perdew-Zunger self-interaction correction on the thermochemical performance of approximate density functionals”, J. Chem. Phys. **121**, 8187 (2004).

Grant Numbers and Grant Titles: DE-SC0001330 The Physics and Chemistry of Cluster-based Catalyst Systems

Postdoc(s): Der-You Kao

Student(s): Kushantha Withanage

Publications acknowledging this grant in the last 3-4 years

[1] *Si clusters are more metallic than bulk Si.* K. Jackson and J. Jellinek, J. Chem. Phys. **145**, 244302 (2016).
[2] *Local spin density treatment of Substitutional Defects in Ionic Crystals with Self-Interaction Corrections.* K. Jackson, Advances in Atomic, Molecular, and Optical Physics **64**, 15 (2015).
[3] *Site specific atomic polarizabilities in endohedral fullerenes and carbon onions.* R. Zope, S. Bhusal, T. Baruah and K. A. Jackson, J. Chem. Phys. **143**, 084306 (2015).
[4] *H_2 Saturation on Palladium Clusters.* A. Pelzer, K. A. Jackson, and J. Jellinek, J. Phys. Chem. A **119**, 3594 (2015).
[5] *Site-specific polarizabilities from analytic linear response theory.* J. E. Peralta, V. Barone, and K. A. Jackson, Chem. Phys. Lett. **608**, 24 (2014).
[6] *Investigating the metallic behavior of Na clusters using site specific polarizabilities.* L. Ma, K. A. Jackson, M. Yang, J. Jellinek, and M. Horoi, Phys. Rev. B **89**, 035429 (2014).
[7] *H_2 reactions on Palladium clusters.* A. Pelzer, K. A. Jackson, and J. Jellinek, J. Phys. Chem. A **117**, 10407 (2013).

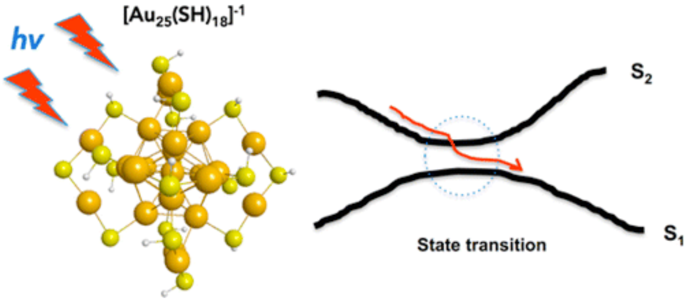
Electron and Electron-Nuclear Dynamics in Gold and Silver Nanoparticles

Christine M. Aikens

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

Abstract

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



In this work, photoexcitation in the $Au_{25}(SR)_{18}^-$, $Au_{38}(SR)_{24}$, and $Au_{22}(SR)_{16}$ 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 differences in the time scales for the observed electron dynamics are apparent for the methyl and ethyl ligands. Additional work is underway to understand the origins of these differences. This work will be presented during the poster session (if applicable). NA calculations are also in progress for the $Au_{25}(SH)_{18}^-$ system on a $(TiO_2)_{38}$ cluster.

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.

Electron dynamics within pure silver and gold clusters have also been examined. Electronic excitation can move among excited state modes, yielding one mechanism for plasmon decay. Furthermore, nuclear motion contributes to dephasing of the plasmon.

Grant Numbers and Grant Titles

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

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

Publications

- Photoluminescence Origin of $Au_{38}(SR)_{24}$ and $Au_{22}(SR)_{18}$ Nanoparticles: A Theoretical Perspective. K. L. D. M. Weerawardene, E. B. Guidez, C. M. Aikens, submitted to *J. Phys. Chem. C*.
- Theoretical Investigation of Electron and Nuclear Dynamics in the $[Au_{25}(SH)_{18}]^{-1}$ Thiolate-Protected Gold Nanocluster. R. Senanayake, A. V. Akimov, C. M. Aikens, *J. Phys. Chem. C*, DOI: 10.1021/acs.jpcc.6b09731 (Special Issue for ISSPIC XVIII: International Symposium on Small Particles and Inorganic Clusters 2016). http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.6b09731
- Theoretical Insights into the Origin of Photoluminescence of $Au_{25}(SR)_{18}^{-}$ Nanoparticles. K. L. D. M. Weerawardene, C. M. Aikens, *J. Am. Chem. Soc.*, **2016**, *138*, 11202-11210. http://pubs.acs.org/doi/abs/10.1021/jacs.6b05293
- Real-time TDDFT Studies of Exciton Transfer and Decay in Silver Nanowire Arrays. B. Peng, D. Lingerfelt, F. Ding, C. M. Aikens, X. Li, *J. Phys. Chem. C*, **2015**, *119*, 6421-6427. http://pubs.acs.org/doi/abs/10.1021/acs.jpcc.5b00263

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

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

Program Scope

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

Recent Progress

Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames. In a recent *J. Phys. Chem. A* Feature Article,[9] we addressed the formation mechanisms of naphthalene and indene, which represent prototype PAH carrying two six-membered and one five- plus a six-membered ring. Theoretical studies of the relevant chemical reactions were overviewed in terms of their potential energy surfaces, rate constants, and product branching ratios; these data were compared with experimental measurements in crossed molecular beams and in the pyrolytic chemical reactor emulating the extreme conditions in the interstellar medium (ISM) and the combustion-like environment, respectively. The outcome of the reactions potentially producing naphthalene and indene was shown to critically depend on temperature and pressure or collision energy and hence the reaction mechanisms and their contributions to the PAH growth can be rather different in the ISM, planetary atmospheres, and in combustion flames at different temperatures and pressures. Specifically, this paradigm was illustrated with new theoretical results for rate constants and product branching ratios for the reaction of phenyl radical with vinylacetylene. The analysis of the formation mechanisms of naphthalene and its derivatives shows that in combustion they can be produced via Hydrogen-Abstraction-aCetylene-Addition (HACA) routes, recombination of cyclopentadienyl radical with itself and with cyclopentadiene, the reaction of benzyl radical with propargyl, methylation of indenyl radical, and the reactions of phenyl radical with vinylacetylene and 1,3-butadiene. In extreme astrochemical conditions, naphthalene and dihydronaphthalene can be formed in the C_6H_5 + vinylacetylene and C_6H_5 + 1,3-butadiene reactions, respectively. Ethynyl-substituted naphthalenes can be produced via the ethynyl addition mechanism beginning with benzene (in dehydrogenated forms) or with styrene.

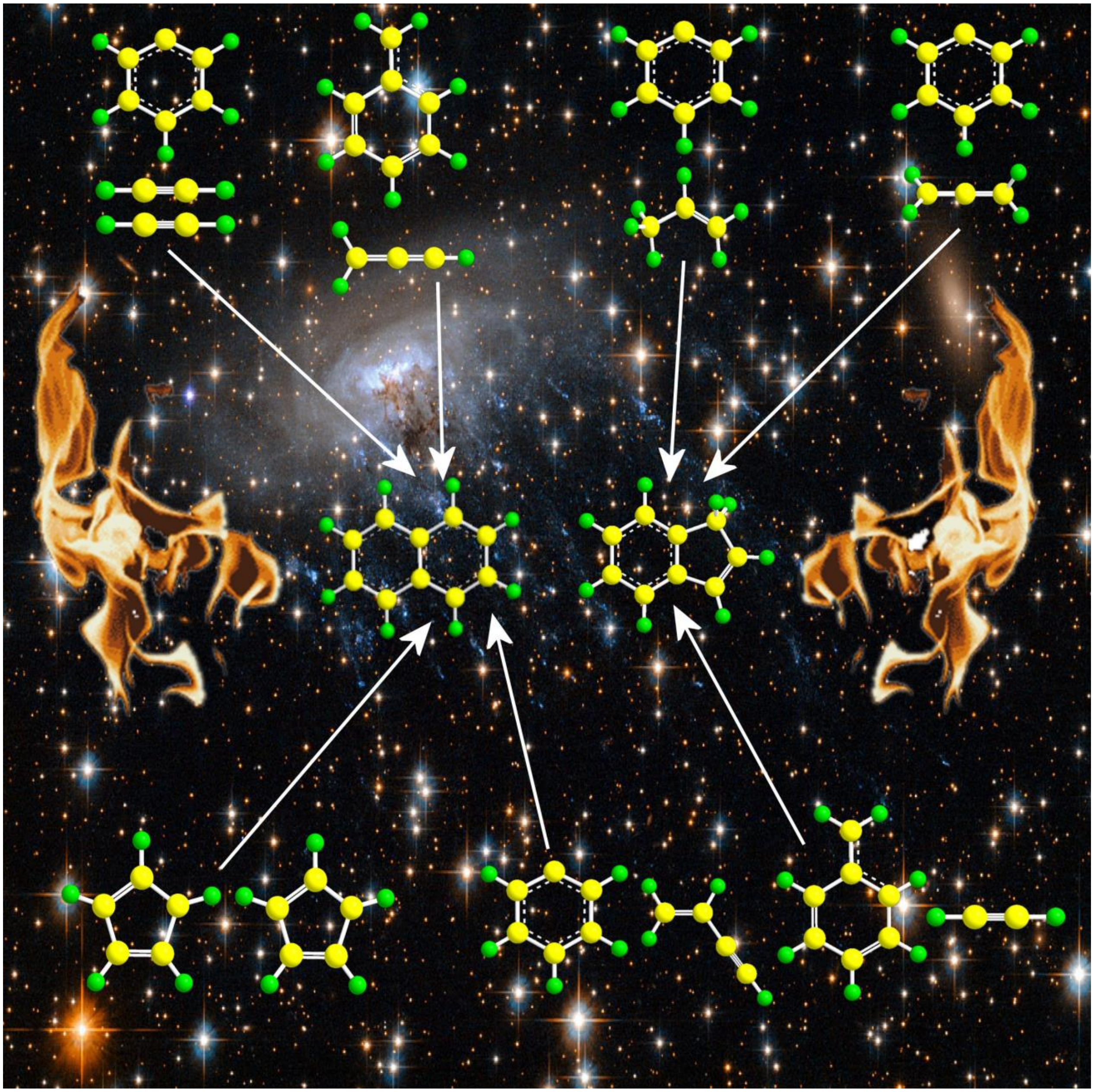


Figure 1. Chemical reactions forming naphthalene and indene in interstellar space and in combustion (cover art from *J. Phys. Chem. A*, volume 121, issue 6, February 16, 2017).

We employed the ab initio RRKM - Master Equation approach to predict the rate constants involved in the formation of indene and its conversion to naphthalene.[7] The reactions eventually leading to indene involve C_9H_x (x = 8-11) potential energy surfaces (PESs) and include $C_6H_5 + C_3H_4$ (allene and propyne), $C_6H_6 + C_3H_3$, benzyl + C_2H_2, $C_6H_5 + C_3H_6$, $C_6H_6 + C_3H_5$, and $C_6H_5 + C_3H_5$. These predictions allowed us to make a number of valuable observations on the role of various mechanisms. For instance, we demonstrated that reactions which can significantly contribute to the formation of indene include phenyl + allene and H-assisted isomerization to indene of its major product, 3-phenylpropyne, benzyl + acetylene, and the reactions of the phenyl radical with propene and allyl radical, both proceeding via the 3-phenylpropene intermediate. 3-phenylpropene can be activated to 1-phenylallyl radical, which in turn rapidly decomposes to indene. Next, indene can be converted to benzofulvene or naphthalene under typical combustion conditions via its activation by H atom abstraction and methyl substitution on the five-member ring followed by isomerization and decomposition of the resulting 1-methylindenyl radical, $C_{10}H_9 \rightarrow C_{10}H_8 + H$. Alternatively, the same region of the $C_{10}H_9$ PES can be accessed through the reaction of benzyl with propargyl, $C_7H_7 + C_3H_3 \rightarrow C_{10}H_{10} \rightarrow C_{10}H_9 + H$, which therefore can also contribute to the formation of benzofulvene or naphthalene. Benzofluvene easily transforms to naphthalene by H-assisted isomerization. An analysis of the effect of pressure on the reaction outcome and relative product yields was given and modified Arrhenius fits of the rate constants were reported for the majority of the considered reactions. Ultimately, the implementation of such expressions in detailed kinetic models will help quantify the role of these reactions for PAH growth in various environments.

Combined experimental and theoretical studies of the formation of naphthalene and phenanthrene 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 revealed the fundamental chemistry of the styrenyl and the ortho-vinylphenyl radicals (C_8H_7)—key transient species of the HACA mechanism—with acetylene and provided the first solid experimental evidence on the facile formation of naphthalene in a simulated combustion environment validating the previously theoretically proposed HACA mechanism for these two radicals.[5,8] Our study highlighted, at the molecular level spanning combustion and astrochemistry, the importance of the HACA mechanism to the formation of the prototype PAH naphthalene. In another work, by exploring the previously unknown chemistry of the ortho-biphenylyl radical with acetylene, we demonstrated the efficient synthesis of phenanthrene in carbon-rich circumstellar environments.[10] However, the lack of formation of the anthracene isomer implies that HACA alone cannot be responsible for the formation of PAHs in extreme environments.

Future Plans

The main goal of this project will continue to be unraveling reaction mechanisms and generating reliable temperature- and pressure-dependent rate constants for various processes in PAH formation, growth, and oxidation. To accomplish this goal we will convert PESs of the pertinent reactions into pressure- and temperature-dependent rate constants using the eigenvalue-based RRKM-ME code developed by Klippenstein and co-workers. In the new three-year project period we will focus on the following systems: 1) the remaining reactions and pathways leading to the formation of naphthalene and indene, such as $C_5H_5 + C_5H_5/C_5H_6$, $C_7H_7 + C_3H_3$, and $C_6H_5 + C_3H_5$, the kinetics of which have not yet been explored; 2) reactions producing three-ring PAHs, such as anthracene, phenanthrene, and acenaphthalene, including HACA routes and the reactions of naphthyl and indenyl radicals with C_4H_6, C_3H_4, and C_4H_4; 3) HACA mechanism in larger PAHs via acetylene addition to zigzag and arm-chair edges; 4) oxidation of six- and five-member rings in aromatic and PAH radicals such as phenanthryl, anthracyl, cyclopentadienyl, indenyl, and acenaphthyl. The rate constants will be included in the latest combustion models in collaboration with S. Klippenstein, L. Harding, Y. Georgievskii, R. Sivaramakrishnan, J. Miller, and M. Frenklach. We will continue our collaborations with R. Kaiser's and M. Ahmed's groups on the studies of combustion-relevant bimolecular reactions in crossed beams and in the pyrolytic reactor at LBNL, with A. Suits on photodissociation of pyridine, and with R. Tranter on the roaming dynamics of Cl reactions with hydrocarbons.

Grant Number and Grant Title

DE-FG02-04ER15570 Theoretical studies of chemical reactions related to the formation and growth of polycyclic aromatic hydrocarbons and molecular properties of their key intermediates
Postdoc: None
Students: Joao Marcelo Ribeiro, Daniel Belisario-Lara

DOE/BES sponsored publications (2014-2017)

1. Kislov V.V., Singh R.I., Edwards D.E, Mebel A.M., Frenklach M., “Rate coefficients and product branching ratios for the oxidation of phenyl and naphthyl radicals: A theoretical RRKM-ME study”, Proc. Int. Combust. Inst. 2015, 1861-1869.
2. Singh R.I., Mebel A.M., Frenklach M., “Oxidation of graphene-edge six- and five-member rings by molecular oxygen”, J. Phys. Chem. A 2015, 119, 7528-7547.
3. Mebel A.M., Kaiser R.I., “Formation of resonantly stabilised free radicals via the reactions of atomic carbon, dicarbon, and tricarbon with unsaturated hydrocarbons: Theory and crossed molecular beams experiments”, Int. Rev. Phys. Chem. 2015, 34, 461-514.
4. Ribeiro J.M., Mebel A.M., “Reaction mechanism and product branching ratios of the CH + C_3H_6 reaction: A theoretical study”, J. Phys. Chem. A 2016, 120, 1800-1812.
5. Yang T., Troy T.P., Xu B., Kostko O., Ahmed M., Mebel A.M., Kaiser R.I., “Hydrogen-Abstraction/Acetylene-Addition Exposed”, Angew. Chem. Int. Ed. 2016, 55, 14983-14987.
6. Thomas A.M., Yang T., Dangi B.B., Kaiser R.I., Kim G.S., Mebel A.M., “Oxidation of the para-Tolyl Radical by Molecular Oxygen under Single-Collision Conditions: Formation of the para-Toloxy Radical”, J. Phys. Chem. Lett. 2016, 24, 5121-5127.
7. Mebel A.M., Georgievskii Y., Jasper A.W., Klippenstein S.J., “Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene”, Faraday Discuss. 2016, 195, 637-670.
8. Mebel A.M., Georgievskii Y., Jasper A.W., Klippenstein S.J., “Temperature- and Pressure-Dependent Rate Coefficients for the HACA Pathways from Benzene to Naphthalene”, Proc. Int. Combust. Inst. 2017, 36, 919-926.
9. Mebel A.M., Landera A., Kaiser R.I., “Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames”, Feature Article, J. Phys. Chem. A 2017, 121, 901–926.
10. Yang T., Kaiser R.I., Troy T.P., Xu B., Kostko O., Ahmed M., Mebel A.M., Zagidullin M.V., Azyazov V.N., “HACA’s Heritage: A Free Radical Pathway to Phenanthrene in Circumstellar Envelopes of Asymptotic Giant Branch Stars”, Angew. Chem. Int. Ed. 2017, DOI: 10.1002/ange.201701259.

Modeling photoionization and photodetachment phenomena in the gas and condensed phase

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

Summary of recent major accomplishments

During the past year, we conducted several computational studies of open-shell and electronically excited species. The common theme in these studies is interactions between states of different character and intersections between the corresponding potential energy surfaces. We also continued to develop and benchmark computational methods for modeling electronic structure and spectroscopy of open-shell species. Particular emphasis was placed on determining spectroscopic signatures of transient species, to facilitate comparisons with experimental data. The following representative publications supported by DOE highlight selected recent results.[1–10]

Highlight: Dyson orbitals and absolute cross sections for photoionization

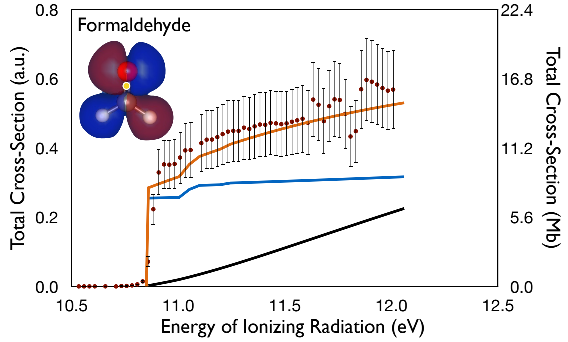


Figure 1: Absolute photoionization cross-section (in atomic units) for formaldehyde. Red dots show the experimental values. Blue and black lines correspond to the cross-sections computed using the Coulomb (Z=1) and plane (Z=0) waves, respectively. Orange line denotes cross-sections computed using the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

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

$$\phi^d(1) = \sqrt{N} \int \Psi^I(1,2,\ldots,N)\Psi^F(2,\ldots,N)d2\ldots dNy \tag{1}$$

We employed correlated Dyson orbitals and tested approximate treatments of the photoelectron wave function, that is, plane and Coulomb waves, by comparing computed and experimental photoionization/photodetachment spectra.[2] Using this simple description of the ejected electron, we were able to reproduce experimental cross-sections for a large set of molecules. This model is implemented in the *ezDyson* code, which is a free software available for download from the *iOpenShell* website; it provides a convenient tool for quick evaluations of the electronic cross-sections. We have applied this approach to aid the interpretation of experiments conducted in Prof. Kaiser group[6] and to study electronic structure of solvated electrons.[7]

Highlight: Photoionization of amino-acids in the gas and condensed phase

In collaboration with Dr. M. Ahmed from LBNL, we are investigating VUV and X-ray photoionization of amino-acids in the gas and condensed phases. Our calculations have shown that VUV photoionization of arginine leads to prompt and extensive fragmentation, explaining low observed yield of the parent ion. Our calculations of arginine in aqueous solution quantified the spectroscopic signatures of different protonation states.

We have also developed new coupled-cluster based approach for core-ionized states. Our benchmark calculations of core-ionized glycine in aqueous solutions have shown that our approach is capable of describing chemical shifts with quantitative accuracy. The results highlight the importance of specific solvent interactions.

Research highlight: Current developments and future plans

In the near future, we plan to complete the following:
(i) finalize the paper on modeling core-ionized states of glycine for publication;
(ii) finalize the paper on modeling arginine photoionization in the gas and condensed phase for publication;
(iii) finalize the implementation of non-adiabatic couplings (NACs) within EOM-CC framework;
(iv) benchmark EOM-CC NACs against MRCI;
(v) continue investigations of spin-forbidden channels in combustion (Cvetanovic diradicals).

Grant numbers and grant titles

Theoretical modeling of spin-forbidden channels in combustion reactions, DE-FG02-05ER15685.
Simulating the Generation, Evolution and Fate of Electronic Excitations in Molecular and Nanoscale Materials with First Principles Methods, coPI, joint with M. Head-Gordon *et al.*
Postdocs: Dr. Samer Gozem, Dr. Ilya Kaliman.
Students: Anastasia Gunina, Arman Sadybekov, Natalie Orms, Xintian Feng.

References

[1] E. Epifanovsky, K. Klein, S. Stopkowicz, J. Gauss, and A.I. Krylov, Spin-orbit couplings within the equation-of-motion coupled-cluster framework: Theory, implementation, and benchmark calculations, J. Chem. Phys. **143**, 064102 (2015).

[2] S. Gozem, A.O. Gunina, T. Ichino, D.L. Osborn, J.F. Stanton, and A.I. Krylov, Photoelectron wave function in photoionization: Plane wave or Coulomb wave?, J. Phys. Chem. Lett. **6**, 4532 (2015).

[3] N.V. Korovina, S. Das, Z. Nett, X. Feng, J. Joy, A.I. Krylov, S.E. Bradforth, and M.E. Thompson, Singlet fission in a covalently linked cofacial alkynyltetracene dimer, J. Am. Chem. Soc. **138**, 617 (2016).

[4] X. Feng and A.I. Krylov, On couplings and excimers: Lessons from studies of singlet fission in covalently linked tetracene dimers, Phys. Chem. Chem. Phys. **18**, 7751 (2016).

[5] X. Feng, D. Casanova, and A.I. Krylov, Intra- and inter-molecular singlet fission in covalently linked dimers, J. Phys. Chem. C **120**, 19070 (2016).

[6] M.J. Abplanalp, S. Gozem, A.I. Krylov, C.N. Shingledecker, E. Herbst, and R.I. Kaiser, Formation of interstellar aldehydes and enols - tracers of a cosmic-ray driven non-equilibrium synthesis of complex organic molecules, Proc. Nat. Acad. Sci. **113**, 7727 (2016).

[7] A.O. Gunina and A.I. Krylov, Probing electronic wave functions of sodium-doped clusters: Dyson orbitals, anisotropy parameters, and ionization cross-sections, J. Phys. Chem. A **120**, 9841 (2016).

[8] I. Kaliman and A.I. Krylov, New algorithm for tensor contractions on multi-core CPUs, GPUs, and accelerators enables CCSD and EOM-CCSD calculations with over 1000 basis functions on a single compute node, J. Comput. Chem. **38**, 842 (2017).

[9] S. Manzer, E. Epifanovsky, A.I. Krylov, and M. Head-Gordon, A general sparse tensor framework for electronic structure theory, J. Chem. Theory Comput. **13**, 1108 (2017).

[10] E.S. Subramaniam Iyer, A. Sadybekov, O. Lioubashevski, A.I. Krylov, and S. Ruhman, Rewriting the story of excimer formation in liquid benzene, J. Phys. Chem. A **121**, 1962 (2017).

Tunna Baruah

DFT for molecular ground and excited states

Yoh Yamamoto, Kamal Nyaupane, Tunna Baruah

Department of Physics, University of Texas at El Paso, El Paso, TX, 79968
Email: tbaruah@utep.edu

Abstract

The accurate description of the molecular states using density functional theory approximations is important for accurate predictive capability. In this regard, recent developments of new functional and methods require extensive testing on various properties. We have applied the recently developed SCAN functional to describe various properties such as magnetic anisotropy energies, excited state properties, and spin states. Another recent novel idea is the incorporation of self-interaction corrections to DFT calculations through a set of local orbitals known as Fermi-Lowdin orbitals. We have also tested the Fermi orbital self-interaction method to describe the various spin states of atoms and molecules. The work presented here were carried out using the NRLMOL code.

Recently, a number of pure GGA and meta-GGA functionals, as implemented in LIBXC exchange-correlation library was incorporated in to the NRLMOL code as part of the project. Apart from these we have also implemented recently published Strongly Constrained and Appropriately Normed (SCAN) meta-GGA functional. The SCAN functional is strongly constrained to satisfy all the known 17 constraints for density functionals. One of the preliminary applications of the SCAN functional is on the spin state of the de-oxy heme molecule. The GGA functionals generally tend to stabilize the low-spin states, which is reversed with the meta-GGA functionals. However, we found that with TPSS functional the low-spin state is preferred. On the other hand the situation is rectified with the application of the SCAN functional. This is also in excellent agreement with a recent application of self-interaction correction through Fermi-orbitals to the de-oxy heme molecule. In another application, the exchange couplings in model H-He-H system was tested at different separations and similarly for $[Cu_2Cl_6]^{2-}$ with different angles. The magnetic anisotropy energies of Mn12 magnetic molecule also showed significantly different barrier from other GGA functionals.

We have also tested the spin states of molecules using this functional. One of the test systems is $Fe(O_2)_2$ molecule in its neutral state. We have earlier reported that the SCAN results do not compare with the multi-reference calculations. This leads to the question whether the application of self-interaction can help in the correct description of the spin states. We have applied the recently developed Fermi-Lowdin orbital based self-interaction correction method to the FeO4 clusters where the Fe is in various charge states. The Fermi-Lowdin orbital based SIC method has earlier been applied to closed shell molecular systems such as benzene, porphyrin, C60, and pentacene by our group. The challenges in this method basically arises from the positions of the Fermi orbital descriptors which need to be optimized to variationally determine the total energy. Depending on the charge states of the Fe ion, the clusters can have different geometries. The correct description of the spin states and energy ordering of the clusters is where the traditional DFT functionals do not compare with multi-reference methods. The Fermi orbital descriptors for a closed shell atom follow the shell structure with the descriptors for sp3 hybridized orbitals forming a tetrahedral around the atom. The partially filled 3d orbitals can be

challenging with many possibilities. Below we show one set of the descriptor positions for Fe in +3 charge state. This work is in progress.

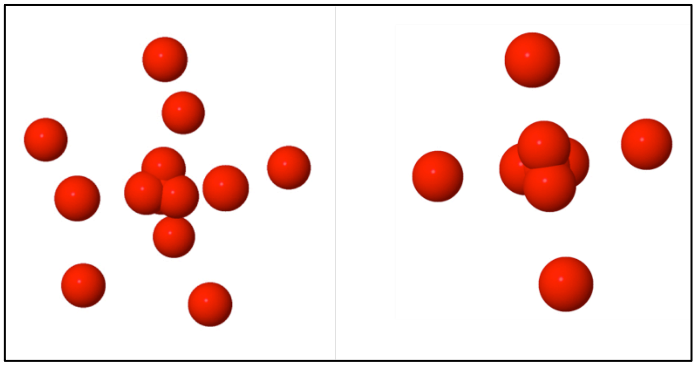


Fig.1 : Fermi orbital descriptor positions for majority and minority sin channels in Fe^{3+}.

One of the recently completed projects involved the description of the excited states of a set of porphyrin and extended porphyrin-like macrocycle called smaragdyrin linked to acceptor molecules. The acceptor molecules are fullerenes and graphene oxide nanoflake. The results showed that the graphene oxide interacts strongly with the donor molecules compared to a fullerene. Although the donor components have similar macrocycles, their interactions with the nano-carbons are quite dissimilar.

The future plan is to extend the applications of the SIC method to extended systems with transition metals and also for light harvesting molecules. This is important from the point that the correct description of the electronic levels particularly the frontier levels is important for light harvesting or excited state properties.

DE-SC0002168: DFT based methods for light harvesting molecules

Postdoc(s): Yoh Yamamoto

Student(s): Kamal Nyaupane

1. Spin states of FeO4 molecule using self-interaction correction, Y. Yamamoto, K. Nyaupane, T. Baruah (in preparation).
2. Excited States of Light-Harvesting Systems Based on Fullerene/Graphene Oxide and Porphyrin/Smaragdyrin, Gloria Cárdenas-Jirón , Merlys Borges-Martínez, Ember Sikorski, and Tunna Baruah, Journal of Physical Chemistry C, DOI: 10.1021/acs.jpcc.6b12452.
3. *Electronic and Optical Properties of VSc2N@C68 Fullerene* Shusil Bhusal, Rajendra R. Zope, Surendra Bhatt, Tunna Baruah, J. Phys. Chem. C (2016).
4. *Electronic and Structural Properties of C60 and Sc3N@C80 Supported on Graphene Nanoflakes*, J. U. Reveles-Ramirez, Nakul N. Karle, Tunna Baruah, and Rajendra R. Zope, J. Phys. Chem. C 120, 26083 (2016).
5. *Density functional study of the electronic structure of dye-functionalized fullerenes and their model donor-acceptor complexes containing P3HT*, Tunna Baruah, Amanda Garnica, Marina Paggen, Luis Basurto, and Rajendra Zope, J. Chem. Phys. 144, 144304 (2016).
6. *Density functional investigation of the electronic structure and charge transfer excited states of a multichromophoric antenna*, L. Basurto, Rajendra R. Zope, Tunna Baruah, Chem. Phys. 469, 1 (2016).
7. *Site specific atomic polarizabilities in endohedral fullerenes and carbon onions* Rajendra R. Zope, S. Bhusal, L. Basurto, Tunna Baruah, and Koblar Jackson, J. Chem. Phys. 143 084306 (2015).
8. *Crystalline Alloys of Organic Donors and Acceptors Based on TIPS-Pentacene*

Jes B. Shrman, Kai Moncino, Tunna Baruah, Guang Wu, Sean R. Parkin, Balaji Purushothaman, Rajendra Zope, John Anthony,and Michael Chabinyc, J. Phys. Chem C 119, 20823 (2015).

9. *The electronic structure and charge transfer excited states of the endohedral trimetallic nitride C80 (Ih) fullerenes–Zn-tetraphenyl porphyrin dyads*, Luis Basurto, Fatemeh Amerikheirabadi, Rajendra Zope and Tunna Baruah, Phys. Chem. Chem. Phys. 17, 5832 (2015).
10. *Al12Cu Superatom as Stable Building Block of Ionic Salts*, J. U. Reveles, T. Baruah, and Rajendra Zope, Jounal of Physical Chemistry C 119, 5129 (2015).
11. *FeO2/MgO(1 0 0) supported cluster: Computational pursual for a low-cost and low-temperature CO nanocatalyst*, A.Y. Zamora, J.U. Reveles, R. Mejia-Olvera, T. Baruah, and R.R. Zope, Chemical Physics Letters, 612, 117 (2014).
12. *The effect of structural changes on charge transfer states in a light-harvesting carotenoid-diaryl-porphyrin-C60 molecular triad*, Marco Olguin, Luis Basurto, Rajendra R. Zope, and Tunna Baruah, Journal of Chemical Physics, 140, 204309 (2014).
13. Excited Electronic States of Porphyrin-Based Assemblies Using Density Functional Theory Gloria I. Cárdenas-Jirón, Tunna Baruah, Rajendra R. Zope, in Handbook of Porphyrin Science (World Scientific Publishing Company), Volume 42: Towards Tuned Properties of Porphyrinoids, Edited by: Karl M Kadish (University of Houston, USA), Kevin M Smith (Louisiana State University, USA), Roger Guilard (Université de Bourgogne, France), September 2016, pp. 233-289.

Margaret S. Cheung

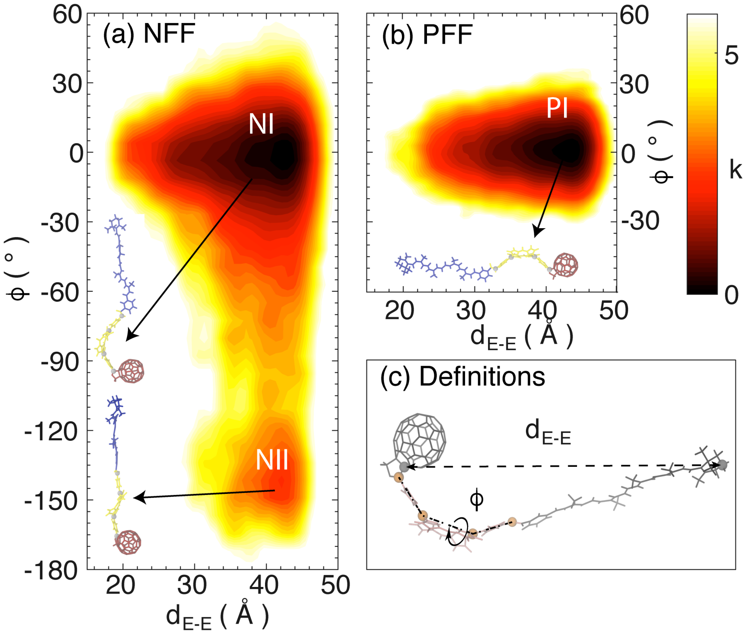
Induced Polarization Restricts Conformational distribution of Conformation of a Light-Harvesting Molecular Triad in Ground State

Oleg N. Starovoytov,[1] Pengzhi Zhang,[1] Piotr Cieplak,[2] and Margaret S. Cheung[1,]

[1] Department of Physics, University of Houston, Houston, Texas 77204, United States
[2] Sanford Burnham Prebys Medical Discovery Institute, La Jolla, California 92037, United States

Abstract

A light-harvesting molecular triad consisting of carotenoid polyene (C), diaryl-porphyrin (P) and pyrrole-fullerene (C_{60}) is a donor-acceptor molecule capable of absorbing incident light in the visible range. Its ability of converting chemical energy from solar energy suggests its great potential in turning into a real-world application. The ensemble of its conformations in ambient conditions varies widely according to its electronic states. However, due to lack of polarization that impacts the subtle charge distribution on atoms, the molecular simulations fail to produce accurate average dipole moments. We developed the first polarizable model for a molecular triad to investigate the structural and dynamic properties of a molecular triad in the ground state in explicit organic solvent, tetrahydrofuran (THF). We performed the first-principles electronic structure calculations of the individual components from a triad as well as THF, followed by fitting the partial atomic charges to the electrostatic potential using an i-RESP methodology. We validated these force field parameters by comparing thermodynamic and dynamic properties obtained from molecular dynamics simulations with those from experiments. We enhanced the sampling of the triad conformations with replica exchange molecular dynamics simulations. We characterized the effects of induced polarization on structural stability of the triad by analyzing the free energy landscapes constructed with polarizable force fields. Furthermore, by using principal component analyses, we found that conformations of the molecular triad were adopted within a small range of torsional angle with induced polarization. The triad conformation solvated in polar solvent with polarizable force field qualitatively agrees with those from nuclear magnetic resonance spectroscopy.



Grant title: STUDIES OF ELECTRON TRANSFER AND TRANSPORT IN ORGANIC SEMICONDUCTORS (OPV), MOLECULAR BRIDGES, AND THERMOELECTRONIC ENERGY CONVERSION

Grant number: Basic Energy Sciences through the Chemical Sciences Geosciences and Biosciences Division: Award number DE-SC0016501 (09/15/2016 - 09/14/2017).

Postdoc(s): Oleg N. Starovoytov (2014-2016) Pengzhi Zhang (2017-)

Publications:

(1) O.N. Starovoytov, P. Zhang, P. Cieplak, M.S. Cheung, Computational investigations of a light-harvesting molecular triad in explicit tetrahydrofuran solvent using molecular dynamics simulations (2017) submitted.

(2) 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).

(3) D. Balamurugan, A. J. A. Aquino, F. De Dios, L. Flores Jr., H. Lischka, M. S. Cheung, "Multiscale simulation of the ground and photo-induced charge-separated states of molecular triad in polar organic solvent: exploring the conformations, fluctuations and the free energy landscapes", Journal of Physical Chemistry, B, 117, 12065-12075 (2013).

Multiple Coupled Potential Energy Surfaces with Application to Combustion

Richard Dawes
Missouri University of Science and Technology
400 W. 11th Street, Rolla, MO 65409
dawesr@mst.edu

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 $\rightarrow$ 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 2016. The initial start date of this project was 07-15-2013.

Two new review articles are now in the literature. The first is a *Molecular Physics* review of methods for *Automated Construction of Potential Energy Surfaces* and includes an author profile.[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, came out last year (JPC A review on fitted PESs and the quantum dynamics of X + H_2O (X = F, Cl and O) reactions).[3]

Experimental and theoretical studies of the electronic transitions of MgC.[4] In the 2014 report a previous study of BeC[5] was described in which vibronic calculations were able to help assign and interpret electronic spectra of that system recorded by the group of Michael C. Heaven (Emory). Last year's report and presentation at the PI meeting described MRCI/CBS level calculations for valence-isoelectronic MgC performed by graduate student Phalgun Lolur.

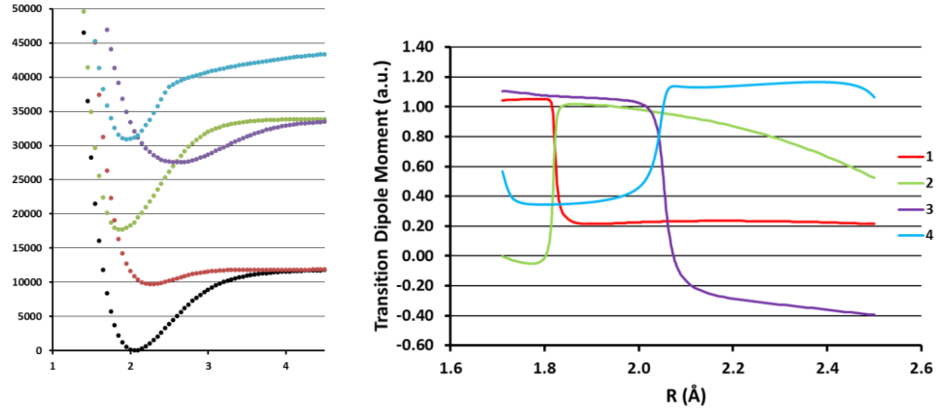


Figure 1. Electronic states of MgC plotted in the diabatic representation (left). At (right) the rapidly switching transition dipole moments are plotted.

A collaboration with Alan Aspuru-Guzik (another PI in the CTC program) was initiated at the 2016 PI meeting to explore to what extent laser control of excited electronic state dynamics is possible in this system. A joint publication is in preparation.

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 a benchmark study of N_2 and CO.[6] The PECs compare well with the best ab initio references and experimental quantities (vibrational levels etc). However, the cost was found not to be competitive with standard electronic structure approaches for small systems. (The scaling with number of electrons is n^3 for QMC so it will certainly be more competitive for larger systems where the e.g. n^7 scaling of traditional methods becomes prohibitive). We have found the QMCPACK code (Paul Kent, Oak Ridge) to be advantageous for multiconfigurational trial wavefunctions (due to the Table method algorithm).
Andrew Powell will graduate in June and is preparing to submit an article describing his recent work which benchmarks and compares the DMC and FCIQMC methods for reaction profiles that are sensitive to dynamic correlation, are strongly multireference and are perturbed by avoided state crossings.

MCTDH: **Rovibrationally and electronically inelastic scattering.** Previously, a time-dependent quantum dynamics method called MCTDH was applied to studying inelastic scattering at high collision energies where more typical time-independent calculations (Molscat) become prohibitively expensive.[7] Using an IMLS-based PES for CO+CO constructed for a previous ro-vibrational spectroscopy study,[8] time-independent Molscat calculations (for the low energy range) were combined with time-dependent MCTDH calculations to cover an extended energy range. Where the two approaches overlap, reasonable agreement was obtained between the two. We have now extended this approach in two significant ways: 1) We are treating larger systems in full-dimensionality. A publication is in preparation describing rovibrationally inelastic collisions for H_2O + Ar on a newly developed high-accuracy PES.[9] Preliminary calculations are underway for $H_2O + H_2O$ (water dimer) collisions using the PES of Paesani. 2) 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.[10] The new coupled PESs have been used to study photodissociation and scattering dynamics and multiple publications are in preparation. In the new studies, effects due to the coupled excited electronic state are being assessed. Since interference effects are noted in both the collisional and photodissociation dynamics, it seems possible that quantum control may be achieved in this and similar systems.

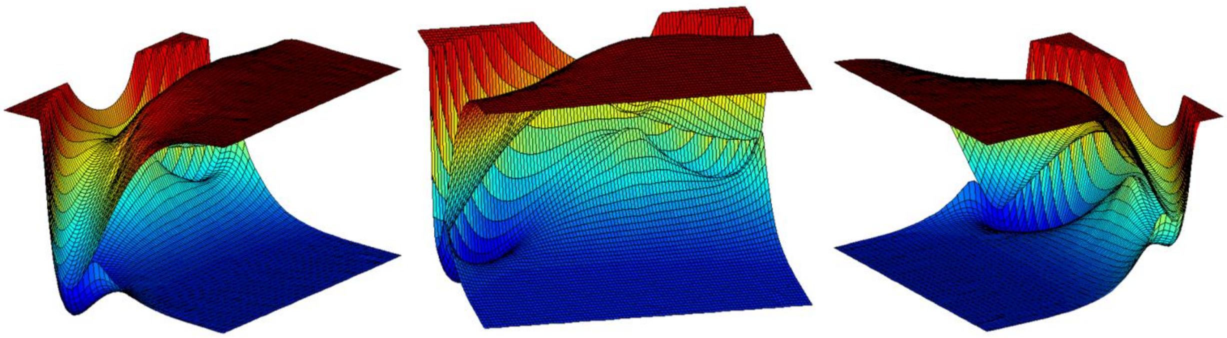


Figure 2. Sequence of surface plots of the fitted adiabatic *X* and *A* state PESs for HCO in Jacobi coordinates as a function of $R_{\mathrm{H—CO}}$ and theta. The Renner-Teller coupled states are degenerate along collinear seams for both HCO (left side of plots), and HOC (right side of plots). A third accidental intersection at a bent geometry (middle of plots) is avoided for r_{CO} = 1.18 Å fixed distance used in the plots.

Table I: Effect of Davidson correction and Renner-Teller coupling on HCO bound states.[10]

(v_1, v_2, v_3)	No Davidson	Davidson	Davidson + RT	Expt[a]
0,0,0	0.0	0.0	0.0	0.0
0,0,1	1106.5	1079.0	1081.4	1080.8
0,1,0	1920.0	1862.4	1862.3	1868.2
0,0,2	2167.5	2139.5	2144.7	2142.0
1,0,0	2548.5	2440.9	2439.2	2434.5
0,1,1	3021.2	2937.6	2939.8	2942.0
0,0,3	3209.2	3178.2	3187.3	3171.0
1,0,1	3642.7	3477.3	3477.8	3476.0
0,2,0	3811.5	3701.5	3701.4	3709.0
0,1,2	4085.8	3993.5	3998.5	3997.0
0,0,4	4254.2	4188.9	4203.6	4209.0
1,1,0	4478.3	4306.3	4304.4	4302.0
1,0,2	4651.9	4479.4	4481.3	4501.0
2,0,0	4788.3	4572.7	4570.2	4570.0
0,2,1	4905.9	4773.9	4776.0	4783.0
MAD	87.9	6.1	4.9	
RMSE	108.8	8.7	7.4	

[a] J. D. Tobiason, *et al.* JCP **103**,1448 (1995).

Table II: Spectroscopic accuracy of HCO resonance states computed on new PESs.[10]

(v_1,v_2,v_3)	Davidson	Davidson + RT	Expt
0,1,3	5026	5035	5032
0,0,5	5171	5194	5204
1,1,1	5331	5330	5324
0,3,0	5517	5517	5530
0,2,2	5825	5830	5834
0,1,4	6032	6046	6038
1,2,0	6167	6164	6156
0,3,1	6587	6589	6598
1,2,1	7171	7171	7166
0,4,0	7309	7309	7323
0,3,2	7633	7637	7643
0,2,4	7853	7867	7854
0,1,6	7946	7977	7957
1,2,2	8167	8168	8156
0,4,1	8368	8365	8390
0,3,3	8655	8663	8666
1,3,1	8993	8993	8988
0,5,0	9077	9076	9092
0,4,2	9419	9423	9431
MAD	11.14	9.87	
RMSE	13.08	11.46	

References (* denotes publications supported by the DOE)

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

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

[3] * Jun Li, Bin Jiang, Hongwei Song, Jianyi Ma, Bin Zhao, Richard Dawes and Hua Guo, From ab initio Potential Energy Surfaces to State Resolved Reactivities: The X + H2O ↔ HX + OH (X=F, Cl, and O(3P)) Reactions. *J. Phys. Chem. A* **119**, 4667 (2015).

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

[5] B. J. Barker, I. O. Antonov, J. M. Merritt, V. E. Bondybey, M. C. Heaven, R. Dawes, *J. Chem. Phys.* **137**, 214313 (2012)**.**

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

[7] * Steve A. Ndengue, Richard Dawes and Fabien Gatti, Rotational Excitations in CO-CO Collisions at Low Temperature: Time Independent and Multiconfigurational Time Dependent Hartree Calculations, *J. Phys. Chem. A* **119**, 7712 (2015).

[8] R. Dawes, X.-G. Wang and T. Carrington Jr., *J. Phys. Chem. A*, **117**, 7612 (2013).

[9] * Steve Ndengué, Richard Dawes and Moumita Majumder, A new flexible intermolecular Potential Energy Surface for the H_2O-Ar complex: Rovibrational States ad Inelastic scattering.

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

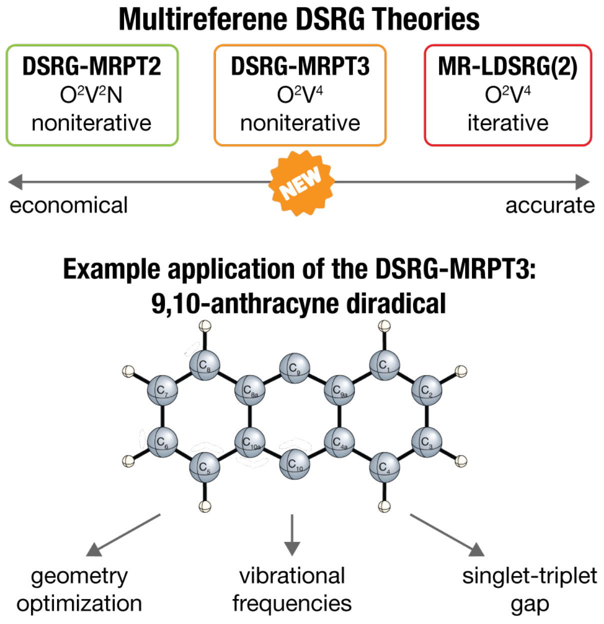
Francesco A. Evangelista

Driven similarity renormalization group: Recent developments and applications

Chenyang Li, Kevin P. Hannon, Jeffrey B. Schriber, Francesco A. Evangelista

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

Abstract



The focus of this project is to create a new set of many-body theries that can be applied to study bond-breaking reactions, transition metal complexes, and near-degenerate excited states. We have recently demonstrated that it is possible to combine conventional Quantum Chemistry many-body approaches with flow renormalization group methods to produce a new family of electronic structure theories. These methods have several advantages: (i) they are numerically-robust and avoid intruder states, (ii) they lead to equation that are relatively simple, and (iii) they are easily generalized to multi-determinantal reference states. An important aspect of our work has been to reformulate the similarity renormalization group (SRG) of Głazek and Wilson and Wegner[1] into a practical quantum chemistry approach, the *driven* SRG (DSRG).[2] The DSRG approach brings the Hamilton into a block-diagonal form via a *continuous* unitary transformation that is a function of a flow parameter (s). As s goes from 0 to ∞, the DSRG transformation produces a controlled downfolding of many-body interactions by decoupling high-energy processes from low-energy ones. This feature allows the reduction of a full many-body Hamiltonian with strongly and weakly interacting electrons to a compact effective Hamiltonian that describes a set of strongly interacting electrons with modified many-body interactions. Since the DSRG performs a renormalization transformation, it avoids numerical instabilities introduced by internally-contracted excited configurations that become near-degenerate with the reference wave function. After implementing a single-reference version of the DSRG truncated to one- and two-body operators [SR-DSRG(2)],[2] we proceeded to generalize the DSRG to the case of a complete active space zeroth-order wave function.[3] We have implmented both a second-order perturbative approximation to the multireference DSRG (DSRG-MRPT2)[3,4] and a non-perturbative scheme that include one- and two-body excitation and de-excitation operators [MR-LDSRG(2)].[5]

Recent progress

In the past year, we examined new approximation schemes for the DSRG that are both accurate and economical. We ultimately decided to pursue a third-order multireference scheme based on the DSRG (DSRG-MRPT3). In the early stages of this project, we derived the DSRG-MRPT3 equations and develop a new code that implements this method using density-fitted or Cholesky-decomposed two-electron integrals. We have also performed a detailed comparison of all our multireference DSRG methods using a benchmark set proposed by the Truhlar group.[7] This study showed that third-order correction helps improve upon the accuracy of the DSRG-MRPT2 scheme. Because of its non-iterative nature, the DSRG-MRPT3 approach was found to be significantly cheaper than the MR-LDSRG(2) method. We also showed that the DSRG-MRPT3 is a versatile approach that can be applied to interesting problems involving open-shell species. For example, we used the DSRG-MRPT3 to characterize the low-lying electronic states of 9,10-anthracyne (9,10-didehydroanthracene). This system was recently shown to undergo retro-Bergman cyclization on a NaCl/Cu surface when manipulated with the tip of an atomic force microscope. With our efficient DSRG-MRPT3 implementation we were able to optimize the geometry of 9,10-anthracyne and compute its harmonic vibrational frequencies. Adiabatic singlet-triplet splittings were then computed and compared to other multireference approaches.

Another project is exploring applications of the DSRG-MRPT methods to excited states. We are currently benchmarking a simplified scheme to compute vertical excitation energies. This study is in preparation for our future work on more general excited state formalisms based on the DSRG.

Future plans

- Benchmark vertical excitation energies obtained from a simplified DSRG-MRPT2.
- Implement state-averaged and multi-state variants of the DSRG-MRPT2 to compute near-degenerate ground and electronic excited states.
- Implement a low-scaling Laplace-transformed atomic orbital-based implementation of the DSRG-MRPT2 for systems with hundreds of atoms.

References

1. Głazek, S. D. and Wilson, K. G. Perturbative renormalization group for Hamiltonians. *Phys. Rev. D* **49,** 4214–4218 (1994). Wegner, F. Flow-equations for Hamiltonians. *Ann. Phys.* **506,** 77–91 (1994).
2. Evangelista, F. A. A driven similarity renormalization group approach to quantum many-body problems. *J. Chem. Phys.* **141,** 054109 (2014).
3. Li, C. and Evangelista, F. A. Multireference Driven Similarity Renormalization Group: A Second-Order Perturbative Analysis. *J. Chem. Theory Comput.* **11,** 2097–2108 (2015).
4. Hannon, K. P.; Li, C.; Evangelista, F. A. An Integral-Factorized Implementation of the Driven Similarity Renormalization Group Second-Order Multireference Perturbation Theory. *J. Chem. Phys.* **144**, 204111 (2016).
5. Li, C.; Evangelista, F. A. Towards Numerically Robust Multireference Theories: the Driven Similarity Renormalization Group Truncated to One- and Two-Body Operators. *J. Chem. Phys.* **144**, 164114, (2016).
6. Yang, K. R.; Jalan, A.; Green, W. H.; Truhlar, D. G. Which Ab Initio Wave Function Methods Are Adequate for Quantitative Calculations of the Energies of Biradicals? The Performance of Coupled-Cluster and Multi-Reference Methods Along a Single-Bond Dissociation Coordinate. *J. Chem. Theory Comput.* **9**, 418–431 (2012).

Grant Numbers and Grant Titles

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

Postdoc(s): Chenyang Li

Student(s): Kevin P. Hannon, Jeffrey B. Schriber

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

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

Non-Adiabatic Molecular Dynamics Methods for Materials Discovery

Mikko Muuronen, Shane M. Parker, Jordan C. Vincent, Saswata Roy, Filipp Furche
University of California, Irvine, Department of Chemistry,
1102 Natural Sciences II, Irvine, CA 92697-2025
Email: filipp.furche@uci.edu

Abstract

The direct conversion of sunlight to chemical energy by photocatalysis underlies solar fuel generation, efficient energy storage, and artificial photosynthesis. However, as opposed to ground-state reactions, mechanistic details of excited state processes in real materials have remained elusive, because short-lived excited state species are exceedingly difficult to characterize both experimentally and theoretically. For example, when this project started, the rate-limiting step of the photooxidation of water on TiO_2 nanoparticles was still under debate [1], it was unknown if and how divalent lanthanides may be generated through photoreduction [2], and the relation between the structure and the emission intensity of luciferin-derived fluorescent probes was poorly understood [3]. The leading cause of losses in TiO_2 photocatalysts and other light driven materials are non-adiabatic transitions that convert excitation energy into heat. Such non-adiabatic radiationless transitions between electronic states are notoriously hard to control and proceed through “dark”, experimentally elusive conical intersections (CIs).

The work performed under this project led to significant methodological improvements enabling the study of non-adiabatic photocatalytic processes in molecular materials using non-adiabatic molecular dynamics (NAMD) simulations with hybrid time-dependent density functional theory (TDDFT) and Tully’s fewest switches surface hopping algorithm [4, 5]. Our recently developed non-orthonormal Krylov space algorithm speeds up TDDFT simulations by up to a factor of five [6], and a new broken-symmetry algorithm makes both simulations of homolytic and heterolytic bond dissociations possible using TDDFT [7]. These improvements extend the applicability of TDDFT in NAMD simulations of real materials and photochemical reactions that cannot be tackled by existing methodology.

The newly developed methods were validated by simulations of acetaldehyde photodissociation reaction [7], which reproduced experimental branching ratios and kinetic energy probability distributions (KEPDs) from molecular beam experiment semi-quantitatively. While the branching ratios are relatively insensitive to non-adiabatic effects, the reaction mechanisms and the experimental KEPDs are explained only by non-adiabatic simulations. This demonstrates that the strong correlation between nuclear and electronic motion due to non-adiabatic effects is important even for simple photodissociation reactions.

The improved efficiency of our nonorthonormal Krylov space methods [6] enabled the first unconstrained NAMD simulations of the photooxidation of water on TiO_2 nanoparticles [1]. In these simulations, we identified a novel photooxidation mechanism involving the S_1 potential energy surface (PES) close to the S_1-S_0 CI see Fig. 1. The simulations show that unbound water is directly oxidized by the nanoparticles, yielding mobile hydroxyl radicals in agreement with the recent experiments. The calculations also revealed an important reason for the relatively low activity of undoped TiO_2 photocatalysts: Exciton binding and proximity of the particle-hole pair are required for lowering the oxidation reaction barrier, but also greatly

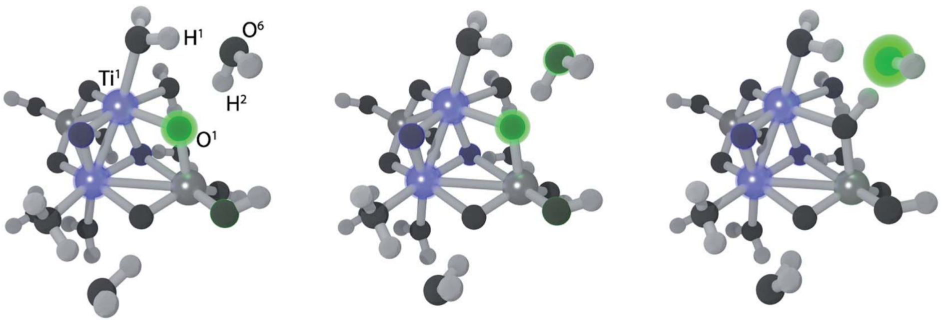


Figure 1: Snapshots from a NAMD trajectory at 200 fs (left), 213 fs (middle) and 218 fs (right) showing electron-proton transfer between water and TiO_2 nanoparticle. Blue and green colors indicate negative and positive computed excitonic (electron-hole pair) charges, respectively. Reproduced from [1] - Published by The Royal Society of Chemistry.

enhance nonradiative exciton decay. These results may be valuable for future developments of more efficient photocatalysts.

Since transitions between adiabatic electronic states result from derivative couplings, and thus simulations involving more than two excited states require couplings between all pairs of excited states. We showed that derivative couplings between two TDDFT excited states (state-to-state) can be obtained from the quadratic response function [8]. However, implementation of the state-to-state couplings also uncovered severe defects in the analytical structure of the quadratic response function within TDDFT: spurious poles in the quadratic response function give rise to unphysical divergences in state-to-state properties whenever the energy difference between the two states, Ω_{mn}, matches *any other* excitation energy from the ground state [9]. We further showed that these divergences are not limited to TDDFT, but affect state-to-state properties from any response theory based on a nonlinear effective Hamiltonian, including response theories based on multiconfigurational self-consistent field and coupled cluster approaches.

We also developed an efficient method for simulating vibronic absorption spectra that includes Dushinsky rotation and avoids the explosion of computational cost limiting brute-force Franck-Condon approaches. The method was applied simulate the ultraviolet-visible spectrum of the black absorber 7,7,8,8-tetracyanoquinodimethane anion ($TCNQ^-$) [10]. Simple Gaussian broadening of vertical electronic excitations produces only one single band in the visible region, failing catastrophically. However, inclusion of vibronic effects produces nearly quantitative agreement with the experimental spectrum of $TCNQ^-$. These results underline the importance of vibronic effects for predicting the absorption spectra of molecules with many vibrational degrees of freedom.

Grant Numbers and Grant Titles

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

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

10 Publications (out of 13)

[1] M. Muuronen, S. M. Parker, E. Berardo, A. Le, M. Zwijnenburg, and F. Furche: Mechanism of Photocatalytic Water Oxidation on Small TiO_2 Nanoparticles, *Chem. Sci.* **8**, 2179–2183, 2017.

[2] M. E. Fieser, J. E. Bates, J. W. Ziller, F. Furche, and W. J. Evans: Dinitrogen reduction via photochemical activation of heteroleptic tris(cyclopentadienyl) rare-earth complexes, *J. Am. Chem. Soc.* **135**, 3804–3807, 2013.

[3] R. C. Steinhardt, C. M. Rathbun, B. T. Krull, J. M. Yu, Y. Yang, B. D. Nguyen, J. Kwon, D. C. McCutcheon, K. A. Jones, F. Furche, and J. A. Prescher: Brominated Luciferins Are Versatile Bioluminescent Probes, *ChemBioChem* **18**, 96–100, 2017.

[4] 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.

[5] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, and F. Weigend: Turbomole, *WIREs Comput. Mol. Sci.* **4**, 91–100, 2014.

[6] F. Furche, B. Krull, B. D. Nguyen, and J. Kwon: Accelerating molecular property calculations with nonorthonormal Krylov space methods, *J. Chem. Phys.* **144**, 174105, 2016.

[7] J. C. Vincent, M. Muuronen, K. C. Pearce, L. N. Mohanam, E. Tapavicza, and F. Furche: That Little Extra Kick: Nonadiabatic Effects in Acetaldehyde Photodissociation, *J. Phys. Chem. Lett.* **7**, 2016.

[8] Q. Ou, G. D. Bellchambers, F. Furche, and J. E. Subotnik: First-order derivative couplings between excited states from adiabatic TDDFT response theory, *J. Chem. Phys.* **142**, 064114, 2015.

[9] S. M. Parker, S. Roy, and F. Furche: Unphysical divergences in response theory, *J. Chem. Phys.* **145**, 134105, 2016.

[10] E. Tapavicza, F. Furche, and D. Sundholm: Importance of vibronic effects in the UV-Vis spectrum of the 7,7,8,8-tetracyanoquinodimethane anion, *J. Chem. Theory Comput.* **12**, 5058–5066, 2016.

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 developed in this direction, which include: (i) development of an enriched finite element (FE) basis; (ii) development of efficient computational algorithms for the solution of the Kohn-Sham equations. In particular, 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 enriched FE basis thus provides a systematically improvable, yet efficient basis for all-electron KS DFT calculations. Despite the significant advantage the enriched FE basis provides in terms of the number of basis functions, the integrals involved in the evaluation of the discrete KS Hamiltonian and the overlap matrix need to be computed accurately and efficiently using numerical quadrarture. To this end, we adopt the approach of using adaptive quadrature grids, where the quadrature points are constructed based on the characteristics of the enrichment functions. In addition, we compute the inverse of the overlap matrix efficiently by using a block matrix inversion in conjunction with special reduced-order quadrature rules, which is required to transform the generalized eigenvalue problem to a standard eigenvalue problem. We solve the resulting discrete KS problem by using a Chebyshev polynomial based filtering technique to compute the eigenspectrum of interest. The use of enriched FE basis significantly reduced the spectral width of the discrete Hamiltonian in comparison to a classical FE basis, thereby improving the computational efficiency afforded by the Chebyshev filtering.

The numerical results [1] demonstrate the accuracy, efficiency and parallel scalability of the enriched FE basis on benchmark problems of varying sizes, which include semiconducting and heavy metallic systems, with the largest system containing ~10,000 electrons. Table I shows the comparison of the classical FE basis and enriched FE basis for Silicon nanoclusters consisting of 1x1x1 (252 electrons), 2x1x1 (434 electrons) and 2x2x2 (1334 electrons) diamond unit cells, which demonstrates the significant savings realized by the enriched basis both in terms of the number of basis functions as well as computational time. Table II shows the comparison of the enriched FE basis with pc-3 and pc-4 basis computed using NWChem for a series of Si nanoclusters consisting of 1x1x1 - 4x4x4 (8694 electrons) diamond unit cells. The enriched basis is found to significantly outperform the Gaussian-type basis with increasing computational savings realized for larger clusters. Finally, Figure 1 shows the scalability of the enriched basis, for a benchmark problem of a Silicon nanocluster containing 3920 electrons with ~4

million basis functions. The scalability is close to ideal for this benchmark problem up to 384 processors. Beyond this, the degrees of freedom on each processor fall below 5,000, which is too low to achieve good parallel scalability.

In the next year, we plan to extend the capability of all-electron calculations using enriched FE basis to periodic calculations. Further, we will work towards combining the developed framework for enriched FE basis with localization techniques [2] to realize reduced-order computational complexity in the solution of KS equations.

TABLE I: Comparison of classical and enriched finite element (FE) basis: Energy per atom (E in Ha), degrees of freedom per atom (DoF), and total computation CPU time (in CPU hours) for various silicon nano-clusters.

Si 1 × 1 × 1	Classical FE	Enriched FE
E	−288.320035	−288.319450
DoF	402, 112	14, 728
CPU Hrs	1599.15	24.81
Si 2 × 1 × 1	Classical FE	Enriched FE
E	−288.334123	−288.333872
DoF	386, 205	13, 557
CPU Hrs	16441.43	57.10
Si 2 × 2 × 2	Classical FE	Enriched FE
E	−288.359459	−288.359266
DoF	360, 467	10, 642
CPU Hrs	75936.4	553.13

TABLE II: Comparison of enriched finite element, pc-3 and pc-4 basis: Energy per atom (E in Ha) and total computation CPU time (in CPU hours) for various silicon nano-clusters.

Si 1 × 1 × 1	Enriched FE	pc-3	pc-4
E	−288.319450	−288.318996	−288.319448
CPU Hrs	24.81	8.39	98.88
Si 2 × 1 × 1	Enriched FE	pc-3	pc-4
E	−288.333872	−288.333447	−288.333898
CPU Hrs	57.10	151.74	1817.30
Si 2 × 2 × 2	Enriched FE	pc-3	pc-4
E	−288.359266	−288.360045	FTC[a]
CPU Hrs	553.13	4097.29	–
Si 3 × 3 × 3	Enriched FE	pc-3	pc-4
E	−288.374721	FTC	FTC
CPU Hrs	6252.15	–	–
Si 4 × 4 × 4	Enriched FE	pc-3	pc-4
E	−288.381425	FTC	FTC
CPU Hrs	45053.82	–	–

[a] FTC: Failed to converge

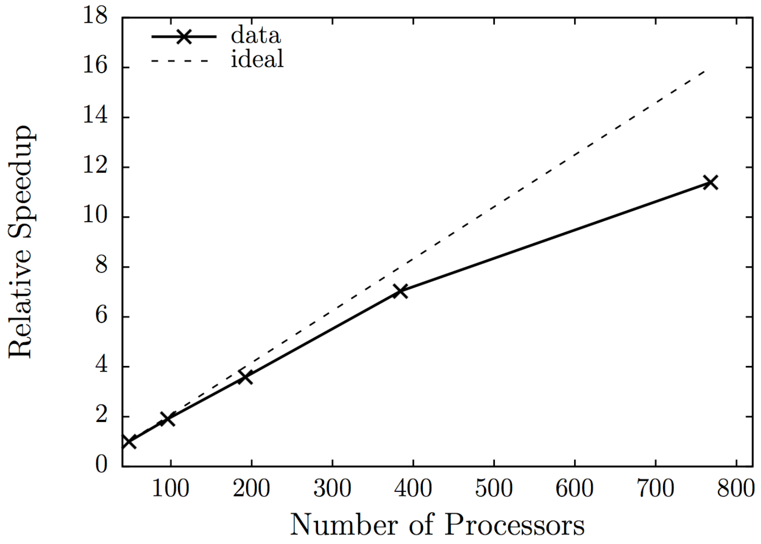


Figure I : Parallel scaling of enriched FE basis on bechchmark Si nanocluster containing 3920 electrons.

References:

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).

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

Postdoc(s): None yet

Student(s): None yet; Grant starts 05/01/2017

DE-SC0008637: Software center for predictive theory and modelling

Postdoc(s): Phani Motamarri

Student(s): Sambit Das; Mrinal Iyer

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, in press (2017). DOI: 10.1016/j.jmps.2017.03.010

Surface Plasmon Enhanced Chemistry

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

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

Recent Progress: Our primary activity during the last year has involved the development of semiempirical electronic structure methods to describe the properties of silver clusters that show plasmon excitations[1-3]. Such clusters have been known for several years based on TDDFT calculations, and they are useful in many different ways for modeling optical properties such as extinction and Raman scattering processes that are influenced by plasmon excitation, and for describing plasmon induced photochemistry. However a serious limitation of TDDFT calculations for describing silver (or gold) clusters with ligands is that charge transfer excited state energies are seriously underestimated (often by several eV) due to self-interaction errors. This has limited what could be done with these clusters, as often the charge transfer states are below the plasmon excitations, leading to physical results. However there is a way around this, which involves using a Hartree-Fock-based method such as INDO, where there is no self-interaction error. This idea has been around for a long time, however it was never implemented as the standard parameters available in INDO to describe silver excited states produced excited state energies of poor quality. What we found is that there is a systematic way to adjust these parameters to give plasmon excited states for bare clusters that match both experiment and results from TDDFT,[2] and once these parameters have been defined for one cluster, the agreement of INDO with TDDFT is good for all clusters. In addition, the INDO code that we are developing is capable of doing both singles and doubles CI calculations (i.e., INDO/S and INDO/SD) which enabled us to determine (for the first time) if doubles excitations make an important contribution to plasmon excited states. But we found that doubles are unimportant, which is very useful for doing further work as the singles-only calculation is much more efficient. With these capabilities we have been able to systematically explore plasmon excitation for a wide variety of silver clusters, and in the process of doing this, we discovered that there can be quadrupole plasmon excited states[2] in addition to the standard dipole excited states. Fig. 1 shows the transition density associated with the quadrupole plasmon of a Ag_{55}^{+} nanorod, and contrasts this transition density with the corresponding results for two dipole plasmons modes, and with other nonplasmonic quadrupole states. This is the first example of a "dark" plasmon based on electronic structure calculations, and knowing this

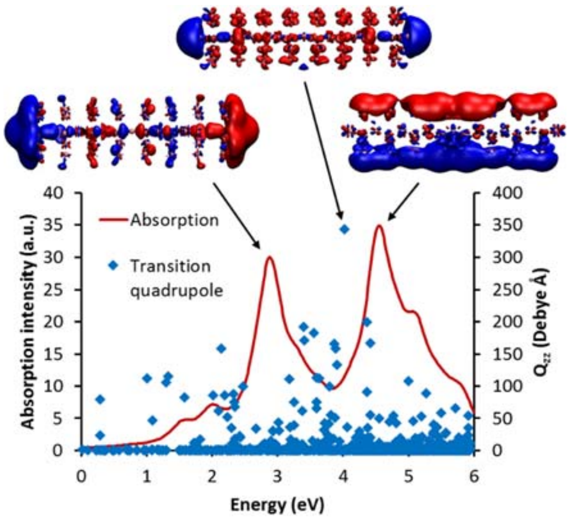


Figure 1. Top: transition densities for three plasmonic excitations (two dipolar and one quadrupolar) associated with a pentagonal Ag_{55}^+ nanorod. Bottom: Absorption spectrum of the nanorod (red curve), and transition quadrupole intensity for each electronic state in the nanorod. Note that the plasmonic transition quadrupole is much more intense that any of the others, and the two dipole modes have only small transition quadrupoles.

result will enable us to model the role of dark mode excitation in plasmonic properties. Our initial calculations were for clusters in vacuum, but we have since modified our semiempirical code to incorporate continuum solvation [3] at the COSMO level for both ground and excited states. In that work, we demonstrated for a series of prototypical π-conjugated molecules, that our newly implemented INDO/SCI/COSMO model yields more accurate absorption energies and comparably accurate solvatochromic shifts to those computed using TD-ωB97XD and CIS with COSMO solvation at a substantially lower computational cost. These studies are just the beginning of a series of projects that we can do with INDO-based methods, as further described below in our future plans.

Another cluster-based electronic structure study involved a TDDFT study of the impact of ligand passivation on plasmon excitation in silver clusters.[4] There has been confusion for some time as to the relation between the absorption spectra of ligand-protected clusters and the corresponding spectra of bare cores associated with the same clusters. In this study we discovered that the plasmonic excitations in ligand-protected silver clusters (considering both amine and thiolate ligands) are mostly associated with silver cores that are perturbed by the ligands, with essentially no contribution coming from excitations associated with the shell around the core where there are staple bonds and other structures that mix together the metal and ligand atoms. This study further shows that the ligands lead to two effects on plasmon excitation of the bare core: (1) dielectric screening that reduces excitation energies and (2) ligand field splitting that reduces plasmonic character. The dielectric screening can be thought of as a simple dielectric effect, and this lowers the silver plasmon excitation energy from 3.75 eV to 1.8 eV. The ligand field splitting leads to a breakup of the plasmon into groups of plasmons, each of which is less coherent.

We also have used metal clusters to study the coupling of acoustic mode excitation and plasmon excitation.[5] Experiments related to this topic have been done many times over the last 10 years, and in all cases it has been found that ultrafast laser excitation leads to acoustic mode excitation (when the initial electronic excitation gets converted to phonons),and this results in oscillating plasmon wavelengths (on the ps timescale) that are easily detected. These experiments have been interpreted using a combination of continuum mechanics and electrodynamics, but these theories are not capable of describing the coupling of these effects to chemistry in molecules on the surfaces of the nanoparticles. However our TDDFT-based work with bare silver clusters has now been extended to describe the oscillating plasmon experiments from first principles. We generally find good agreement with the continuum theories after correction for quantum size effects in the small clusters, but more information is provided by the quantum calculations, such the atom motions during oscillations, and the coupling of plasmons to modes other than acoustic modes. This methodology now gives us the capability to expand our work to the effect of plasmon-induced coupling of acoustic motions to molecules adsorbed onto the clusters.

In a different direction, we developed a Landauer-Büttiker-based theory for plasmonic hot-carrier solar cells (HCSCs)[6] that has provided important insights into fundamental limitations on solar cell efficiency for this type of solar cell. Fig. 2 shows the structural model used for this work, in which is assumed that plasmon excitation produces carriers that transfer through a Schottky barrier to a semiconductor, and then the built-in potential separates electrons and holes for transfer to the external current. The calculation assumes a simple free electron model for the metal, an oscillator model for the plasmon, and a two-state model for the semiconductor. Other important parameters include the electron/plasmon coupling, the electron/semiconductor interaction, hot electron relaxation times, and coupling of the semiconductor to the leads. These parameters are generally known from earlier work and from comparisons with experiment for other device applications. Note that an advantage of this formalism is that the plasmon, electron, and semiconductor degrees of freedom are treated on an equal footing. The results of this application show that HCSC photocurrent rises at energies below the bandgap, as the only significant constraint to the generation of carriers in the semiconductor is that the electrons need surmount the Schottky barrier, and this barrier is below the bandgap. This leads to a low threshold which is good for photovoltaic performance, but plasmon excitation produces a broad range of electron energies and as a result the IQE (internal quantum efficiency) is less than 50% even for photon energies well above the bandgap. We have used extensions of this model to study the efficiency of a solar cell developed by a Japanese group that consisted of gold nanoparticles interacting with TiO_2 electrodes, showing that the ~1% external quantum efficiency that they observed is consistent with the low IQE that we predict. Our analysis also shows us what parameters to change in order to improve this result.

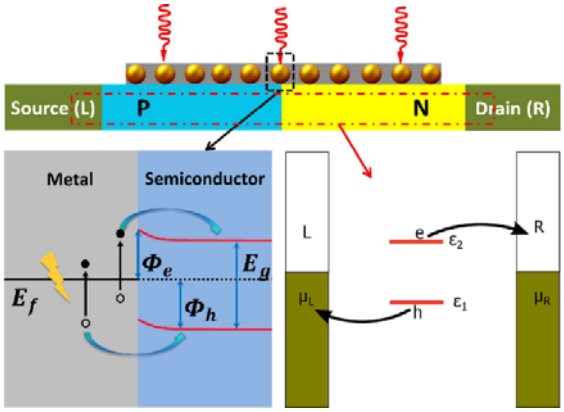


Figure 2. Schematic of hot-carrier solar cell that was studied using Landauer-Buttiker theory. Upper panel: geometry of HCSC. Arrays of spherical nanoparticles are deposited on the top of a pn junction semiconductor. Left bottom panel: Schematic of hot carrier generation and injection over a Schottky barrier to a semiconductor; Right bottom panel: A two-level system is used to model the conduction and valence band of semiconductor. The collected hot-carriers in the semiconductor are driven in different directions by the built-in potential, resulting in photocurrent generation.

Additional studies have involved electrodynamics calculations for a variety of nanoparticle structures and compositions, often involving collaborations with experimentalists [7-8]. We also worked on the development of a new functional (LDA0) that we now use routinely for TDDFT calculations [9] that combines local density functionals with long range corrected functionals, thereby avoiding unnecessary work to include gradient-corrected contributions at short range. We have applied this functional to determine excited state energies for a variety of benchmark molecules, giving results that are in quantitative agreement with calculations that include gradient effects. Finally we wrote a review article concerned with plasmon-induced hot electron effects, and related SERS studies[10]

Future Plans: Our semiempirical calculations are now at the point where there are a myriad of opportunities available to us for addressing fundamental issues in the plasmonics field. This will begin with a detailed study of the chemical effect in SERS where we properly include for the role of resonant charge transfer effects for the first time, thus addressing a nagging question in the SERS community. Another capability that we will consider is the ability to vary the Fermi energy in INDO by simply shifting the atomic orbital energies of the metal atoms while not changing the corresponding energies of the adsorbates. This capability can be used to study SERS enhancements for electrochemical experiments, which is an important first step for eventually studying hot electron effects for experiments under potential control. Such experiments are perhaps the best class of experiments relevant to hot electron effects. And this further gives us the capability of distinguishing electron transfer that occurs when the Fermi energy of the metal matches the LUMO of the molecule, compared to "hot" electron transfer that occurs for electrons that are produced by plasmon excitation well above the Fermi energy. And a key activity of the INDO work will be to determine the "action spectrum" associated with hot electrons, meaning the population of negative ion states of an adsorbate molecule that are produced following plasmon excitation.

Grant Numbers and Grant Titles

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

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

1. Postdocs: Rebecca Gieseking (12), Yu Zhang (6), Martin Mosquera (1), Clotilde Lethiec (1)
2. Students: Lindsey Madison (12,p), Adam Ashwell (12), Mike Ross (12,p)

Up to Ten Publications Acknowledging the Grant (all in the last year)

[1]Semiempirical Modeling of Ag Nanoclusters: New Parameters for Optical Property Studies Enable Determination of Double Excitation Contributions to Plasmonic Excitation, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, J. Phys. Chem. A 120, 4542-49 (2016). DOI:10.1021/acs.jpca.6b04520

[2]Quantum mechanical identification of quadrupolar plasmonic excited states in silver nanorods, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, J. Phys. Chem. A, 120, 9324-29 (2016). DOI:10.1021/acs.jpca.6b09649

[3]Implementation of INDO/SCI with COSMO implicit solvation and benchmarking for solvatochromic shifts, Rebecca L. Gieseking, Mark A. Ratner, George DC. Schatz, J. Phys. Chem. A, 120, 9878-85 (2016) DOI:10.1021/acs.jpca.6b10487

[4]A time-dependent density functional theory study of the impact of ligand passivation on the plasmonic behavior of Ag nanoclusters, Adam P. Ashwell, Mark A. Ratner and George C. Schatz, Adv. Quantum. Chem. 1-29 (2017) DOI: 10.1016/bs.aiq.2017.01.011

[5]Dependence of plasmon energies on acoustic normal modes of Ag_n (n=20,84,120) clusters. Clotilde M. Lethiec, Lindsey R. Madison, George C. Schatz, JPC C, 120, 20572-78 (2016). DOI:10.1021/acs.jpcc.5b12497

[6]Fundamental limitations to plasmonic hot-carrier solar cells, Yu Zhang, ChiYung Yam, George C. Schatz, J. Phys. Chem. Lett. 7, 1852-58 (2016) DOI: 10.1021/acs/jpclett.6b00879

[7]In solution SERS sensing using mesoporous silica-coated gold nanorods, Zhe Gao, Nathan D. Burrows, Nicholas A. Valley, George C. Schatz, Catherine J. Murphy, Christy L. Haynes, Analyst 141, 5088-95 (2016) DOI:10.1039/C6AN01159D; E DOI:10.1039/c6an90098d E:141, 6604.

[8]Plasmonic metallurgy enabled by DNA, M. B. Ross, J. C. Ku, B. Lee, C. A. Mirkin, G. C. Schatz, Adv. Mat. 28, 2790–2794 (2016) DOI:10.1002/adma.201505806

[9]Connection between Hybrid Functionals and Importance of the Local Density Approximation, M. A. Mosquera, C. H. Borca, M. A. Ratner and G. C. Schatz, J. Phys. Chem. A, 120, 1605-1612 (2016) DOI: 10.1021/acs.jpca.5b10864

[10]Review of plasmon-induced hot-electron dynamics and related SERS-chemical effects, Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz, in **Frontiers of Plasmon Enhanced Spectroscopy**, Volume 1, Ed. Y. Ozaki, G. C. Schatz, D. Graham and T. Itoh, ACS Symposium Series Vols. 1245, American Chemical Society, Washington, D. C., 2016, pp 1-22. DOI: 10.1021/bk-2016-1245.ch001

Jeffrey P. Greeley

Interfacial Electrocatalysis from First Principles

Zhenhua Zeng[1], Hee-Joon Chun[1], Joseph Kubal[1], Siddharth Deshpande[1], Jeffrey Greeley[1]
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907[1]

Abstract

Program scope and definition

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

Recent Progress

We are continuing to explore three major topic areas related to structural and mechanistic analyses of electrochemical phenomena and water/catalyst interfaces (we have also been investigating several side projects that could mature into longer-term research directions, but those are not described here). The first major area of interest relates to the electronic, structural, and catalytic properties of continuous ultrathin (hydroxy)oxide films at the interface between precious metals and aqueous solutions. We have, in the past few years, developed methods that exploit basic van der Waals and self-interaction corrections to DFT-GGA calculations to determine the structure and oxidation states of these films on Pt(111) substrates, as a function of the local pH and applied voltage of the aqueous solutions.

Building upon the above progress, we have very recently developed an energetic decomposition scheme that relates the stability of the supported ultrathin films to both bulk properties of (hydroxy)oxides of similar oxidation state and the adhesion energy between the film and the support; the latter, in turn, stabilizes films with oxidation states that do not exist in bulk. On Pt(111), we have found that these films with unexpected oxidation states, which have been recently verified by *in-situ* crystal truncation rod measurements from our collaborators in the group of Nenad Markovic at Argonne, are ultimately responsible for impressive catalytic activity enhancements of single monolayer Ni (hydroxy)oxide films that have puzzled the fundamental electrocatalysis community for the past five years. The Ni films adopt a structure of NiOH on Pt(111), and this specific structure presents active sites that permit accelerated production of hydrogen, a result that could be of future relevance to the development of alkaline electrolyzers (Nature Energy, in press). We are currently evaluating how systematic permutations of the substrate (for example, formation of binary platinum alloys) changes the structure and energetics of these films and how such changes may ultimately influence the rate of alkaline hydrogen production. Additional, related work involves continuing development of automated schemes to predict the structures of fully developed two-dimensional nanoislands on transition metal substrates as a function of applied potential and pH.

To couple some of the structural considerations, described above, with rigorous analysis of electrocatalytic rates and mechanisms on transition metal surfaces, we are developing a comprehensive reaction mechanism for selected nitrogen-cycle electrochemical processes on both low-index and defected platinum surfaces. We have selected the electroreduction of NO_x species as a model chemistry for which to develop efficient strategies to treat the complexities of the electrocatalytic environment. In previous years, we elucidated several highly active pathways for NO electroreduction on smooth Pt(111) surfaces, as well as identifying a highly unusual solution-mediated pathway for formation of N_2O products. In the past project year, in collaboration with the group of Karoliina Honkala at the University of Jyvaskula in Finland , we have focused on the development and refinement of a kinetic Monte Carlo model that is capable of describing atom-specific reaction events on single crystal platinum surfaces as a function of the applied electrochemical potential. We have very recently incorporated several features into the kMC model, the most significant being the effect of direct interactions between adsorbed NO molecules and other species, as well as the refinement of reaction barrier calculations in explicit models of aqueous solvents, that have led to improved predictions of reaction currents and product distributions compared to experiment, as well as to the identification of the exact probabilities of different possible reaction pathways on the platinum surface. We are currently seeking to extrapolate this detailed study on Pt(100) (ACS Catalysis, in press) to other transition metal surfaces.

Finally, we have made significant progress in the past project year in developing comprehensive descriptions of charge transfer barriers for proton-coupled electron transfer (PCET) across electrochemical double layers to transition metal surfaces. The approach that we have adopted uses an adiabatic-like approximation to compute interfacial capacitance for layers of solvated protons near metal surfaces. The capacitances can be used to extrapolate reaction barriers and thermodynamics for PCET, which must be calculated on finite-sized unit cells, to the case of infinitely large unit cells where the workfunction (and thus voltage) is constant. We have carried out such calculations for two elementary PCET reactions that are central to the NO electroreduction chemistry described above, $N^* + H^+ + e^- \rightarrow NH^*$ and $NO^* + H^+ + e^- \rightarrow NOH^*$. These calculations were performed at three different voltages on approximately eight transition metal surfaces, and from the resulting energetics, Brønsted-Evans-Polanyi correlations relating the reaction activation barriers to the corresponding reaction energy changes were developed. Both reactions show strong linear correlations across all voltages and metals, and the slopes of the correlations are directly related to the fractional location of the transition states along the corresponding reaction coordinates. These correlations confirm, at least for these particular reactions, a long-held, but to our knowledge never verified, assumption in the electrocatalysis community that a single Brønsted-Evans-Polanyi relationship can describe PCET

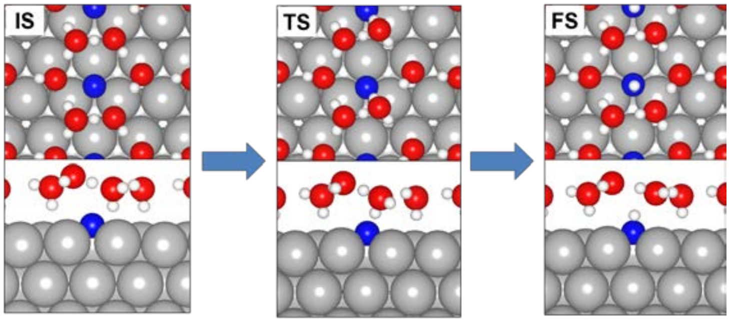


Figure. Top and side views of proton-coupled electron transfer from an electrochemical double layer to adsorbed nitrogen on a Pt(111) surface.

reactions as a function of both voltage and transition metal. We are currently seeking to develop approximate theories that would provide estimates of the transition state structure, and hence BEP slope, without necessitating calculations across many different transition metals for each reaction.

Future Plans

In addition to future work mentioned in the body of the abstract, we have begun 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 will also seek to generalize our kMC model to describe electrocatalysis at the three-phase boundary between the ultrathin films and the metal substrate. We are additionally seeking to move beyond the static electrochemical double layer models that we have used to describe selected elementary reactions in NO electroreduction. In particular, we intend to develop estimates of the entropy of electrochemical double layers using a vibrational density of states method, which will enable us to describe true free energies of solvation at the electrified interface, as opposed to the potential energy analyses that are currently standard in the field. If possible, these efforts will be complemented with increased accuracy in our DFT-based energy calculations, using modified density functionals developed by other CTC PI's.

Grant Numbers and Grant Titles

DE-BES-CTC Interfacial Electrocatalysis from First Principles

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

1. "Stabilization of Ultrathin (Hydroxy)oxide Films on Transition Metal Substrates for Electrochemical Energy Conversion," Z. Zeng, K. Chang, J. Kubal, N. Markovic, and J. Greeley, *Nature Energy, accepted.*
2. "Atomistic Insights into Nitrogen Cycle Electrochemistry: A Combined DFT and Kinetic Monte Carlo Analysis of NO Electrochemical Reduction on Pt(100)," H. Chun, V. Apaja, A. Clayborne, K. Honkala, and J. Greeley, *ACS Catalysis, accepted.*
3. "Platinum-nickel hydroxide nanocomposites for electrocatalytic reduction of water," L. Wang, Y. Zhu, Z. Zeng, C. Lin, M. Giroux, L. Jiang, Y. Han, J. Greeley, C. Wang, and J. Jin, *Nano Energy* **31** (2017) 456-461.
4. "Characterization of oxygenated species at water/Pt(111) interfaces from DFT energetics and XPS simulations," Z. Zeng and J. Greeley, *Nano Energy* **29** (2016) 369-377.
5. "Theoretical Heterogeneous Catalysis: Scaling Relationships and Computational Catalyst Design," J. Greeley, *Annual Review of Chemical and Biomolecular Engineering* **7** (2016) 605-635.
6. "Surface Tension Effects on the Reactivity of Metal Nanoparticles." L. Li, F. Abild-Pedersen, J. Greeley, and J. Nørskov, *Journal of Physical Chemistry Letters* **6** (2015) 3797-3801.
7. "Towards First Principles-Based Prediction of Highly Accurate Electrochemical Pourbaix Diagrams." Z. Zeng, M. Chan, Z. Zhou, J. Kubal, D. Fan, and J. Greeley, *J. Phys. Chem. C* **119** (2015) 18177-18187.
8. "Elucidation of Pathways for NO Reduction on Pt(111) From First Principles." A. Clayborne, H. Chun, R. Rankin, and J. Greeley, *Ang. Chem. Int. Ed.* **54** (2015) 8255-8258.

9. “Ab-initio thermodynamic modeling of electrified metal-oxide interfaces: consistent treatment of electronic and ionic potentials.” Z. Zeng, M. Hansen, J. Greeley, J. Rossmeisl, and M. Bjorketun, *J. Phys. Chem. C* **118** (2014) 22663-22671.

10. “Exceptional Size-Dependent Activity Enhancement in the Electroreduction of CO_2 over Au Nanoparticles.” H. Mistry, R. Reske, Z. Zeng, Z. Zhao, J. Greeley, P. Strasser, and B. Cuenya, *J. Am. Chem. Soc.* **136** (2014) 16473-16476.

Merging symmetry restoration with Coupled Cluster theory

Gustavo E. Scuseria

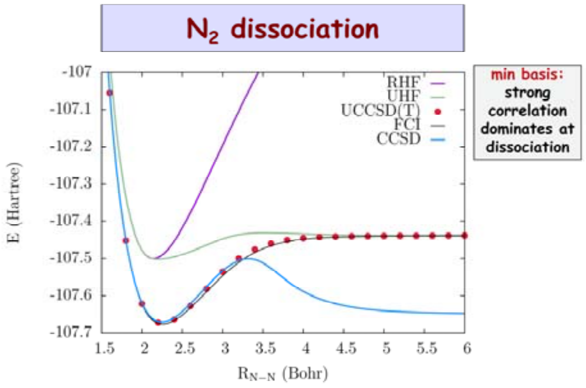
Department of Chemistry
Department of Physics & Astronomy
Department of Materials Science and Nano Engineering
Rice University, Houston, Texas, USA

guscus@rice.edu

Abstract

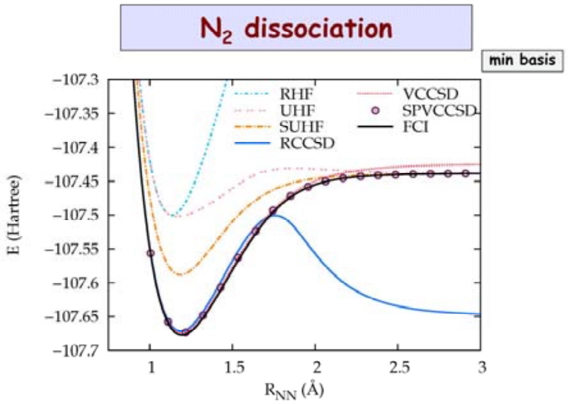
A precise accounting for electronic correlation effects is necessary for quantum mechanical calculations to reliably yield accurate results in molecular and solid-state systems. Correlation can be conceptually divided into weak correlations due to electrons avoiding one another because of the repulsive 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 year 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. In this presentation, I will discuss our current efforts for understanding the problems of restricted coupled cluster theory under strong correlation and designing a meaningful solution using these polynomial of particle-hole excitations.



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

1. Quasiparticle coupled cluster theory for pairing interactions, T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, *Phys. Rev.* **C 89**, 054305 (2014); http://link.aps.org/doi/10.1103/PhysRevC.89.054305

2. Analytic energy gradient for the projected Hartree-Fock method, R. Schutski, C. A. Jiménez-Hoyos, and G. E. Scuseria, *J. Chem. Phys.* **140**, 204101 (2014); http://scitation.aip.org/content/aip/journal/jcp/140/20/10.1063/1.4876490

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

4. Variational description of the ground state of the repulsive two-dimensional Hubbard model in terms of non-orthogonal symmetry-projected Slater determinants, R. R. Rodríguez-Guzmán, C. A. Jiménez-Hoyos, and G. E. Scuseria, *Phys. Rev.* **B 90**, 195110 (2014); http://journals.aps.org/prb/abstract/10.1103/PhysRevB.90.195110

5. Cluster-based mean-field and perturbative description of strongly correlated fermion systems: Application to the one- and two-dimensional Hubbard model, C. A. Jiménez-Hoyos and G. E. Scuseria, *Phys. Rev.* B **92**, 085101 (2015); http://link.aps.org/doi/10.1103/PhysRevB.92.085101

6. Polynomial Similarity Transformation Theory: A smooth interpolation between coupled cluster doubles and projected BCS applied to the reduced BCS Hamiltonian, M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, *Phys. Rev.* **B 93**, 125124 (2016); http://link.aps.org/doi/10.1103/PhysRevB.93.125124

7. Projected Hartree Fock Theory as a Polynomial Similarity Transformation Theory of Single Excitations, Y. Qiu, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **145**, 111102 (2016); http://dx.doi.org/10.1063/1.4963082

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

9. Projected Hartree-Fock as a polynomial of particle-hole excitations and its combination with variational coupled cluster theory, Yiheng Qiu, T. M. Henderson, and G. E. Scuseria; https://arxiv.org/abs/1702.08578

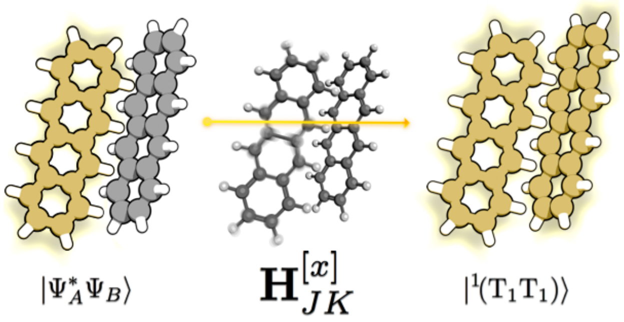
10. Combining symmetry collective states with coupled cluster theory: Lessons from the Agassi model Hamiltonian, M. R. Hermes, J. Dukelsky, and G. E. Scuseria; https://arxiv.org/abs/1703.02123

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

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

Abstract

Project Scope



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

Recent Progress

Over the past several years we have developed a fully *ab initio* version of the old Frenkel-Davydon exciton model, in which a collective excitation in a molecular crystal, aggregate, or other multi-chromophore system is described using an *ansatz* consisting of a linear combination of excitations that are localized on individual chromophores. 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 and aggregates. 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. Although the small models are amenable to traditional TDDFT calculations, they suffer from an artificial heterogeneity of 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. Upon transforming to normal modes, the 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 applied this approach to the problem of singlet fission in crystalline pentacene, where we showed that only when vibronic coupling is included does the (experimentally known) singlet fission pathway, $S_0 \rightarrow {}^1(TT)$, become energetically favorable.

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 with respect to counterpoise-corrected supersystem benchmarks.

Future Plans

We plan to apply the MBE to compute vibrational spectra of strongly-interacting, charged clusters of importance in understanding aerosol nucleation, and also to the prediction of NMR spectra for large carbohydrates of interest in biomass applications. (In both cases we have potential experimental collaborators.) 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 Development of Accurate and Affordable Electronic Structure Methods for the Condensed Phase

Postdoc(s): Jie Liu

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

Publications

1. A. F. Morrison and J. M. Herbert, *Evidence for singlet fission driven by vibronic coherence in crystalline tetracene.* Journal of Physical Chemistry Letters **8**, 1442 (2017).
2. J. M. Herbert, X. Zhang, A. F. Morrison, and J. Liu, *Beyond time-dependent density functional theory using only single excitations: Methods for computational studies of excited states in complex systems.* Accounts of Chemical Research **49**, 931 (2016).
3. K. U. Lao, K.-Y. Liu, and J. M. Herbert, *Understanding the many-body expansion for large systems. II. Accuracy considerations.* Journal of Chemical Physics **144**, 164105 (2016).
4. J. Liu and J. M. Herbert, *Pair-pair approximation to the generalized many-body expansion: An efficient and accurate alternative to the four-body expansion, with applications to* ab initio *protein energetics.* Journal of Chemical Theory and Computation **12**, 572 (2016).
5. J. Liu and J. M. Herbert, *Local excitation approximations to time-dependent density functional theory for excitation energies in solution.* Journal of Chemical Theory and Computation **12**, 157 (2016).
6. J. Liu and J. M. Herbert, *An efficient and accurate approximation to time-dependent density functional theory for systems of weakly coupled monomers.* Journal of Chemical Physics **143**, 034106 (2015).

7. A. F. Morrison and J. M. Herbert, *Low-scaling quantum chemistry approach to excited-state properties via* an ab initio *exciton model: Application to excitation energy transfer in a self-assembled nanotube.* Journal of Physical Chemistry Letters **6**, 4390 (2015).
8. K. U. Lao, R. Schäffer, G. Jansen, and J. M. Herbert, *Accurate description of intermolecular interactions involving ions using symmetry-adapted perturbation theory.* Journal of Chemical Theory and Computation **11**, 2473 (2015).
9. K. U. Lao and J. M. Herbert, *Accurate and efficient quantum chemistry calculations for noncovalent interactions in many-body systems: The XSAPT family of methods*. Journal of Physical Chemistry A **119**, 235 (2015).
10. A. F. Morrison, Z.-Q. You, and J. M. Herbert, *Ab initio implementation of the Frenkel-Davydov exciton model: A naturally parallelizable approach to computing collective excitations in crystals and aggregates.* Journal of Chemical Theory and Computation **10**, 5366 (2014).

DEVELOPMENT OF APPROACHES TO MODEL EXCITED STATE CHARGE AND ENERGY TRANSFER IN SOLUTION: MODELING EXCITED STATES IN THE CONDENSED PHASE

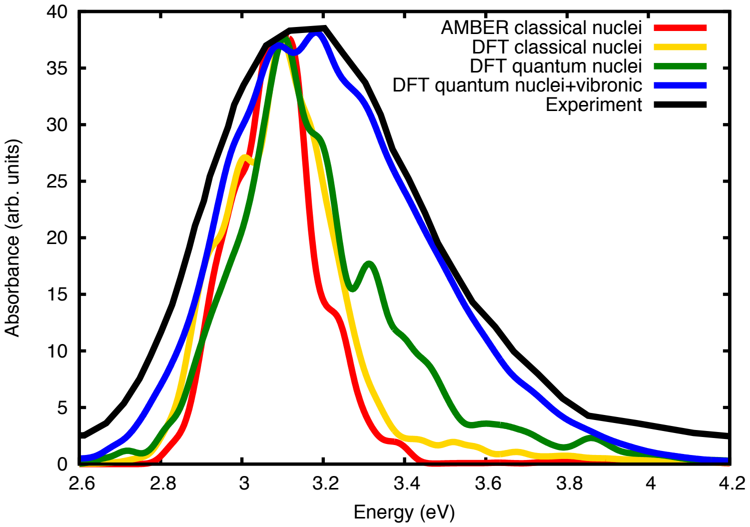
Christine Isborn[1] (PI), Aurora Clark (co-PI)[2], Thomas Markland (co-PI)[3]
1. University of California Merced, Email: cisborn@ucmerced.edu
2. Washington State University, Email: auclark@wsu.edu
3. Stanford University, Email: tmarkland@stanford.edu

Xochitl Sosa Vazquez, Joel Milanese, Makenzie Provorse, Tim Zuehlsdorff, Christine M. Isborn
Department of Chemistry, University of California, Merced

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. For reliable condensed phase simulations, an accurate model that includes both short- and long-range interactions is required. Short- and long-range interactions may be particularly strong in aqueous solution, where hydrogen-bonding and proton transfer may play a large role at short range and polarization may play a large role at long-range. For realistic condensed phase calculations that take into account solute-solvent interactions large-scale quantum mechanical (QM) calculations that include the condensed phase environment are necessary. These large-scale calculations can also help us determine what physics is necessary for more approximate models. The Isborn group is using excited state time-dependent density functional theory calculations that include the condensed phase to determine how to accurately model chromophores in solution. We are exploring various aspects of modeling condensed phase systems, including examination of basis set and density functional dependence [1], the limitations of the adiabatic approximation in time-dependent density functional theory [2], the role of nuclear quantum effects [3] and vibronic effects on computed absorption spectra, the best choice of classical solvent model [4], and how much QM solvent to include in a calculation [4, 5].

To determine how much solvent should be treated with QM in a condensed phase calculation, we have examined convergence trends for solutes of different polarity [4, 5]. Although short-range solute-solvent interactions such as charge-transfer, hydrogen bonding, and solute-solvent polarization can be taken into account with a QM treatment of the solvent, it is unclear how much QM solvent is necessary to accurately model interactions with different solutes. We investigated the effect of explicit QM solvent on absorption spectra computed for a series of solutes with decreasing polarity. By adjusting the boundary between QM and classical molecular mechanical solvent, convergence of the calculated absorption spectra with respect to the size of the QM region is achieved. We found that the rate of convergence does not correlate with solute polarity when excitation energies are calculated using time dependent density functional theory with a range-separated hybrid functional, but does correlate with solute polarity when using configuration interaction singles. We also found that larger basis sets converge the computed spectrum with fewer QM solvent molecules. To optimize the computational cost with respect to convergence, we tested a mixed basis set with more basis functions for atoms of the chromophore and the solvent molecules that are nearest to it and fewer basis functions for the atoms of the remaining solvent molecules in the QM region. Our results show that using a mixed basis sets is potentially an effective way to significantly lower the computational cost while reproducing the results computed with larger basis sets. We also have tested which classical solvation method best interfaces with large amounts of QM solvent, and have found that the convergence of excitation energies is similar for molecular mechanical point charges and a polarizable continuum model. We found that while the van der Waals (VDW) definition of the PCM cavity is adequate for molecular structures with small amounts of QM solvent, larger QM solvent layers had gaps in the VDW PCM cavity, leading to asymptotically incorrect excitation energies. Given that the VDW cavity leads to unphysical solute-solvent interactions, we advise the computational community to instead use a solvent excluded surface cavity for QM/PCM calculations that include QM solvent.



In our work with the Clark and Markland groups, we are analyzing which solvent effects are important to include for accurate simulation of aqueous absorption spectra by comparing our computed spectra to experimental spectra for different chromophores. We are comparing absorption spectra computed from configurations obtained from classical force field molecular dynamics to ab initio density functional theory Born-Oppenheimer molecular dynamics that can simulate proton transfer, and also examining the importance of nuclear quantum effects via path integral molecular dynamics. We will analyze the hydrogen bonding dynamics in these different potentials and explore how hydrogen bonding and solvent environment affects the electronic excitations. We have also developed a computational method to take into vibronic contributions to the absorption spectrum in the presence of explicit solvent. Our initial studies show that including nuclear quantum effects and vibronic effects are important for reproducing experimental results. 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.

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)

Isborn Group Postdoc(s): Makenzie Provorse, Tim Zuehlsdorff

Up to Ten Publications Acknowledging this Grant (since September 2015), Isborn Group

[1] "Size-dependent error of the density functional theory ionization potential in vacuum and solution." X. A. Sosa Vazquez and C. M. Isborn *J. Chem. Phys*. 143, 244105 (2015)

[2] "Electron Dynamics with Real-Time Time-Dependent Density Functional Theory." M. R. Provorse and C. M. Isborn. "*Int. J. Quantum Chem*. 116, 739-749 (2016)

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

[4] "Convergence of Excitation Energies in Mixed Quantum and Classical Solvent: Comparison of Continuum and Point Charge Models." M. R. Provorse, T. Peev, C. Xiong, C. M. Isborn. *J. Phys. Chem. B* 120, 12148-12159 (2016)

[5] "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.* ASAP (2017) **DOI:** 10.1021/acs.jctc.7b00159

Anharmonic Densities of States: A General Dynamics-Based Solution

PI: Julius Jellinek

Chemical Sciences and Engineering Division, Argonne National Laboratory,
Argonne, IL 60439

jellinek@anl.gov

Abstract

This program focuses on theoretical/computational explorations of structural, dynamical, electronic, and chemical reactivity properties of a broad class of finite systems that play a central role in many technologically important areas. Together with applications, our work involves new conceptual and methodological developments aimed at more adequate and more accurate analysis and characterization of nanoscale systems and phenomena. One of our recent efforts targeted the general solution for the long-standing problem of anharmonic densities of states.

Density of states (DOS) is a fundamental characteristic of systems that lies in the very foundation of statistical mechanics and all the theoretical constructs (such, e.g., as kinetic rate theories, phase diagrams, etc.) that derive from them. Knowledge of DOS is central for calculation of entropy, partition function, free energy, reaction rate constants, and other important characteristics. The accuracy of all these depends on the accuracy with which the DOS is defined. Even though virtually all real systems are anharmonic, the current practice in the computation of vibrational DOSs is largely based on the harmonic approximation. The reason is that despite major efforts over more than seven decades a general and exact, yet practical in applications, solution to the problem of anharmonic DOSs stubbornly resisted resolution. The alternatives introduced are mostly limited to cases of weak anharmonicity and/or suffer from other shortcomings.

In a breakthrough development,[7] we formulated a general and exact solution to this long-standing problem, which is applicable to arbitrary degree of anharmonicity (i.e., any system) and that is practical and efficient in applications. The solution and its algorithmic implementations are developed within the frameworks of both classical and quantum mechanics. The quantum implementation involves generalization and significant enhancement in the efficiency of the celebrated Beyer-Swinehart algorithm, which is the fastest to date algorithm used in the computation of the quantum harmonic DOSs. Our solution is based on simulating the actual dynamical behavior of systems on the time scale of interest, short or long, as defined by the experiment and/or the nature of the process or phenomenon at hand. As a consequence, the resulting anharmonic DOSs are fully dynamically informed and, in general, time-dependent. As such, they lay the foundation for formulation of new statistical mechanical frameworks that incorporate time and reproduce exactly the actual time-averaged dynamical behavior of systems on the temporal scale of interest irrespective of whether this behavior is statistical or not in the traditional sense.

The significance of this advance is that it expands the fundamental conceptual and operational arsenals of statistical mechanics with far-reaching and broad implications in chemistry,

physics, materials science, nanoscience and biology. Work has been initiated on extending this development to the general case of rotational(ro)-vibrational DOSs for systems with arbitrary degree of anharmonicity and arbitrarily strong ro-vibrational coupling.

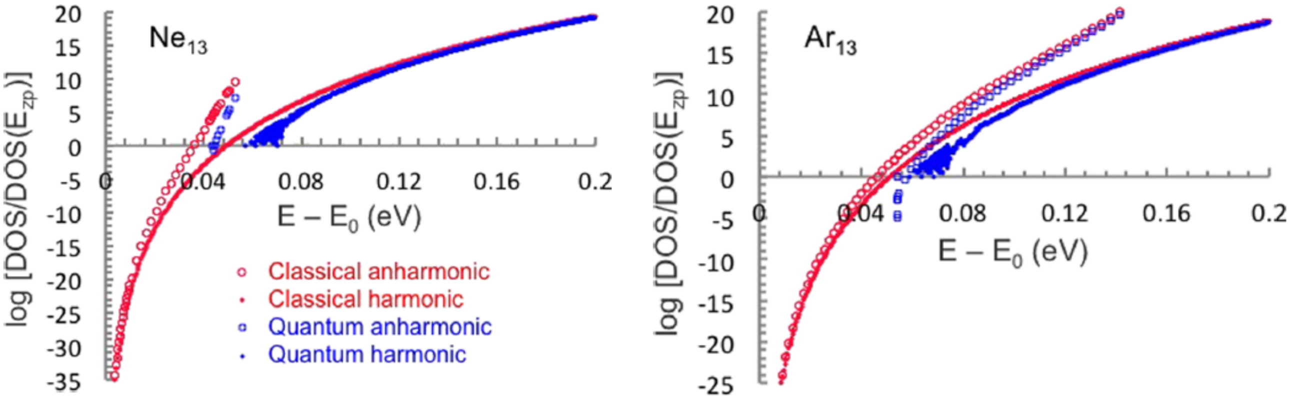


Figure 1. Illustration of the application of the new methodology to two highly anharmonic clusters Ne_{13} and Ar_{13}. The graphs show the anharmonic and harmonic, classical and quantum, DOSs as a function of the internal energy.

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References

1. Investigating the Metallic Behavior of Na Clusters Using Site Specific Polarizabilities
   Li Ma, K. A. Jackson, J. Wang, M. Horoi, and J. Jellinek
   Phys. Rev. B **89**, 035429(1-10) (2014).
2. Dynamic Layer Rearrangement During Growth of Layered Oxide Films by Molecular Beam Epitaxy
   J.-H. Lee, G. Luo, I. C. Tung, S.-H. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S. M. Nakhmanson, J. A. Eastman, H. Hong, J. Jellinek, D. Morgan, D. D. Fong, and J. W. Freeland
   Nature Materials **13**, 879-883 (2014).
3. Transition from Atoms to Clusters to Condensed Matter
   J. Jellinek
   Adv. Chem. Phys. **157**, 25-41 (2015).
4. H_2 Saturation on Palladium Clusters
   A. W. Pelzer, J. Jellinek, and K. A. Jackson
   J. Phys. Chem. A **119**, 3594-3603 (2015).
5. Morphology Tailoring of Pt Nanocatalysts for the Oxygen Reduction Reaction: The Paradigm of Pt_{13}
   W. Zhang, A. Sumer, J. Jellinek and D. Cheng
   ChemNanoMat **1**, 482-488 (2015) [Featured on the cover of the journal].
6. Reactive Scattering Calculations for ^{87}Rb + ^{87}RbHe → $Rb_2(^3\Sigma_u^+, v)$ + He from Ultralow to Intermediate Energies
   R. Rodriguez-Cantano, T. Gonzales-Lezana, R. Prosmiti, G. Delgado-Barrio, P. Villarreal, and J. Jellinek
   J. Chem. Phys. **142**, 164304(1-8) (2015).
7. Anharmonic Densities of States: A General Dynamics-Based Solution
   J. Jellinek and D. Aleinikava
   J. Chem. Phys. **144**, 214103(1-12) (2016).
8. Si Clusters Are More Metallic Than Bulk Si
   K. A. Jackson and J. Jellinek
   J. Chem. Phys. **145**, 244302(1-7) (2016).

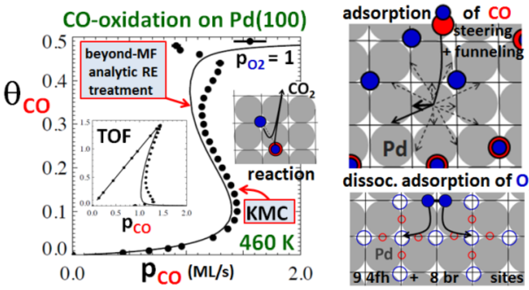
Jim W. Evans

Statistical mechanical and energetic analysis of chemisorption and catalysis on metals

Da-Jiang Liu, F. Zahariev, M.S. Gordon, T.L. Windus, and Jim Evans
Ames Laboratory – USDOE, Division of Chemical & Biological Sciences

Abstract

We describe development of predictive molecular-level models for chemisorption and catalytic reaction-diffusion processes (determining, e.g., reaction yield or TOF) on surfaces. Traditional mean-field (MF) chemicals kinetics can fail due to strong spatial correlations between adsorbed reactants (either of thermodynamic or kinetic origin). Thus, we utilize stochastic multi-site lattice gas models (accounting for distinct adsorption sites), behavior of which is analyzed by KMC simulation. Such modeling must precisely describe (e.g., with ab-initio energetics) adlayer thermodynamics, well as local-environment-dependent kinetics of adsorption, desorption, diffusion, and reaction. Model validation comes from extensive comparison with experiment, e.g., for CO-oxidation on metal(100) surfaces at low pressure (P) recovering and elucidating observed steady-state bifurcations and TPR kinetics. For deeper insight, we have developed beyond-MF rate equations accounting for subtle equilibrium adlayer ordering to describe these systems. In other work, we successfully analyze non-MF CO-oxidation kinetics at high P producing strong non-equilibrium correlations. We also explore the role of chemisorbed species (e.g., catalytic promoters and poisons) such as S which induce dynamic rearrangement of the catalytic surface and possible metal-S complex formation.



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

Personnel associated with the above projects: PIs: J.W. Evans, M.S. Gordon; T.L. Windus
Staff Scientists: D.-J. Liu, F. Zahariev; Students: Andres Garcia, Jeff Boschen, Jiyoung Lee

PROGRAM SCOPE

The theoretical Chemical Physics project at Ames Laboratory pursues molecular-level and coarse-grained modeling of **heterogeneous catalysis and other complex reaction phenomena** at surfaces and in mesoporous materials. The effort incorporates: *electronic structure analysis and non-equilibrium statistical mechanical and multi-scale modeling*. The former includes quantum chemistry studies for large systems, and for homogeneous & heterogeneous catalysis. The latter (by Liu & Evans) described in part below explores molecular-level descriptions of: (i) the interplay between anomalous transport and catalytic reaction in functionalized mesoporous materials; (ii) chemisorption and heterogeneous catalysis on metal surfaces and nanoclusters. These studies also connect molecular-level treatments to mesoscale spatiotemporal mesoscale behavior, and analysis of fundamental non-equilibrium behavior in reaction-diffusion systems.

RECENT PROGRESS

Chemisorption and Catalysis on Extended Surfaces (and Nanoclusters)

Detailed and predictive multisite lattice-gas (msLG) models and efficient KMC simulation algorithms were developed to describe CO-oxidation on unreconstructed metal(100) surfaces under lower-pressure (P) conditions.[1] The msLG models account for multiple stable adsorption sites of some reactant species, and thus allow more accurate treatment of adlayer ordering and reaction configurations. Reactive steady-states are controlled by kinetics as well as adlayer thermodynamics. Thus, guided by DFT, we developed realistic models for dissociative adsorption of oxygen on mixed reactant adlayers on metal(100) surfaces addressing the shortcomings of Langmuir and Brundle-Behm-Barker pictures,[2] and also for CO-adsorption including "steering". Extensive DFT analysis has been performed to determine adspecies adsorption energies and interactions, with higher-level theory (by Zahariev, Gordon) assessing DFT limitations.[3] Model predictions for bifurcations of reactive steady-states, titration, TPD and TPR kinetics were compared extensively with experiment.[1] For deeper insight into behavior controlling reactivity, and for practical utility, we have also developed an analytic beyond-MF rate equation treatment for a slightly simplified msLG model of CO-oxidation on Pd(100), which still accounts for the complex equilibrium adlayer superlattice ordering.[3]

Another effort explored CO-oxidation at high-P on RuO_2(110), an oxidized surface of Ru. Reuter *et al.* noted a dramatic failure of MF-rate equation treatment of kinetics due to strong spatial correlations induced by a combination of reaction and limited mobility. We develop a formalism to precisely describe these correlations and also the sluggish dynamics in this system.[4] We also pursued the BESAC scientific grand challenge to develop a fundamental understanding of non-equilibrium phase transitions (e.g., nucleation/metastability in catalytic poisoning).[5]

Detailed characterization of chemisorption is key to describe reactant ordering in catalysis, but also possible chemisorption-induced restructuring and dynamics of metal surfaces by reactants or impurities (promoters or poisons). We recently focused on the effect of sulfur (S) which can induce reconstruction on terraces and at steps, and metal-S complex formation on Au, Ag, and Cu coinage metal surfaces. Liu has performed extensive DFT analysis is closely integrated with high-resolution low-T STM studies from Japanese and US collaborators for a comprehensive exploration of low-energy structures, sometimes combined with statistical mechanical analysis.[6] For S/Cu, experimental data suggests a preference for motifs both in reconstruction and complex formation suggest a preference for 4-fold (over 3-fold) hollow sites and for S-M-S motifs. With Windus et al., we explore this trend for nanoclusters as well as extended surfaces with both plane-wave and localized atomic orbital bases finding strong quantum size effects with increasing size but emergence of 4fh preference.[7] Separate analysis with Windus explored the stability of X-Au-X "staple" motifs on Au(111) where X = S, CH_3S,..[8]

Catalytic Reactions in Functionalized Nanoporous Materials

Recent efforts have considered catalytic conversion reactions occurring inside linear nanopores of zeolites, functionalized mesoporous silica (by the Ames Lab catalysis group), etc.. Previous analyses had produced limited characterization of low reactivity due to inhibited transport into pores. We showed that mean-field reaction-diffusion equation (RDE) treatments fail to describe such behavior, instead developing a successful "generalized hydrodynamic" treatment. A key parameter is the propensity for reactants and products to pass each other in the pore, a quantity which can be assessed by suitable Langevin simulations or equivalent Fokker-Planck equation analysis.[9] Our recent efforts extended our modeling to treat: concentration-dependent (stereo-) selectivity (with Windus), the effect of interactions between reactant and product species and the porous material, and developed new strategies to determine the generalized tracer diffusivity (the key input to our generalized hydrodynamic formulation).[10]

FUTURE PLANS

Future research efforts will include the following: **(i)** Development of more detailed system-specific models for catalysis in nano- and meso-porous materials. These studies should account for different mobilities of reactants and products, the details of rotational-translational diffusion in controlling passing propensities of molecules in pores, solvent-mediated interactions, etc. In collaboration with the *Gordon group,* we aim to apply EFP-MD analysis to assess both the solvent-mediated diffusivity and interactions of reactant and product species. This key information will provide input to our coarse-grained modeling, in particular for our Langevin simulations of passing propensities. **(ii)** Development of realistic and predictive models for catalytic reactions on metal surfaces addressing limitations of DFT predictions for energetics, and incorporating the local environment dependence of barriers for reactions and of the dynamics of dissociative adsorption, etc. Here, we will collaborate further with *Zahariev and Gordon* comparing predictions of high-level methods including QMC with DFT predictions. **(iii)** Development of appropriate theoretical framework to reliably describe strong correlations due to inhibited mobility in surface reactions at high-pressures. Related more general studies will attempt to provide a fundamental understanding of non-equilibrium poisoning transitions and related phenomena in catalytic reaction systems. **(iv)** Further analysis of the interaction of metal surfaces and nanoclusters with chemisorbed species, particularly S which can act as a promoter or poison. This work involves a collaboration with the *Windus group* to elucidate the nature of the metal-S interaction and the stability of various surface motifs.

Selected Publications Acknowledging this Grant from 2014-present

1. Liu, D.-J.; Garcia, A.; Wang, J.; Ackerman, D.; Wang, C.-J.; Evans, J.W. KMC simulation of statistical mechanical models and coarse-grained mesoscale descriptions of catalytic reaction-diffusion processes: 1D nanoporous and 2D surface systems, *Chemical Reviews*, 2015, *115*, 5979-6050.
2. Liu, D.-J.; Evans, J.W. Dissociative adsorption of O_2 on unreconstructed metal(100) surfaces: Pathways, energetics, and sticking kinetics, *Phys. Rev. B* 2014, *89*, 205406; Also: Statistical mechanical models…with blocking, steering, and funneling, *J. Chem. Phys.* 2014, *140*, 194704.
3. Liu, D.-J.; Zahariev, F.; Gordon, M.S.; Evans, J.W. Predictive Beyond-Mean-Field Rate Equations for… Catalytic Surface Reactions: CO-Oxidation on Pd(100), *J. Phys. Chem. C*, 2016, *120*, 28639-28653.
4. Liu, D.-J.; Evans, J.W. Transitions between strongly correlated and random steady-states for catalytic CO-oxidation on surfaces at high-pressure, *J. Chem. Phys.* 2015, *142*, 134703.
5. Wang, C.-J.; Liu, D.-J.; Evans, J.W. Generic two-phase coexistence and metastability in a threshold version of Schloegl's model for autocatalysis, *J. Chem. Phys.* 2015, *142*, 164105.
6. Walen, H.; Liu, D.-J.; Oh, J.; Lim, H.; Evans, J.W.; Aikens, C.; Kim, Y.; Thiel, P.A. Cu_2S_3 complex on Cu(111) as a candidate for mass transport enhancement, *Phys. Rev. B*, 2015, *91*, 045426.
7. Boschen, J.; Lee, J.; Windus, T.L.; Evans, J.W.; Thiel, P.A.; Liu, D.-J. S-adsorption on (111) & (100) facets of Cu nanoclusters, J. Chem. Phys. 2016, 145, 164312. Also: *J. Phys. Chem. C* 2016, *120*, 10268.
8. Lee, J.; Boschen, J.; Windus, T.; Thiel, P.; Liu, D.-J. Stabilization of X-Au-X complexes on Au(111): a theoretical investigation and comparison of X = S, Cl, CH_3S,.. *J. Phys. Chem. C* 2017, *212*, 3870.
9. Wang, C.-J.; Ackerman, D.M.; Slowing, I.I.; Evans, J.W. Langevin and Fokker-Planck analyses of inhibited molecular passing processes… in nanoporous materials, *Phys. Rev. Lett.* 2014, *113*, 038301.
10. Garcia, A.; Evans, J.W. Catalytic Conversion in Nanoporous Materials: Concentration Oscillations and Spatial Correlations due to Inhibited Transport and Intermolecular Interactions, *J. Chem. Phys.* 2016 *145*, 174705.

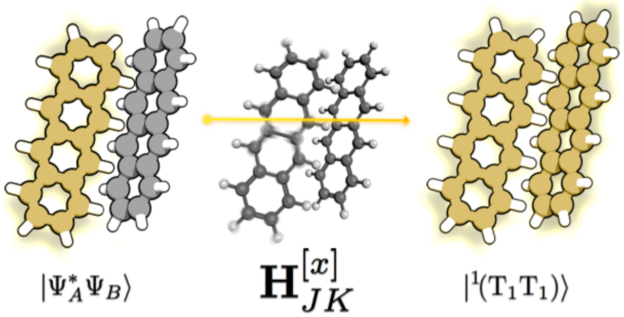
Fragment-Based Quantum Chemistry for Non-Covalent Interactions and Excitation Energy Transfer

John M. Herbert (herbert@chemistry.ohio-state.edu)

Dept. of Chemistry & Biochemistry, The Ohio State University, Columbus, OH 43210

Abstract

Project Scope



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

Recent Progress

Over the past several years we have developed a fully *ab initio* version of the old Frenkel-Davydon exciton model, in which a collective excitation in a molecular crystal, aggregate, or other multi-chromophore system is described using an *ansatz* consisting of a linear combination of excitations that are localized on individual chromophores. 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 and aggregates. 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. Although the small models are amenable to traditional TDDFT calculations, they suffer from an artificial heterogeneity of 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. Upon transforming to normal modes, the 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 applied this approach to the problem of singlet fission in crystalline pentacene, where we showed that only when vibronic coupling is included does the (experimentally known) singlet fission pathway, $S_0 \rightarrow {}^1(TT)$, become energetically favorable.

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 with respect to counterpoise-corrected supersystem benchmarks.

Future Plans

We plan to apply the MBE to compute vibrational spectra of strongly-interacting, charged clusters of importance in understanding aerosol nucleation, and also to the prediction of NMR spectra for large carbohydrates of interest in biomass applications. (In both cases we have potential experimental collaborators.) 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 Development of Accurate and Affordable Electronic Structure Methods for the Condensed Phase

Postdoc(s): Jie Liu

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

Publications

1. A. F. Morrison and J. M. Herbert, *Evidence for singlet fission driven by vibronic coherence in crystalline tetracene.* Journal of Physical Chemistry Letters **8**, 1442 (2017).
2. J. M. Herbert, X. Zhang, A. F. Morrison, and J. Liu, *Beyond time-dependent density functional theory using only single excitations: Methods for computational studies of excited states in complex systems.* Accounts of Chemical Research **49**, 931 (2016).
3. K. U. Lao, K.-Y. Liu, and J. M. Herbert, *Understanding the many-body expansion for large systems. II. Accuracy considerations.* Journal of Chemical Physics **144**, 164105 (2016).
4. J. Liu and J. M. Herbert, *Pair-pair approximation to the generalized many-body expansion: An efficient and accurate alternative to the four-body expansion, with applications to* ab initio *protein energetics.* Journal of Chemical Theory and Computation **12**, 572 (2016).
5. J. Liu and J. M. Herbert, *Local excitation approximations to time-dependent density functional theory for excitation energies in solution.* Journal of Chemical Theory and Computation **12**, 157 (2016).
6. J. Liu and J. M. Herbert, *An efficient and accurate approximation to time-dependent density functional theory for systems of weakly coupled monomers.* Journal of Chemical Physics **143**, 034106 (2015).

7. A. F. Morrison and J. M. Herbert, *Low-scaling quantum chemistry approach to excited-state properties via* an ab initio *exciton model: Application to excitation energy transfer in a self-assembled nanotube.* Journal of Physical Chemistry Letters **6**, 4390 (2015).
8. K. U. Lao, R. Schäffer*,* G. Jansen, and J. M. Herbert, *Accurate description of intermolecular interactions involving ions using symmetry-adapted perturbation theory.* Journal of Chemical Theory and Computation **11**, 2473 (2015).
9. K. U. Lao and J. M. Herbert, *Accurate and efficient quantum chemistry calculations for noncovalent interactions in many-body systems: The XSAPT family of methods*. Journal of Physical Chemistry A **119**, 235 (2015).
10. A. F. Morrison, Z.-Q. You, and J. M. Herbert, *Ab initio implementation of the Frenkel-Davydov exciton model: A naturally parallelizable approach to computing collective excitations in crystals and aggregates.* Journal of Chemical Theory and Computation **10**, 5366 (2014).

J. Karl Johnson

Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO_2 Hydrogenation

Lin Li[1], Jingyun Ye[1], J. Karl Johnson[1]

[1]University of Pittsburgh, Department of Chemical & Petroleum Engineering, Pittsburgh PA 15261

Abstract

Capture and conversion of CO_2 into fuels and other value-added chemicals is an attractive alternative or supplement to carbon sequestration. Carbon capture and conversion has the potential to reduce net CO_2 emissions while generating high-energy density fuels and other valuable commodities. The main roadblock to this approach is that hydrogenation of CO_2 is very challenging because of its kinetic and thermodynamic stability. Hence, reduction of CO_2 typically requires aggressive reaction conditions (high temperature and high pressure). Homogeneous catalytic conversion of CO_2 can be carried out under fairly mild conditions, but has the drawback catalyst recycling and product separation are usually very difficult. An ideal catalyst for large-scale industrial CO_2 hydrogenation would combine the advantages of homogeneous and heterogeneous catalysts. Moreover, if CO_2 capture could be combined in a single process with CO_2 reduction, then the economics could be significantly enhanced through process intensification.

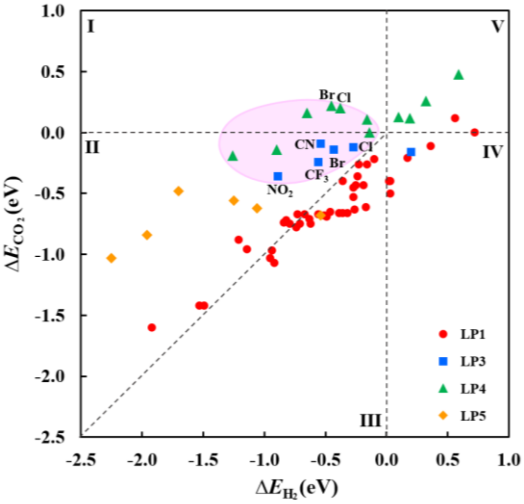


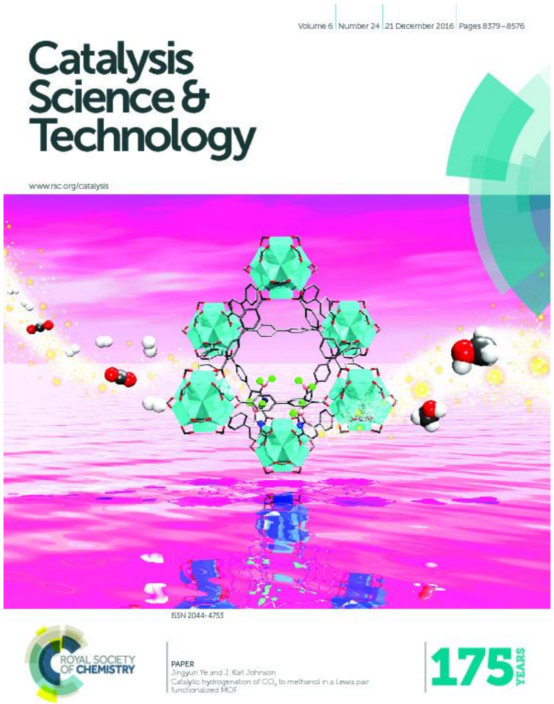
Figure 1. Identification of functional groups that bind H_2 more strongly than CO_2. **LP1**, **LP3**, **LP4**, and **LP5** represent different classes of Lewis pair moieties that have been modified. The groups marked in the pink shaded region are predicted to have lower barriers based on linear scaling relations.[1]

We have used density functional theory to computationally design materials that have advantages of both homogeneous and heterogeneous catalysts. One family of catalysts we have designed is based on Lewis pair functional groups, which have both Lewis acid and Lewis base sites on a single molecule. These molecular catalysts can be covalently attached to porous materials, such as metal organic framework (MOF).[2]

The general mechanism for CO_2 reduction in these functionalized MOFs involves at two-step process. The first step is the heterolytic dissociation of H_2 on the Lewis pair group, leading to a protic hydrogen bound to the Lewis base site and a hydridic hydrogen bound to the Lewis acid site. The second step is the concerted two-hydrogen (two-electron) reduction of CO_2 by the simultaneous addition of the hydridic hydrogen to the carbon of CO_2 and the protic hydrogen to one of the oxygens. We have developed design principles for optimizing catalyst performance based on a Sabatier analysis coupled with descriptors for the elementary reaction barriers for converting CO_2 to formic acid for various Lewis pair functional groups bound to a thermally and chemically stable MOF known as UiO-66.[3]

We found that many of the functional groups identified in our previous work that have favorable rates for CO_2 reduction also tend to chemisorb CO_2 more strongly than H_2, leading to catalyst poisoning due to competitive adsorption of CO_2 over H_2. We utilized the scaling relations identified for UiO-66 functionalized MOFs to explore how to modify the binding energies of CO_2 and H_2 by adjusting the properties of the Lewis pair moieties. We considered five different classes of functional groups. The **LP1** class of functional groups is designed to modify the Lewis acid site. The **LP2** class is designed to modify the base site of the Lewis pair. The **LP3** and **LP4** classes increase steric hindrance of the acid and base sites. The **LP5** class replaces the Lewis base site N with P, which modifies the basicity relative to **LP1**, and also modifies the acidity by substituents attached to the Lewis acid site. Results of our screening are shown in Figure 1.[1]

We have developed a modified catalysts using a larger MOF, UiO-67, which can incorporate multiple functional groups per unit cell. We have also developed new functional groups by incorporating the Lewis base site directly into one of the rings of the linker. We have mapped out reaction pathways for CO_2 reduction to methanol in this new catalytic material.[4] We have also used grand canonical Monte Carlos simulations to demonstrate that this material can selectively adsorb CO_2 from a simulated flue gas mixture of N_2 (85%) and CO_2 (15%).[4] Our paper reporting these results was published in *Catalysis Science & Technology* and was selected for the cover art for issue 24, 21 December 2016 and this cover art is shown in Figure 2. In future work we are identifying new approaches to activating CO_2 in addition to activating H_2.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Catalysis Science & Technology

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ROYAL SOCIETY OF CHEMISTRY

PAPER
Jingyun Ye and J. Karl Johnson
Catalytic hydrogenation of CO_2 to methanol in a Lewis pair functionalized MOF

175 YEARS

Figure 2. Cover of *Catalysis Science & Technology* highlighting our article on conversion of CO_2 to methanol using functionalized UiO-67 as the catalyst.[4]

References

1. Ye, J.; Yeh, B. Y.; Reynolds, R. A.; Johnson, J. K., Screening the activity of Lewis pairs for hydrogenation of CO_2. *Molecular Simulation* 2017, in press, 1-7.
2. Ye, J.; Johnson, J. K., Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO_2 Hydrogenation. *ACS Catalysis* 2015, 5, 2921-2928.
3. Ye, J.; Johnson, J. K., Screening Lewis Pair Moieties for Catalytic Hydrogenation of CO_2 in Functionalized UiO-66. *ACS Catalysis* 2015, 5, 6219-6229.
4. Ye, J.; Johnson, J. K., Catalytic hydrogenation of CO_2 to methanol in a Lewis pair functionalized MOF. *Catalysis Science & Technology* 2016, 6, 8392-8405.

Grant Numbers and Grant Titles

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

Postdocs: Lin Li, Jingyun Ye

Students: Benjamin Y. Yeh (undergraduate), Ronald A. Reynolds (undergraduate)

Publications

1. Jingyun Ye, Benjamin Y. Yeh, Ronald A. Reynolds, J. Karl Johnson, "Screening the Activity of Lewis Pairs for Hydrogenation of CO_2", *Molecular Simulation,* in press, (2017). DOI: 10.1080/08927022.2017.1295457
2. Jingyun Ye, J. Karl Johnson, "Catalytic Hydrogenation of CO_2 to Methanol in a Lewis Pair Functionalized MOF", *Catalysis Science & Technology*, 6, 8392-8405 (2016). DOI: 10.1039/c6cy01245k
3. Jingyun Ye, J. Karl Johnson "Screening Lewis Pair Moieties for Catalytic Hydrogenation of CO_2 in Functionalized UiO-66", *ACS Catalysis*, **5**, 6219–6229 (2015).
4. Jingyun Ye and J. Karl Johnson "Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO_2 Hydrogenation", *ACS Catalysis*, **5**, 2921–2928 (2015).

2017 CTC PI MEETING

ABSTRACT

- **Program Title**: Magnetic and Tunable Band Gap Cluster Building Blocks for Novel Nanostructure Materials and Electron Transport through their Assemblies.
- **Principal Investigator**: Khanna, Shiv
- **Mailing Address**: Physics Department, Virginia Commonwealth University, Box-2000, Richmond, VA 23284-2000, USA
- **Email**: snkhanna@vcu.edu
- **Program Scope**: Extensive research over the past three decades has shown that the electronic, magnetic, and chemical properties of small clusters can be different from the bulk and change with size, composition, and the charged state. A promising direction in nanoscience is then the formation of materials whereby atomic 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 stable motifs with interesting magnetic properties and studying the collective behavior of assemblies of such particles is at the heart of the current proposal.

Our comprehensive program starts from studies of the electronic structure and magnetic properties of free and supported clusters for identifying stable magnetic motifs with different magnetic strengths, magnetic anisotropy energy, and varying band gaps; to investigation the collective behavior of the assemblies of such motifs; to investigate the magnetic coupling and electrical transport through molecules of such motifs; and work with experimental groups to synthesize such assemblies. The program involves four interrelated areas of study, namely: A) magnetic properties of free TM_nC_m/TM_nSi_m (TM=Cr, Mn, Fe, Co, Ni) clusters and TM_n clusters supported on graphene to identify potential magnetic building blocks.; B) studies of metal chalcogenide superatoms and Si_nTM_m (TM= Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, Pd) clusters to identify potential semiconducting magnetic building blocks.; C) studies of ligated cluster assemblies and supported ligated clusters to explore magnetic assemblies with tunable band gaps.; and D) develop computational tools to carry out electronic transport studies. The theoretical studies are carried out in close collaboration with experimental groups.

- **Recent Progress:** This has been a very productive period. Our work was highlighted on the cover of Journal of Materials Chemistry C and on the back cover of Physical Chemistry Chemical Physics journals. The work proceeded along three different directions.

(1) **Magnetic Response of an Assembly of Magnetic Clusters**:

Starting from the bulk magnetic material, the decrease in size to smaller than a typical domain size results in a nanoparticle where the atomic moments are exchange coupled and the particle behaves like a giant magnet with a moment Nμ where N is the number of atoms and μ is the moment per atom. At small sizes, the magnetic anisotropy energy responsible for holding the magnetic moment along certain directions becomes comparable to the thermal energy. The thermal fluctuations can then lead to random flipping of the giant magnetic moment with time, leading to superparamagnetic relaxations and a thermally unstable magnetic order. The first step to stable magnetic order is then to control the magnetic anisotropy. In a recent work (highlighted on the DOE website) we showed that one of the approaches to high anisotropy is to synthesize nanoparticles where the transition metal layers are separated by carbon. Using wet chemical methods, we reported synthesis of iron-cobalt-carbide nanoparticles with blocking temperature, T_B, of 790 K for particles with a domain size as small as 5±1 nm. While the synthesis of nanoparticles with controlled anisotropy is an exciting development for applications such as memory storage, one of the questions is the magnetic behavior of an assembly of magnetic nanoparticles. For example, how can one develop soft or hard magnetic solids by controlling anisotropy and interaction between nano-particles.

In this period, we took the first step towards investigating the nature of collective response that emerges as one assembles magnetic clusters/nanoparticles. We studied the progression of the collective behaviors as the particles are allowed to interact by isotropic and anisotropic interactions. We initially investigate the magnetic response as the particles interact via isotropic exchange interactions including ferromagnetic and anti-ferromagnetic couplings. In finite systems, the spin orbit coupling can lead to anisotropic exchange interactions including the well-known Dzyaloshinskii-Moriya (DM) interaction. The DM interaction between interacting ions that lack inversion symmetry can lead to spin canting and is usually included at surfaces and in small particles characterized by outer sites that do not possess center of symmetry. We focussed our investigations on a recently synthesized assembly consisting of $Ni_9Te_6(PEt_3)_8$ clusters with a Ni_9Te_6 core decorated with 8 tri-ethylphosphine (PEt_3) ligands attached to Ni sites. The cluster forms a rock-salt (NaCl) structure when combined with C_{60}. Experiments indicate that the ionic solid is magnetic and undergoes a ferromagnetic phase transition at low temperatures (4K) while it exhibits Curie-Weiss behavior at higher temperatures (above 10K). The SQUID measurements also indicate that the individual clusters behave as isolated localized magnets with a magnetic moment of around 5.4 μ_B per functional unit.

We first undertook an investigation of the magnetic moment and anisotropy in a $Ni_9Te_6(PEt_3)_8$ cluster using a first- principles approach based. The theoretical studies indicate that the individual clusters have a spin magnetic moment of 5.3 μ_B in agreement with experiment. Further, the clusters were found to be marked by low magnetic anisotropy energy (MAE) of 2.72 meV and a larger intra-exchange coupling exceeding 0.2 eV indicating that the observed paramagnetic behavior around 10K

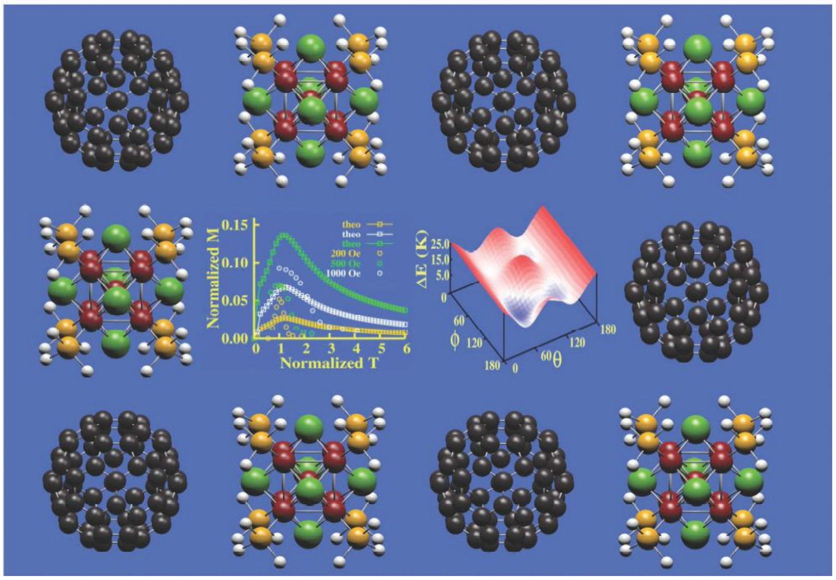

Fig. 1. Magnetic response of magnetic superatom-fullerene assemblies.

is likely due to superparamagnetic relaxations. The magnetic motifs separated by C_{60} experience a weak superexchange interaction that could stabilize a ferromagnetic ground state as observed around 2K. Experiments also indicate that the magnetization first increases and then decreases with increasing temperature in zero field cooled samples and increases with field at a given temperature.

We then investigated the magnetic behavior of an assembly of magnetic clusters using a simple model that progressively includes ferromagnetic/antiferromagnetic interactions, magnetic anisotropy energy, and non-isotropic interactions and examined assemblies of various sizes that allowed magnetic species of different space quantization. Using a model Hamiltonian that incorporated exchange, anisotropy, Zeeman and DMI interactions, we calculated the magnetization of small assemblies at various temperatures. We examined square planar configurations consisting of 16, 24 and 48 sites with 8, 12 and 24 magnetic superatoms respectively. The magnetic atoms were allowed 2 or 5 orientations. The central figure in Fig. 1 shows a comparison of our calculated magnetization values and compares them with experiment. Through a variety of parameters we showed that the inclusion of Dzyaloshinskii-Moriya interaction that cause spin canting is necessary to get qualitative response as observed in experiments. We are currently developing Monte Carlo based programs to study assemblies of larger size.

(2) **Magnetic Coupling and Optical Band Gap in Manganese trimer Metal Organic frameworks.**

The ability to control the optical band gap energy of a material is valuable for synthesizing materials for photocatalytic and optoelectronic applications. Being able to understand the features that control the band gap energy of a material requires the systematic synthesis of a set of materials with variable linkers and/or metal motifs. Previous studies have shown that by varying the linker or the cluster motif, the optical band gap energy of MOFs and cluster solids may be controlled. Generally, one does not expect magnetic materials to have a significant band gap since the majority or minority manifolds are generally not fully occupied. In the present case, we examined assemblies based on Mn^{2+} that has a $3d^5$ configuration in which the majority spin shell is filled, while the minority 3d shell is empty and therefore the system could be expected to show a significant optical band gap. This raises the question whether the optical band gap energy of manganese based materials can be controlled.

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ROYAL SOCIETY OF CHEMISTRY

PAPER
R. Nath, Shiv N. Khanna, Sukhendu Mandal *et al.*
The effect of substituted benzene dicarboxylic acid linkers on the optical band gap energy and magnetic coupling in manganese trimer metal organic frameworks

In a joint effort combining experiments in group of Prof. Mandal in India and theoretical investigations at VCU, we systematically studied a series of Mn based MOFs that are both magnetic and have a controllable optical band gap energy as a first step towards developing multifunctional magnetic materials. Through synergistic studies combining experiments and first principles theory, we reported the synthesis and characterization of eight metal-organic frameworks composed of Mn trimers linked by Benzene-Dicarboxylic Acid (BDC) derivatives. By singly substituting the BDC linker with F, Cl, Br, OH, NH_2, N_3, and NO_2, the effect of the linker on the magnetic and optical properties may be studied. Experimental studies indicate that the resulting solids exhibit interesting magnetic behavior where the susceptibility exhibits a broad feature at low temperatures for several compounds, while in other cases the susceptibility increases continuously down to 2.1 K. These are signatures of antiferromagnetism and paramagnetism, respectively. A Curie-Weiss fit to the data revealed the effective moment and the nature of magnetic interactions. Theoretical studies find that the materials have an antiferromagnetic ground state in which the ferrimagnetic clusters are antiferromagnetically coupled to each other with a low energy transition towards a ferrimagnetic state. The theoretical studies also show that the Mn_3-based motifs are marked by a strong exchange coupling and a weak magnetic anisotropy that results in super-paramagnetic relaxations above few Kelvins. We also find that the linkers form the conduction band edge of the given series of MOFs, and that by changing the functional group of the linker, the position of the conduction band edge may be lowered allowing for the tuning of the optical band gap energy.

(3) **Metal Chalcogenide Clusters as Novel Super Electron Donors and Acceptors:**

In nature, alkali and halogen atoms have open electronic shells. Alkali atoms have one electron passed a filled electronic shell while halogen atoms need an electron to fill the electronic shell. In a startling development that appeared in Journal of American Chemical Society (JACS 139, 1971(2017)), we have demonstrated the existence of metal chalcogenide clusters that have closed electronic shells and yet can be programmed to act as alkalis or halogens by changing the ligands. This new behavior is rooted in the charge transfer characteristics of the ligands. These units therefore possess the ability to donate and receive multiple electrons.

- **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 using the new super donors and acceptors as dopants in semiconductors. In fact, our preliminary studies indicate that such dopings may allow one to change the p- or n- characteristics of a semiconductor. We are also examining magnetic motifs to explore if we can develop novel magnetic semiconductors using such motifs as dopants. In another development, we are developing Monte Carlo based codes to study collective behaviors of assemblies of magnetic nano-clusters in an effort to understand experiments on nano-assemblies. Finally, we are continuing our studies of transport across clusters and cluster molecules to identify the unique features offered by such units.

- **Selected Publications:**

P1. "A Systematic Framework and Nanoperiodic Concept for Unifying Nanoscience: Hard/Soft Nano-Elements, Super Atoms, Meta-Atoms, New Emerging Properties, Periodic Property Patterns, Predictive Mendeleev-Like Nanoperiodic Tables", D. A. Tomalia and S. N. Khanna, *Chem. Rev.* **116,** 2705-2774 (2016). Doi: 10.1021/acs.chemrev.5b00367

P2. "Transforming Ni_9Te_6 from Electron Donor to Acceptor via Ligand Exchange", Vikas Chauhan, Arthur C. Reber, and Shiv N. Khanna, *J. Phys. Chem. A* **120,** 6644-6649 (2016). Doi: 10.1021/acs.jpca.6b05701

P3. "Magnetic Behavior of Superatomic-Fullerene Assemblies", Pallabi Sutradhar, Vikas Chauhan, Shiv N Khanna, and Jayasimha Atulasimha, *Phys. Chem. Chem. Phys.***19,** 996-1002 (2017). Doi: 10.1039/c6cp05196k

P4. "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). Doi: 10.1039.

P5. "Reactivity of Metal Clusters", Z. Luo, A. W. Castleman, Jr. and S. N. Khanna, *Chem. Rev. (in Press).* doi: 10.1021/acs.chemrev.6b00230

P6. "Symmetry and Magnetism in Ni_9Te_6 clusters ligated by CO and Phosphine Ligands.", Arthur C. Reber, Vikas Chauhan, and Shiv N. Khanna, *J. Chem. Phys.* **146**, 024302 (2017). Doi: 10.1063/1.4973609.

P7. "Superatoms: Electronic and Geometric Effects on Reactivity" Arthur C. Reber and S. N. Khanna, Acc. Chem. Res. **50**, 255-263 (2017). doi**:** 10.1021/acs.accounts.6b00464

P8. "Metal Chalcogenide Clusters with Closed Electronic Shells and the Electronic Properties of Alkalis and Halogens", V. Chauhan, A. C. Reber, and S. N. Khanna, *Jour. Amer. Chem. Soc.* **139**, 1871-1877 (2017). Doi: 10.1021/jacs6b09416

Metal-Chalcogenide Clusters with Closed Electronic Shells as Super Donors and Acceptors for Novel Doped Semiconductors

S. N. Khanna
Physics Department, Virginia Commonwealth University, Richmond, VA 23284-2000

Due to quantum confinement, the electronic states in compact clusters are grouped into shells much in the same way as in atoms. Clusters with filled electronic shells and a large gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are highly stable mimicking inert gases that are chemically inert. Clusters (like atoms) with one electron past the filled shell exhibit alkaline behavior offering low ionization potential while clusters requiring an electron to fill the electronic shell behave as halogen atoms with high electron affinities. These behaviors are at the heart of the conventional periodic classification of elements. Finding novel clusters that can donate or accept multiple electrons and forming materials using such building blocks is a promising direction to create nanoscale materials with novel properties. The presentation will focus on our recent work on two different assemblies that offer promise for a new class of doped semiconductors and another development leading to magnetic assemblies for hard and soft magnets.

I will first focus on the identification of chalcogen based ligated clusters that have filled electronic shells and yet exhibit alkali or halogen characteristics defying the conventional viewpoints of stability and reactivity. I will show that some of these can act as super donors allowing donation or acceptor of multiple electrons. Such a feature can have important implications. For example, they can alter n- or p-characteristics through doping of semiconductors. Our theoretical findings follow the recent developments that have enabled synthesis of molecular building blocks composed of a central core of transition and chalcogen atoms ligated by various ligands, by Roy et al. (SCIENCE 341) (Fig. 1). These highly stable building blocks, can be prepared in solutions, have charge donor/acceptor characteristics, and can form either unary solids or binary solids with complementary units maintaining identity of the internal structure. This class of clusters includes $Co_6Se_8(PEt_3)_6$, $Cr_6Te_8(PEt_3)_6$, and $Ni_9Te_6(PEt_3)_8$ where

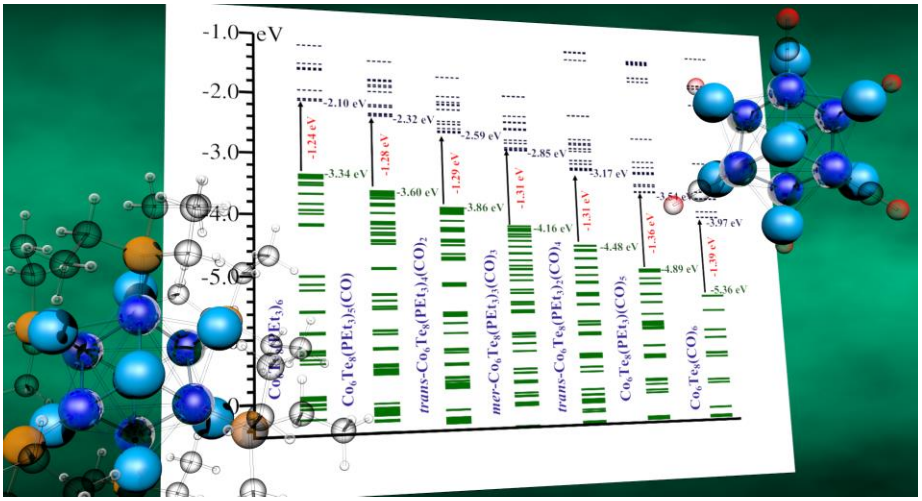

Fig. 1. One electron energy levels of ligated $Co_6Te_8(PEt_3)_m(CO)_n$; (m+n=6) clusters. Solid and dashed lines represent the occupied and empty energy levels. The values of HOMO, LUMO and HOMO-LUMO gap are also given.

metal-chalcogenide cores are decorated with triethylphosphine (PEt_3) ligands attached to metal sites. Theoretical studies indicate that the phosphine ligands bind to the cluster motif by forming charge transfer complexes. More recent studies have focused on manipulating metal-ligand bonds to create motifs offering newer feature. This includes replacing electron donor PEt_3 ligands by electron acceptor CO ligands or isonitriles to form their dimers. One of the fundamental issues is how the metal-ligand bonding can be used to control the cluster properties?

I will show that the ligand manipulation can be used to transform a cluster from an electron acceptor to an electron donor without changing the effective valence count. I will illustrate this by considering a $Co_6Te_8(PEt_3)_6$ cluster that has a closed electronic shell with a high HOMO-LUMO gap of 1.24 eV. This cluster has a low ionization energy and a low electron affinity. Replacement of PEt_3 ligands by CO will be shown to monotonically increase the ionization energy from 4.91 to 7.03 eV for $Co_6Te_8(CO)_6$. The increase in ionization energy is followed by an increase in the electronic affinity from 1.19 eV for $Co_6Te_8(PEt_3)_6$ to 2.60 eV for $Co_6Te_8(CO)_6$. The unusual feature is that irrespective of the combination of ligands, the ligated species always have a closed shell electronic configuration with a high HOMO-LUMO gap varying from 1.24 to 1.39 eV. By changing the ligand, the polarity of the interaction between the Co 4s orbital and the lone pair of the ligand change, but the effective valence electron count remains the same. As I will show, the change in the electronic character is not associated with a change in the electron count but due to a shift in the electronic spectrum that can be rationalized as ligands forming a coulomb well that surrounds the cluster and may raise or lower the energy of the states depending on the donor-acceptor characteristics of the ligand. The ability to stabilize the different charged states can not only crucial for forming solids with different classes of counter ions (donors or acceptors) but also in photovoltaic applications requiring control over oxidation states, and use of donors/acceptors as dopants to create novel doped semiconductors. I will illustrate this feature by considering a doped two-dimensional transition metal chalcogenides using Co_6Se_8 $(PEt_3)_6$ superatoms as electron donors to dope a MoS_2 layer semiconductors.

I will also present our recent work on the magnetic response of an assembly of magnetic nanoparticles. These developments follow our recent work on mixed Fe-Co systems where we collaborated with experimental groups to provided experimental evidence substantiating the synthesis of a novel cobalt iron carbide phase ($CoFe_2C$) of nanoparticles that revealed a blocking temperature, T_B, of 790 K for particles with a domain size as small as 5 ± 1 nm. The particles have magnetocrystalline anisotropy of $4.6 \pm 2 \times 10^6$ J/m^3, which is 10 times larger than that of Co nanoparticles. I will present our results on the magnetic behavior of an assembly of such nanoparticles as a first step towards developing hard and soft magnetic materials.

We are currently exploring the potential of using the new super donors and acceptors as dopants in semiconductors In fact, our preliminary studies indicate that such dopings may allow one to change the p- or n- characteristics of a semiconductor. We are also examining magnetic motifs to explore if we can develop novel magnetic semiconductors using such motifs as dopants. In another development, we are developing Monte Carlo based codes to study collective behaviors of assemblies of magnetic nano-clusters in an effort to understand experiments on nano-assemblies. Finally, we are continuing our studies of transport across clusters and cluster molecules to identify the unique features offered by such units.

Grant Number and Grant Title

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

Post Doc: Vikas Chauhan

Student: Cameron Grover (Fees for Graduate Student)

Selected Publications:

P1. “Experimental evidence for the formation of $CoFe_2C$ phase with colossal magnetocrystalline- anisotropy”, Ahmed A. El-Gendy, Massimo Bertino, Dustin Clifford, Meichun Qian, Shiv N. Khanna, Everett E. Carpenter, *Appl. Phys. Lett.* **106**, 213109 (2015). doi: 10.1063/1.4921789.

P2. “Making sense of conflicting magic numbers in WSi_n clusters”, M. B. Abreu, A. C. Reber, and S. N. Khanna, *J. Chem. Phys.* **143**, 074310 (2015). doi: 10.1063/1.4928755.

P3. “Geometry controls the stability of $FeSi_{14}$”, V. Chauhan, M. B. Abreu, A. C. Reber, and S. N. Khanna, *Phys. Chem. Chem. Phys.* **17,** 15718-15724 (2015). doi: 10.1039/c5cp01386k

P4. “$Ni_9Te_6(PEt_3)_8C_{60}$ is a Superatomic Superalkali Superparamagnetic Cluster Assembled Material (S^3-CAM)”, V. Chauhan, S. Sahoo, and S. N. Khanna, *J. Amer. Chem. Soc.* **138,** 1916-1921 (2016). Doi: 10.1021/jacs.5b10986

P5. ““Transforming Ni_9Te_6 from Electron Donor to Acceptor via Ligand Exchange”, Vikas Chauhan, Arthur C. Reber, and Shiv N. Khanna, *J. Phys. Chem. A* **120,** 6644-6649 (2016). Doi: 10.1021/acs.jpca.6b05701

P6. “Magnetic Behavior of Superatomic-Fullerene Assemblies”, Pallabi Sutradhar, Vikas Chauhan, Shiv N Khanna, and Jayasimha Atulasimha, *Phys. Chem. Chem. Phys.* **19**, 996-1002 (2017). Doi: 10.1039/c6cp05196k

P7. “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). Doi: 10.1039..

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P9. “Superatoms: Electronic and Geometric Effects on Reactivity” Arthur C. Reber and S. N. Khanna, *Acc. Chem. Res.* **50**, 255-263 (2017). doi**:** 10.1021/acs.accounts.6b00464

P10. “Metal Chalcogenide Clusters with Closed Electronic Shells and the Electronic Properties of Alkalis and Halogens” , V. Chauhan, A. C. Reber, and S. N. Khanna, *Jour. Amer. Chem. Soc.* **139**, 1871-1877 (2017). Doi: 10.1021/jacs6b09416

Quantum Monte Carlo calculations for chemical bonding and reactions

Henry Krakauer and Shiwei Zhang

College of William & Mary
Williamsburg, VA 23187

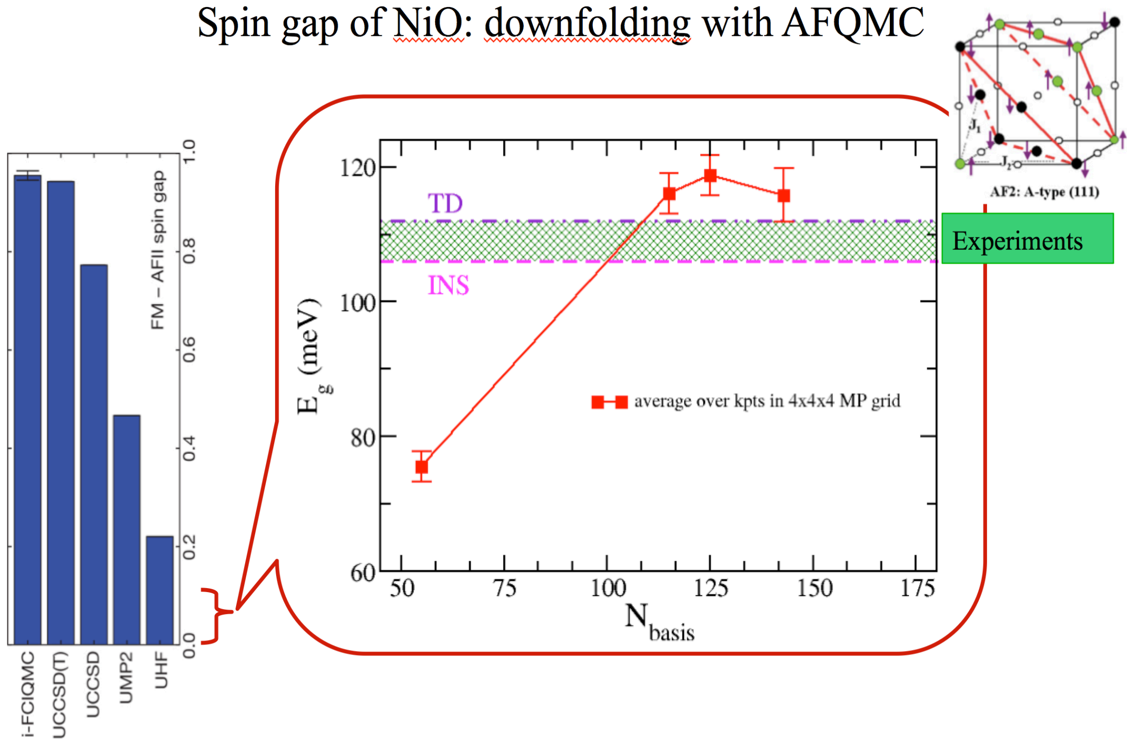
Abstract

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 (see figure)
- 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-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

Spin gap of NiO: downfolding with AFQMC



NiO spin gap. *An accurate NiO spin gap is obtained with AFQMC, in good agreement with experiment. The bar graph (*Booth et al, Nature (London) 493, 365 (2013)*) shows the inadequacy of existing theories, either in the treatment of correlation effects or from lack of basis set convergence, and the high accuracy required by the small energy scale. The main graph shows rapid convergence to the experimental value (neutron scattering and thermodynamic measurements) with the size of the downfolded basis.*

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.

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. 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.
2. Purwanto, Wirawan, Shiwei Zhang, and Henry Krakauer, 2016. "Auxiliary-Field Quantum Monte Carlo Calculations of the Molybdenum Dimer." *The Journal of Chemical Physics* 144 (24). AIP Publishing: 244306. doi:10.1063/1.4954245.
3. Ma, Fengjie, Wirawan Purwanto, Shiwei Zhang, and Henry Krakauer, 2015. "Quantum Monte Carlo Calculations in Solids with Downfolded Hamiltonians." *Physical Review Letters* 114 (22): 226401. doi:10.1103/PhysRevLett.114.226401.
4. Purwanto, Wirawan, Shiwei Zhang, and Henry Krakauer, 2015. "An Auxiliary-Field Quantum Monte Carlo Study of the Chromium Dimer." *The Journal of Chemical Physics* 142 (6). AIP Publishing: 64302. doi:10.1063/1.4906829.
5. Hao Shi, Carlos A. Jimenez-Hoyos, R. Rodriguez-Guzman, Gustavo E. Scuseria, and Shiwei Zhang, 2014. "Symmetry-projected Wave Functions in Quantum Monte Carlo Calculations," Phys. Rev. B 89, 125129 (2014) [CMCSN]
6. Virgus, Yudistira, Wirawan Purwanto, Henry Krakauer, and Shiwei Zhang, 2014. "Stability, Energetics, and Magnetic States of Cobalt Adatoms on Graphene." *Physical Review Letters* 113 (17). American Physical Society: 175502. doi:10.1103/PhysRevLett.113.175502.
7. Shiwei Zhang, 2013. "Auxiliary-Field Quantum Monte Carlo for Correlated Electron Systems," chapter in *Emergent Phenomena in Correlated Matter Modeling and Simulation Vol. 3*, Ed. by E. Pavarini, E. Koch, and U. Schollwock, Forschungszentrum Julich, 2013, ISBN 978-3-89336- 884-6, http://www.cond-mat.de/events/correl13.

8. Wirawan Purwanto, Shiwei Zhang, and Henry Krakauer, 2013. “Frozen-orbital and downfolding calculations with auxiliary-field quantum Monte Carlo,” *J. Chem. Theory Comput*. 9, 4825 (2013).
9. Hao Shi and Shiwei Zhang, “Symmetry in auxiliary-field quantum Monte Carlo calculations,” Phys. Rev. B 88, 125132 (2013). [CMCSN]
10. Ma, Fengjie, Shiwei Zhang, and Henry Krakauer, 2013. “Excited State Calculations in Solids by Auxiliary-Field Quantum Monte Carlo.” *New Journal of Physics* 15 (9). IOP Publishing: 93017. doi:10.1088/1367-2630/15/9/093017.

Machine Learning for Evaluating Reaction Coordinates from Nonadiabatic Molecular Dynamics Simulations

James P. Lewis

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

Program Scope

We have successfully developed and implemented a machine-learning approach to evaluate reaction coordinates from non-adiabatic molecular dynamics (NAMD) simulations. We utilize data generated within FIREBALL (a local orbital density functional theory code); however, the methodology can be easily applied to any molecular dynamics simulation package. The benefits of our machine-learning approach is that we can evaluate reaction coordinates with **zero** human bias added to the methodology. The efficiency of our NAMD approach means that we can also explore significantly statistical ensembles of excitation processes.

RECENT PROGRESS

The azobenzene molecule is composed of two phenyl rings connected by a double N=N bond. This molecule exhibits two isomers, *cis*- and *trans*- confirmations, switching from one to the other under light irradiation (the *cis*-*trans* isomerization can also occur under thermal fluctuations). These photoisomerization processes take place in the sub picosecond time-scale and the detailed mechanism for these transitions are still under debate. In our published work, we have created and analyzed several ensembles of nonadiabatic molecular dynamic (NAMD) simulations of this azobenzene and other azo-functional molecule systems. In our methodology, we explicitly calculate the nonadiabatic coupling vectors. Fig. 1 (top) shows the PES for the ground state (E_0) and the first excited state (E_1); E_1 is obtained by means of a constrained DFT calculation in which one electron from the HOMO is occupying the LUMO orbital. A conical intersection between E_0 and E_1 at the C-N=N-C dihedral angle, α, ~ 96° is clearly observed; the nonadiabatic coupling vector, d_{ij}^{α}, between the HOMO and LUMO states presents a *sharp* increase at the conical intersection. The largest contributions to d_{ij}^{α} are related to the double N=N bond and to the C atoms adjacent to the N atoms. Fig. 1 (bottom) shows the modulus, $|d_{ij}^{\alpha}|$, of the projection on these atoms as function of the dihedral angle α. We clearly observed that the C-N=N-C dihedral angle is a significant reaction coordinate in the photoisomerization of azobenzene by analyzing the nonadiabatic coupling vectors.

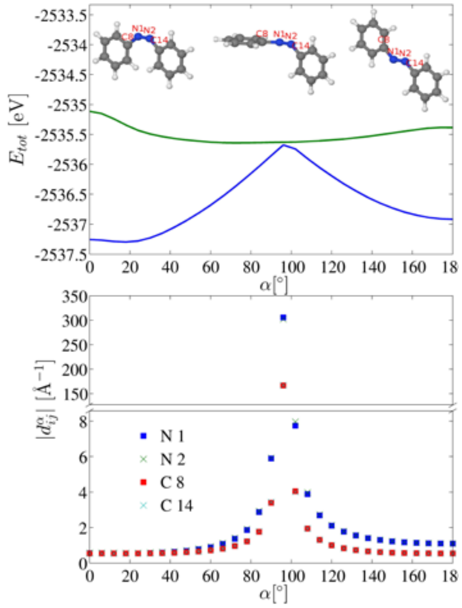


Figure 1. (*top*) Potential energy surface, E_0 and E_1, as a function of the dihedral angle α. (*bottom*) Modulus of the projection on some atoms (N1, N2, C8 and C14, top figure) of the nonadiabatic coupling vector between the HOMO and LUMO Kohn-Sham states along the isomerization as a function of the dihedral angle α.

Building Datasets. We have applied a machine-learning framework to predict the reaction coordinates in the photoisomerization of azobenzene – the method can be readily applied to other systems. First, we build our datasets and examine the mutual information (correlations of the system) by defining the internal coordinates (Z-matrix representation) as the attributes of our system. A dataset includes all the bonds, angles, and dihedrals corresponding to each time step. The data are the internal coordinates for a given time step and each time step defines a row of the matrix ***X***. For example, in our NAMD simulations of azobenzene we build a matrix of 400,000 datasets (rows), each containing 116 columns of attributes – from an ensemble of 100 simulations (50 simulations starting from the *cis*-conformation and 50 simulations starting from the *trans*-conformation) where each simulation has 4000 time steps and the 116 attributes define the 116 internal coordinates representing all bonds, angles, and dihedrals of the azobenzene molecule.

The matrix ***Y*** also contains a matrix of 400,000 rows (datasets), but the columns (attributes of the system) are the electronic energy eigenvalues. The matrix ***Y*** (see Fig. 2) may contain as many eigenvalues as we would like to track. For photoisomerization of azobenzene we choose to track only the HOMO as the attribute of interest - an electron relaxes from the LUMO to the HOMO; therefore, we are interested in tracking the HOMO and discovering how the internal coordinates correlate to the HOMO. We may also include the LUMO as one of our attributes; however for simplicity we focus only on the HOMO as an attribute for the matrix ***Y***.

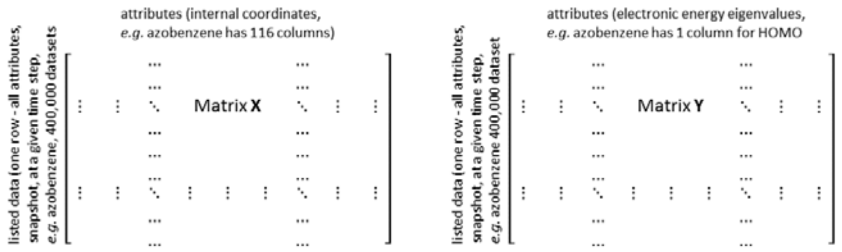


Figure 2. Building the datasets into the **X** and **Y** matrices.

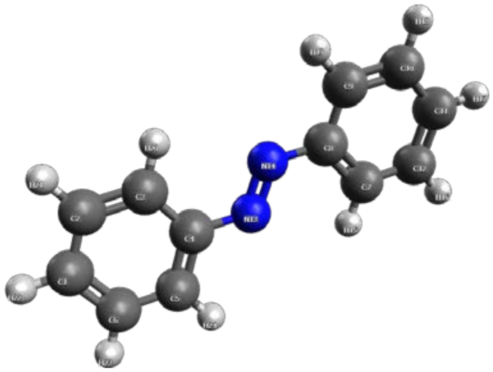


Figure 3. Top panel shows the azobenzene molecule in the cis-conformation and labels the atoms discussed in Table 1.

Calculating the Mutual Information. Now that we have datasets of attributes representing the internal coordinates (***X***) and datasets of attributes representing the HOMO (***Y***), we proceed to calculating the mutual information (MI) of ***X*** and ***Y***. We can interpret the MI between ***X*** and ***Y*** as the reduction of uncertainty about ***X*** after observing ***Y***, or, by symmetry, the reduction in uncertainty about ***Y*** after observing ***X***, essentially an entropic correlation between internal coordinates and the HOMO. After calculating, we rank order the MI data. From our rankings we discover the following – **1)** the largest value of MI is the C8-N14=N13-C4 (atom labels defined in Fig. 3) dihedral angle with MI = 0.244; **2)** the next higher values are the dihedral angles N13=N14-C8-C7, N13=N14-C8-C9, N14=N13-C4-C5, and N14=N13-C4-C3, all with MI ~ 0.12; **3)** the third ranking internal coordinates are the angles C4-N13=N14 and C8-N14=N13 with MI ~ 0.10; **4)** the fourth ranking internal coordinates are the double N=N bond and the neighboring N-C bonds, all with MI ~0.05. The MI results are remarkable in that 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. However, interestingly, the mutual information results also suggest that there are two other mechanisms involved – one mechanism is a concerted motion including the dihedral angles N13=N14-C8-C7 and N13=N14-C8-C9 together with the angle C8-N14=N13; the second mechanism is a concerted motion including the dihedral angles N14=N13-C4-C5 and N14=N13-C4-C3 together with the angle C4-N13=N14. That is, using mutual information, we predict that the global reaction coordinate includes a rotation-inversion mechanism involving the two angles C4-N13=N14 and C8-N14=N13 and their corresponding paired dihedral angles. Results of the rotation-inversion mechanism are reported from experimental observations. Finally, the mutual information greatly decreases for other internal coordinates; the double N=N bond and the neighboring N-C bonds are half as important (subsequently all other internal coordinates do not contribute significantly) to the photoisomerization mechanism.

Finding Reaction Coordinates. After performing the mutual information calculations, we remove redundancies in the data via a principle component analysis (PCA). However, before applying PCA, we first reduce the dimensions by choosing only the k attributes which have the highest MI values. Of these k attributes, some of these may be correlated internal coordinates; PCA will enable us to merge any correlations and further reduce the dimensionality of our attributes. Primarily, for the example of azobenzene, we find redundancies in four dihedral angles (N13=N14-C8-C7, N13=N14-C8-C9, N14=N13-C4-C5, and N14=N13-C4-C3) and two angles (C4-N13=N14 and C8-N14=N13) In many respects this makes perfect sense – in rotation-inversion assisted mechanisms the angle C4-N13=N14 (or C8-N14=N13) rotates to assist in the change of the primary dihedral C8-N14=N13-C4 which contains the double N=N bond. The rotation of C4-N13=N14 equally involves the change in dihedrals N13=N14-C8-C7 and N13=N14-C8-C9; therefore, it would be repetitive to include both of these internal coordinates in the analysis of the reaction coordinates.

Calculating the MI and filtering using PCA only recommend the internal coordinates involved in the reaction mechanisms. We would like to get a sense of what the combined reaction coordinate looks like. Doing this requires that we build a potential energy surface; we use a neural network approach (shown in Fig. 4). In our example of photoisomerization of azobenzene, we are able to reduce the dimensionality of azobenzene from 116 internal coordinates down to only 5 internal coordinates – the C8-N14=N13-C4 dihedral angle, the non-redundant dihedral angles N13=N14-C8-C7 and N14=N13-C4-C5 (or we could have just as easily chosen the pair N13=N14-C8-C9 and N14=N13-C4-C3), the two angles C4-N13=N14 and C8-N14=N13. We could obtain a geodesic (*i.e.*, the shortest route between two points in a multi-dimensional space) from one node to another node on the hypersurface via the neural network. From this reduced dimensionality, we build the network. To build the network, we represent a series of nodes where each node, $\vec{q}_i$, represents a (reduced dimensionality) single data point with a “distance”, an edge with width w_{ij}, between each of the nodes.

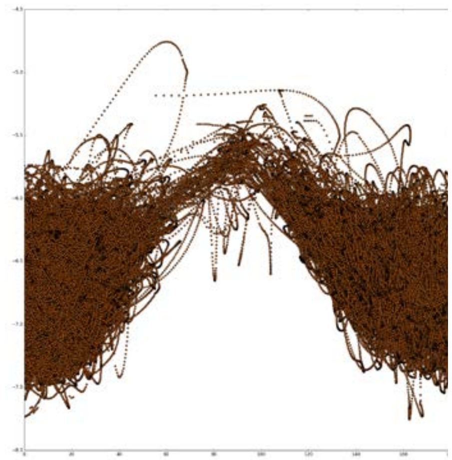


Figure 4. Two-dimensional representation of the multi-dimensional nodal network for the example of azobenzene photoisomerization.

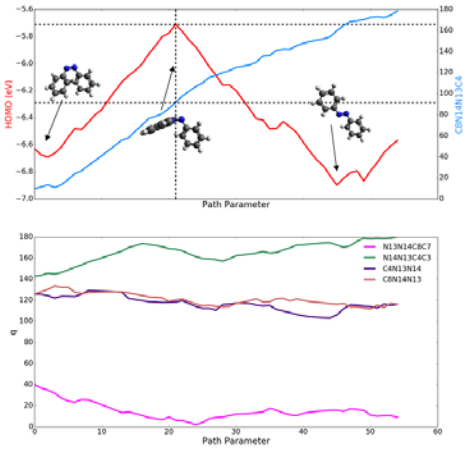


Figure 5. Results of the machine-learning network. (*top*) Plot of the HOMO versus the C8-N14=N13-C4 dihedral angle, one of the reactions coordinates found in the photoisomerization of azobenzene. (*bottom*) Plot of the HOMO versus reaction coordinates – the dihedral angles, N13=N14-C8-C7 and N14=N13-C4-C3, and the angles, C4-N13=N14 and C8-N14=N13.

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 shortest path between minima. After finding the shortest path, we create a list of nodes which need to be passed from the starting node to reach the final node. Once we have the shortest path, then we have all the features and the energies corresponding to each node – putting these features together will provide the reaction coordinate and the change in the energy via photoisomerization.

Results of the Machine-Learning Network. The results of our machine-learning approach are now presented for the photoisomerization of azobenzene. The top plot of Fig. 5 shows how the C8-N14=N13-C4 dihedral changes with respect to the change in the HOMO energy level. We note three regions in the

HOMO energy level - 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 a 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. 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 anticipate based on experimental results. The other internal coordinates that contribute to the reaction coordinate are also plotted in the bottom of Fig. 5. Here we observe some interesting characteristics that warrant later significant analysis.

In conclusion, many researchers have proposed methods for calculating reaction coordinates and some are automated. What we propose is unique in that our method 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 **zero** human decisions made within our approach other than to determine the threshold of MI for building the network. Algorithms can easily be put into place to remove this decision as well. Our methodology can be applied to photoisomerization, photo-reactions, as well as transition state searching.

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

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Student(s): Amanda J. Neukirch, Olivia Pavlic, and Pedram Tavozohi

Publications Acknowledging this Grant in 2013-2016

1. J.I. Mendieta-Moreno, D.G. Trabada, J. Mendieta, J.P. Lewis, P. Gómez-Puertas, and J. Ortega. **2016**. "Quantum mechanics/molecular mechanics free energy maps and nonadiabatic simulations for a photochemical reaction in DNA: Cyclobutane thymine dimer. *J. Phys. Chem. Lett.* 7:4391-4397.
2. V. Zobač, J.P. Lewis, and P. Jelínek. **2016**. "Nonadiabatic molecular dynamics simulations of opening reaction of molecular junctions," *Nanotechnology* 27:285202.
3. O. Ranasingha, H. Wang, V. Zobač, P. Jelínek, G. Panapitiya, A. Neukirch, O.V. Prezhdo, and J.P. Lewis. **2016**. "Slow relaxation of surface plasmon excitations in Au_{55}: The key to efficient plasmonic heating in Au/TiO2. *J. Phys. Chem. Lett.* 7: 1563-1569.
4. L. Wang, H. Wang, A.E. Rice, W. Zheng, X. Li, M. Chen, X. Meng, J.P. Lewis, and F.-S. Xiao. **2015**. "Design and preparation of supported Au catalyst with enhanced catalytic activities by rationally positioning Au nanoparticles on anatase," *J. Phys. Chem. Lett.*, 6:2345-2349.
5. V. Zobač, J.P. Lewis, E. Abad, J.I. Mendieta-Moreno, P. Hapala, P. Jelínek, and J. Ortega. **2015**. "Photo-induced reactions from efficient molecular dynamics with electronic transitions using the FIREBALL local-orbital density functional theory formalism," *J. Phys.: Cond. Mat.* 27:175002.
6. A.J. Neukirch, J. Park, V. Zobac, H. Wang, P. Jelinek, O.V. Prezhdo, H.-C. Zhou, and J.P. Lewis. "Non-adiabatic ensembles of azo-functional organic linkers for porous coordinated polymers," *J. Phys.: Cond. Matt.* **2015**, 27:134208. Special Issue - *Theory of Solar Energy Materials*
7. J.I. Mendieta-Moreno, R.C. Walker, J.P. Lewis, P. Gómez-Puertas, J. Mendieta, and J. Ortega. "An efficient local-orbital DFT QM/MM method for biomolecular systems: FIREBALL/AMBER," *J. Chem. Theory Comp.* **2014**, 10:2185-2193. (Most accessed article: #12/20 in Jun 2014).
8. L. Wang, H. Wang, F. Liu, J. Zhang, Q. Sun, J.P. Lewis, L. Zhu, X. Meng, and F.-S. Xiao. "Selectively catalytic production of 5-hydroxymethylfurfural from glucose by adjusting catalyst wettability," *Chem. Sus. Chem.* **2014**, 7:402-406. (Most Accessed Article: #12/15 Jan 2014)
9. A.J. Neukirch, L.C. Shamberger, E. Abad, B.J. Haycock, H. Wang, J. Ortega, O.V. Prezhdo, and J.P. Lewis. "Ab initio non-adiabatic simulations of the photo-isomerization of *cis*-stilbene and *cis*-azobenzene," *J. Chem. Theory Comp.* **2014**, 10:14-23. (Most Accessed Article: #16/20 in Dec 2013)
10. E. Abad, J.P. Lewis, V. Zobač, P. Hapala, P. Jelínek, and J. Ortega. "Calculation of non-adiabatic coupling vectors in a local-orbital basis set," *J. Chem. Phys.* **2013**,138:154106.
11. L. Wang, H. Wang, W. Zhang, J. Zhang, D.S. Su, J.P. Lewis, X. J. Meng, and F.S. Xiao. "Aerobic homo-coupling of phenylboronic acid on Mg-Al mixed oxides supported Au nanoparticles", *J. Catal.* **2013**, 298:186-197.

Two-Component Non-Collinear Time-Dependent Spin Density Functional Theory

Franco Egidi, Xiaosong Li

xsli@uw.edu

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

Abstract

In recent years, we have witnessed an ever-expanding research effort in the modeling of spin-related phenomena, which are at the basis of magnetic materials and spintronic devices. An accurate theoretical description of the variety of spin phenomena involved in these fields requires enough flexibility to allow the spin magnetization vector to move about and reorient itself along any axis. In some cases, the direction of the spin magnetization may not be the same at every point in space, a situation often referred to as non-collinear spin. This flexibility in the spin orientation is unfortunately not found in most common quantum chemical methods, which implicitly assume that the spin magnetization is uniformly oriented along an axis, conventionally taken to be the z-axis. Therefore, generalizations of widely available theoretical and computational methods specifically designed to describe these spin arrangements are greatly appreciated.

The objective of this research program is to develop a hierarchy of time- and spin-dependent electronic structure methods to accurately model and simulate the electronic spin dynamics in molecules. This will open up new computational and theoretical tools to be applied to the development and understanding of spin-dependent chemical processes. By developing methods to study spin dynamics from first principles, new molecular systems will be made amenable to theoretical investigation.

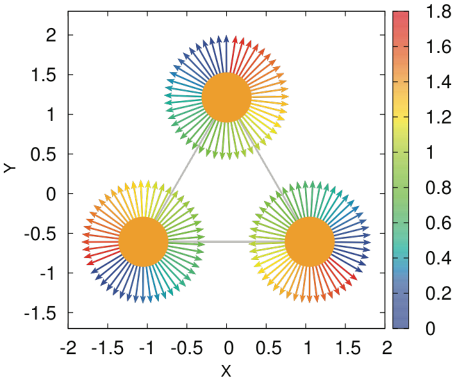


Figure 1. The time evolution of the non-collinear spin magnetization (in the unit of Bohr magneton) of a Li_3 in a uniform magnetic field applied perpendicular to the *xy* plane (the time-evolution is represented as the progression of coloration in the unit of picosecond).[6]

On the development of spin-dependent electronic dynamics, we have formulated an *ab initio* time-dependent spinor theory,[1-6] to study the spin dynamics of many-electron systems. In the time-dependent spinor theory, the time-dependent spin orbitals are expressed in a two-component formalism, represented as a vector in the α- and β-spin space. Time-dependent Hartree-Fock and density functional theory that utilize such a spinor basis gives rise to the time-dependent two-component approach (2c-TDHF/2c-TDDFT). The two-component method allows electron spins to rotate freely in response to any external (e.g. magnetic field) and internal (e.g. spin-orbit coupling) perturbations. The *non-relativistic* 2c-TDHF has been developed to study spin-dynamics of a non-collinear system subject to an external magnetic field (Fig. 1), and the spin-coherence during dissociative reaction dynamics by means of the two component Ehrenfest dynamics.[4] More recently, for the first time, a *relativistic* real-time 2c-TDHF/2c-TDDFT method has been developed and applied to investigations of spin-orbit driven electron dynamics.[2]

The long-term scientific objective is to be able to accurately and realistically predict non-equilibrium many-electron phenomena driven by external perturbations (e.g. electromagnetic fields and dielectric medium) and internal spin couplings (e.g. spin-spin, spin-orbit and spin-other-orbit). Recent developments in the PI's research group lays the groundwork to achieve this long-term goal. Future developments will include the development of two-electron spin dependent terms (spin-own-orbit, spin-other-orbit and spin-spin-spin) in the spin dynamics, and new density functional engines that are variationally tuned to support the relativistic DFT methods.

In this presentation, we introduce a linear response formalism for the description of the electronic excitations of a non-collinear reference defined via Kohn-Sham spin density functional methods. A set of auxiliary variables, defined using the density and non-collinear magnetization density vector, allows the generalization of spin density functional kernels commonly used in collinear DFT to non-collinear cases, including local density, GGA, meta-GGA and hybrid functionals. Working equations and derivations of functional second derivatives with respect to the non-collinear density, required in the linear response non-collinear TDDFT formalism, are presented in this work. This formalism takes all components of the spin magnetization into account independent of the type of reference state (open or closed shell). As a result, the method introduced here is able to afford a non-zero local *xc* torque on the spin magnetization, while still satisfying the zero-torque theorem globally. The formalism is applied to a few test cases using the variational exact-two-component reference including spin-orbit coupling to illustrate the capabilities of the method.

References

1. D. Williams-Young, F. Egidi, X. Li, "Relativistic Two-Component Particle-Particle Tamm-Dancoff Approximation," *J. Chem. Theory Comput.*, **2016**, *12*, 5379.
2. J. J. Goings, J. Kasper, F. Egidi, S. Sun, X. Li, "Real Time Propagation of the Exact Two Component Time-Dependent Density Functional Theory," *J. Chem. Phys.*, **2016**, *145*, 104107.
3. F. Egidi, J. J. Goings, M. Frisch, X. Li, "Direct Atomic-Orbital Based Relativistic Two-Component Linear Response Method for Calculating Excited State Fine Structures," *J. Chem. Theory Comput.*, **2016**, *12*, 3711.
4. F. Ding, J. J. Goings, H. Liu, D. B. Lingerfelt, X. Li, "*Ab Initio* Two-component Ehrenfest Dynamics," *J. Chem. Phys.*, **2015**, *143*, 114105.
5. J. J. Goings, F. Ding, M. Frisch, X. Li, "Stability of the Complex Generalized Hartree-Fock Equations," *J. Chem. Phys.*, **2015**, *142*, 154109.
6. Ding, F.; Goings, J. J.; Frisch, M. J.; Li, X. "Ab Initio Non-Relativistic Spin Dynamics." *J. Chem. Phys.* **2014**, *141*, 214111.

DE-SC0006863 First-Principles Spin-Dependent Many-Electron Dynamics: Dielectric Response and Dirac Formalism

Postdoc(s): Franco Egidi, Alessio Petrone

Student(s): Joshua Goings, Joseph Kasper, Torin Stetina, David Williams-Young

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

1. J. J. Goings, D. B. Lingerfelt, X. Li, "Can Quantized Vibrational Effects be Obtained from Ehrenfest Mixed Quantum-Classical Dynamics?," *J. Phys. Chem. Lett.*, **2016**, *7*, 5193–5197.
2. A. Petrone, D. B. Lingerfelt, D. B. Williams-Young, X. Li, "Ab Initio Transient Vibrational Spectral Analysis," *J. Phys. Chem. Lett.*, **2016**, *7*, 4501.
3. D. Williams-Young, F. Egidi, X. Li, "Relativistic Two-Component Particle-Particle Tamm-Dancoff Approximation," *J. Chem. Theory Comput.*, **2016**, *12*, 5379.
4. G. Donati, D. B. Lingerfelt, A. Petrone, N. Rega, X. Li, ""Watching" Polaron Pair Formation from First-Principles Electron-Nuclear Dynamics," *J. Phys. Chem. A*, **2016**, *120*, 7255–7261.
5. J. J. Goings, J. Kasper, F. Egidi, S. Sun, X. Li, "Real Time Propagation of the Exact Two Component Time-Dependent Density Functional Theory," *J. Chem. Phys.*, **2016**, *145*, 104107.
6. F. Egidi, J. J. Goings, M. Frisch, X. Li, "Direct Atomic-Orbital Based Relativistic Two-Component Linear Response Method for Calculating Excited State Fine Structures," *J. Chem. Theory Comput.*, **2016**, *12*, 3711.
7. J. J. Goings, X. Li, "An Atomic Orbital Based Real-Time Time-Dependent Density Functional Theory for Computing Electronic Circular Dichroism Band Spectra," *J. Chem. Phys.*, **2016**, *144*, 234102.
8. J. J. Goings, F. Ding, E. R. Davidson, X. Li, "Approximate Singly Excited States from a Two-component Hartree-Fock Reference," *J. Chem. Phys.*, **2015**, *143*, 144106.
9. F. Ding, J. J. Goings, H. Liu, D. B. Lingerfelt, X. Li, "*Ab Initio* Two-component Ehrenfest Dynamics," *J. Chem. Phys.*, **2015**, *143*, 114105.
10. J. J. Goings, F. Ding, M. Frisch, X. Li, "Stability of the Complex Generalized Hartree-Fock Equations," *J. Chem. Phys.*, **2015**, *142*, 154109.

Modeling ionic effects at solid/liquid interfaces

Alenka Luzar and Dusan Bratko

Department of Chemistry, Virginia Commonwealth University,
1001 West Main Street, Richmond, VA 23284-2006

aluzar@vcu.edu

Program scope

The project is advancing molecular level understanding of nanoscale hydration in salt solutions under the influences of electric stimuli or 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

Solubilization of graphitic nanoparticles, including fragments of graphene, carbon nanotubes, fullerenes, and their derivatives holds promise for exciting new applications. Soluble fullerenes have been synthesized by adding dissociating moieties like carboxylic groups to modulate dispersibility through pH control. Cationic fullerenes can be synthesized by amino substitutions. Analogous functionalization of carbon nanotubes and graphene fragments have been reported but guidelines for the design of nanoparticles with tailored wetting and solubility remain to be established. Our modeling studies of functionalized nanoparticles strive toward this goal. Our preceding work on extended planar surfaces determined the relation between the wetting free energy and populations of planted polar or ionic functionalities. Surface pattern proved significant with maximal wettability obtained at regular charge distribution. Saturation set in at high ionization. An important outstanding question is how does the effect of functionalization depend on particle's *curvature,* and what are the consequences on inter-particle forces in different geometries?

Using atomistic simulations to calculate average interparticle forces, we find the geometry of the nanoparticles is a significant determinant of the effect of functionalization by ionizing groups. At identical head-group densities at the solute/solvent contact plane, solubilization by planted ionic moieties eases with decreasing curvature. With only a fraction of surface groups carrying a charge, dispersed platelets are easier to solubilize than nanotubes than spherical particles. About twice as high threshold surface charge has to be reached to stabilize a dispersion of spherical than planar particles. At high charge density, the impact of planted ionizing groups becomes nonmonotonic. In the window of 1-2 ionic groups per nm squared, the potential of mean force between the nanoparticles reaches saturation. In this regime, ionic screening gradually blurs the differences among distinct geometries until an essentially curvature-independent dispersion environment is created. Strong screening underlying the saturation behavior is due to ion condensation. The phenomenon takes place at a geometry-dependent critical charge density, beyond which ions localize near the surface, offsetting the effects of further ionization. The saturation charge density increases from planar to cylindrical to spherical solutes consistent with our main result that the effectiveness of functionalization decreases with the curvature of the solute.

The asymmetry in cation and anion mobilities in solution, and in their binding to solid surfaces, underlies the generation of electric current under the pressure-driven electrolyte flow through a porous material. Nanoporous media can maximize the overlap of velocity and concentration gradients in the pores. We explore the viability of nanoscale electrokinetic devices using nonequilibrium Molecular Dynamics of salt solutions in model silica pores. We examine the effects of pore deprotonation on electrokinetic current and the efficiency of energy conversion. Our calculations illustrate how subtle differences between conventional and polarizable force fields translate into distinct electrokinetic behaviors as the differences, rather than absolute strengths, of cation and anion binding determine net contributions to the current. In view of high hydrodynamic dissipation manifested in the simulations, the primary usage is envisaged in converting waste mechanical work, e.g. in hydraulic shock absorption. Alternating current can be generated during electrolyte infiltration and retraction cycles in the absorbing porous medium. Introduction of slip-conducive pore coating can pave the way to improved efficiency of energy conversion.

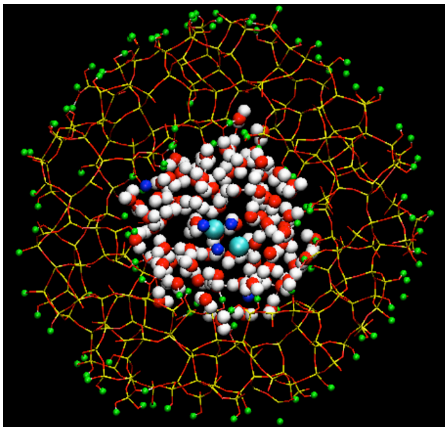


Fig. 1 Cross-section of an electrolyte-filled silica nanopore used in the nonequilibrium MD approach to the electrokinetic effect.

Future plans

Nanoporosity can significantly increase electrode/electrolyte contact area, improving the performance of storage devices like batteries and supercapacitors. To enable predictions of electrolyte uptake in the pores, we are developing an adaptation of the Expanded Ensemble Grand Canonical Monte Carlo to address the equilibria between anode and cathode compartments responding to the imposed voltage between the subsystems. This requires the control of electric potentials. Appropriate algorithms rely on the method of fluctuating atomic charges, or the inclusion of multiple-order images in idealized pore geometries. In a parallel development, we will continue working on algorithms to incorporate multi-body effects due to molecular polarizabilities in the fractional insertion technique supporting the Expanded Ensemble GCMC simulations to cover open electrolyte systems at extreme concentrations known to optimize surface-energy absorption.

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

Postdoc(s): B. Shadrack Jabes

Publications Acknowledging the Award DE-SC-0004406 from 2013 – 2016:

(1) M. von Domaros, D. Bratko, B. Kirchner, A. Luzar, Dynamics at a Janus interface, *J. Phys. Chem. C* **117**, 4561 (2013).

(2) D. Vanzo, D. Bratko, A. Luzar, Nanoconfined water under electric field at constant chemical potential undergoes electrostriction, *J. Chem. Phys*. **140**, 074710 (2014).

(3) J. Driskill, D. Vanzo, D. Bratko, A. Luzar, Wetting transparency of graphene in water, *J. Chem. Phys*. **141**, 18C517 (2014).

(4) D. Vanzo, D. Bratko, A. Luzar, Dynamic Control of Nanopore Wetting in Water and Saline Solutions under Electric Field *J. Phys. Chem. B*. **119**, 8890 (2015).

(5) F. Moucka, D. Bratko, A. Luzar, Electrolyte pore/solution partitioning by Expanded Grand Canonical Ensemble Monte Carlo Simulation, *J. Chem. Phys*. **142**, 124705 (2015).

(6) F. Moucka, D. Bratko, A. Luzar, Salt and water uptake in nanoconfinement under applied electric field: An open ensemble Monte Carlo study, *J. Phys. Chem. C* **119**, *20416* (2015).

(7) B. S. Jabes, D. Bratko, A. Luzar, Universal Repulsive Contribution to the Solvent-Induced Interaction Between Sizable, Curved Hydrophobes, *J. Phys. Chem. Lett.* **7**, 3158 (2016)

(8) B. S. Jabes, D. Bratko, A. Luzar, Metastable vapor in a Janus nanoconfinement, *J. Phys. Chem. C.,* accepted (2017).

Neepa T. Maitra

Electron-Ion Dynamics with Time-Dependent Density Functional Theory

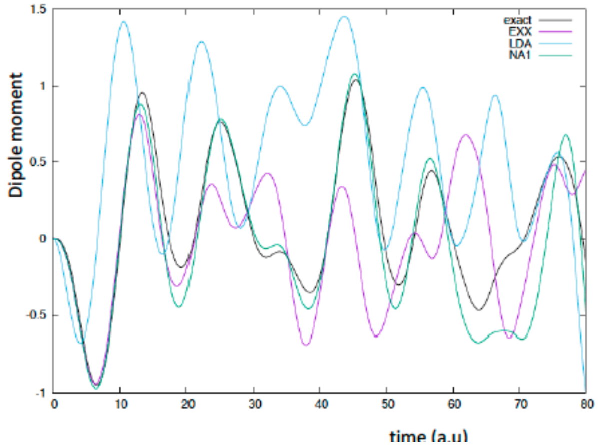
Neepa T. Maitra

Hunter College and the Graduate Center Physics Program, City University of New York
New York, NY 10065

Abstract

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

We have recently started a new direction for the development of time-dependent exchange-correlation functionals that breaks free of the adiabatic approximation. These non-adiabatic approximations are derived beginning with a decomposition of the exact exchange-correlation potential into kinetic and interaction components, and approximating the pieces in each with self-consistent way. For example, the exact interaction component involves the exact exchange-correlation hole, which, in the approximation, we replace with the Kohn-Sham exchange correlation hole. This 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 (e.g. see Figure).



The dipole moment under driving by a non-resonant field, in a model He atom. NA1 denotes a new non-adiabatic functional derived from the exact decomposition, and does considerably better than the standard adiabatic approximations shown.

We are preparing this work now for submission, and future work includes plans to use adiabatic time-dependent density-matrix functional theory to build a better approximation for the kinetic component.

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. We examined the nuclear-mass dependence of these correlation terms in the potential driving the electron in charge-resonance enhanced ionization processes, and found that rather than the nuclear:electron mass ratio, the relative nuclear velocity is critical in determining the size of these dynamical correlation terms. We have begun to investigate mixed quantum-classical schemes based on these equations, as well as 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.

Grant Numbers and Grant Titles

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Postdoc(s): Johanna I. Fuks, Lionel Lacombe, 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) *Studies of Spuriously Time-Dependent Resonances in Time-Dependent Density Functional Theory,* K. Luo, J. I. Fuks, and N. T. Maitra, J. Chem. Phys. **145**, 044101 (2016).
(2) *Perspective: Fundamental Aspects of Time-Dependent Density Functional Theory,* N. T. Maitra, J. Chem. Phys. **144,** 220901 (2016).
(3) *Time-Dependent Density Functional Theory Beyond Kohn-Sham Slater Determinants,* J. I. Fuks, S. E. B. Nielson, M. Ruggenthaler, and N. T. Maitra, for special issue honoring Evert Jan Baerends, Phys. Chem. Chem. Phys. **18**, 20976 (2016).
(4) *The exact potential driving the electron dynamics in enhanced ionization*, E. Khosravi, A. Abedi, and N. T. Maitra, Phys. Rev. Lett. **115**, 263002 (2015).
(5) *Laser-induced electron localization in* H_2^+*: Mixed quantum-classical dynamics based on the exact time-dependent potential energy surface,* Y. Suzuki, A. Abedi, N. T. Maitra, and E.K.U. Gross, Phys. Chem. Chem. Phys. **17**, 29271 (2015).
(6) *Time-resolved spectroscopy in time-dependent density functional theory: An exact condition,* J. I. Fuks, K. Luo, E. D. Sandoval, N. T. Maitra, Phys. Rev. Lett. **114**, 183002 (2015).
(7) *The exact forces on classical nuclei in non-adiabatic charge transfer*, F. Agostini, A. Abedi, Y. Suzuki, S. K. Min, N. T. Maitra, E. K. U. Gross, J. Chem. Phys. **142**, 084303 (2015).
(8) *Challenging adiabatic time-dependent density functional theory with a Hubbard dimer: the case of time-resolved long range charge transfer*, J. I. Fuks and N. T. Maitra, Phys. Chem. Chem. Phys. **16**, 14504 (2014).
(9) *Charge-transfer in time-dependent density functional theory: Insights from the Asymmetric Hubbard Model,* J. I. Fuks and N.T. Maitra, Phys. Rev. A. **89**, 062502 (2014).
(10) *Exact time-dependent Kohn-Sham potentials: Analysis of kinetic and hole contributions***,** K. Luo, J. I. Fuks, E. Sandoval, P. Elliott, and N. T. Maitra, (special DFT developments issue), J. Chem. Phys. **140**, 18A515 (2014).

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

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

Program Scope. Our research effort combines new theory and 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. Recently, the EFP method has been combined with nonlinear time-dependent density functional theory to facilitate the investigation of solvent effects on nonlinear optical properties[1]. 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[5]. In the latter study, the EFP method was shown to outperform density functional theory (DFT) methods.

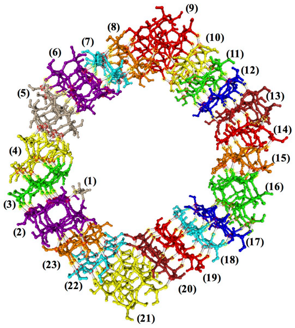
Another (fully quantum) fragmentation approach is the fragment molecular orbital (FMO) method. The FMO method divides a large species into fragments to facilitate accurate QM calculations on very large systems. The FMO method can be used in concert with any electronic structure method in GAMESS. In order 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[7,9]. 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.[5] 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)[9]. 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[9]. Also, a new method, the effective fragment molecular orbital (EFMO) method has been developed that replaces the bath potential with the EFP[10]. 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[10].

Another approach to making high-level electronic structure calculations is to use localized molecular orbitals (LMOs), because correlation is local. So, one can design LMO domains or subsystems and only perform the correlation calculation within those domains. Carter (Princeton) has developed a multi-configurational (MR) configuration interaction (CI) code called TigerCI to perform such calculations. In collaboration with the Carter group, a preliminary parallel version of TigerCI code has been implemented[2]. The TigerCI code has now been incorporated into GAMESS. A manuscript that describes this effort is in preparation. 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[6].

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[4]. The FMO method has been used to study the formation of carbinolamine, catalyzed by a section of MSN[8].



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.

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

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

A collaboration with the Evans group at the Ames Laboratory on reactions that occur on the Pd surface will combine 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 are carrying 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.

References to 10 recent publications of DOE sponsored research

1. F. Zahariev and M.S. Gordon, “Non-linear Response Time-Dependent Density Functional Theory combined with the Effective Fragment Potential Method”, J. Chem. Phys., 140, 18A523 (2014)

2. J. Dieterich, D. Krisiloff, A Gaenko, F.Libisch, T. Windus, M. Gordon, E. Carter, “Shared-memory parallelization of a local correlation multi-reference CI program”, Comp. Phys. Comm., 185, 3175 (2014)

3. K.R. Brorsen, S.R. Pruitt, and M.S. Gordon, “Surface affinity of the hydronium ion: The effective fragment potential and umbrella sampling”, J. Phys. Chem B., 118, 14382 (2014).

4. J. Wang, A. Garcia, D.M. Ackerman, M.S. Gordon, I.I. Slowing, T. Kobayashi, M. Pruski, and J.W. Evans, “Multi-functionalization of nanoporous catalytic materials to enhance reaction yield: Statistical mechanical modeling for conversion reactions with restricted diffusive transport”, Mater. Res. Soc. Symp. Proc. Vol. 1641 (2014)

5. K.R. Brorsen, S.Y. Willow, S.S. Xantheas, and M.S. Gordon, “The melting temperature of liquid water with the effective fragment potential”, J. Phys. Chem. Lett., 6, 3555 (2015).

6. A. Findlater, F. Zahariev, and M.S. Gordon, “A Combined Fragment Molecular Orbital-Cluster in Molecule Approach to Massively Parallel Electron Correlation Calculations for Large Systems”, J. Phys. Chem. A, 119, 3587 (2015)

7. H. Nakata, D.G. Fedorov, F. Zahariev, M.W. Schmidt, M.S. Gordon, and S. Nakamura, “Analytic second derivative of the energy for density functional theory based on the three-body fragment molecular orbital theory”, J. Chem. Phys., 142, 124101 (2015)

8. Ana P. de Lima Batista**,** Federico Zahariev, Igor I. Slowing, Ataualpa A. C. Braga, Fernando R. Ornellas, Mark S. Gordon, “Silanol-Assisted Carbinolamine Formation in an Amine-Functionalized Mesoporous Silica Surface: Theoretical Investigation by Fragmentation Methods”, J. Phys. Chem. B, 120, 1660 (2016).

9. S.R. Pruitt, H. Nakata, T. Nagata, M. Mayes, Y. Alexeev, G.D. Fletcher, D.G. Fedorov, K. Kitaura, and M.S. Gordon, “The Importance of Three-Body Interactions in Molecular Dynamics Simulations of Water”, J. Chem. Theory Comp., 12, 1423 (2016)

10. C. Bertoni and M.S. Gordon, “Analytic gradients for the Effective Fragment Molecular Orbital method”, J. Chem. Theory Comp., in press.

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

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

Program Scope

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

Recent Progress

Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames. In a recent *J. Phys. Chem. A* Feature Article,[9] we addressed the formation mechanisms of naphthalene and indene, which represent prototype PAH carrying two six-membered and one five- plus a six-membered ring. Theoretical studies of the relevant chemical reactions were overviewed in terms of their potential energy surfaces, rate constants, and product branching ratios; these data were compared with experimental measurements in crossed molecular beams and in the pyrolytic chemical reactor emulating the extreme conditions in the interstellar medium (ISM) and the combustion-like environment, respectively. The outcome of the reactions potentially producing naphthalene and indene was shown to critically depend on temperature and pressure or collision energy and hence the reaction mechanisms and their contributions to the PAH growth can be rather different in the ISM, planetary atmospheres, and in combustion flames at different temperatures and pressures. Specifically, this paradigm was illustrated with new theoretical results for rate constants and product branching ratios for the reaction of phenyl radical with vinylacetylene. The analysis of the formation mechanisms of naphthalene and its derivatives shows that in combustion they can be produced via Hydrogen-Abstraction-aCetylene-Addition (HACA) routes, recombination of cyclopentadienyl radical with itself and with cyclopentadiene, the reaction of benzyl radical with propargyl, methylation of indenyl radical, and the reactions of phenyl radical with vinylacetylene and 1,3-butadiene. In extreme astrochemical conditions, naphthalene and dihydronaphthalene can be formed in the C_6H_5 + vinylacetylene and C_6H_5 + 1,3-butadiene reactions, respectively. Ethynyl-substituted naphthalenes can be produced via the ethynyl addition mechanism beginning with benzene (in dehydrogenated forms) or with styrene.

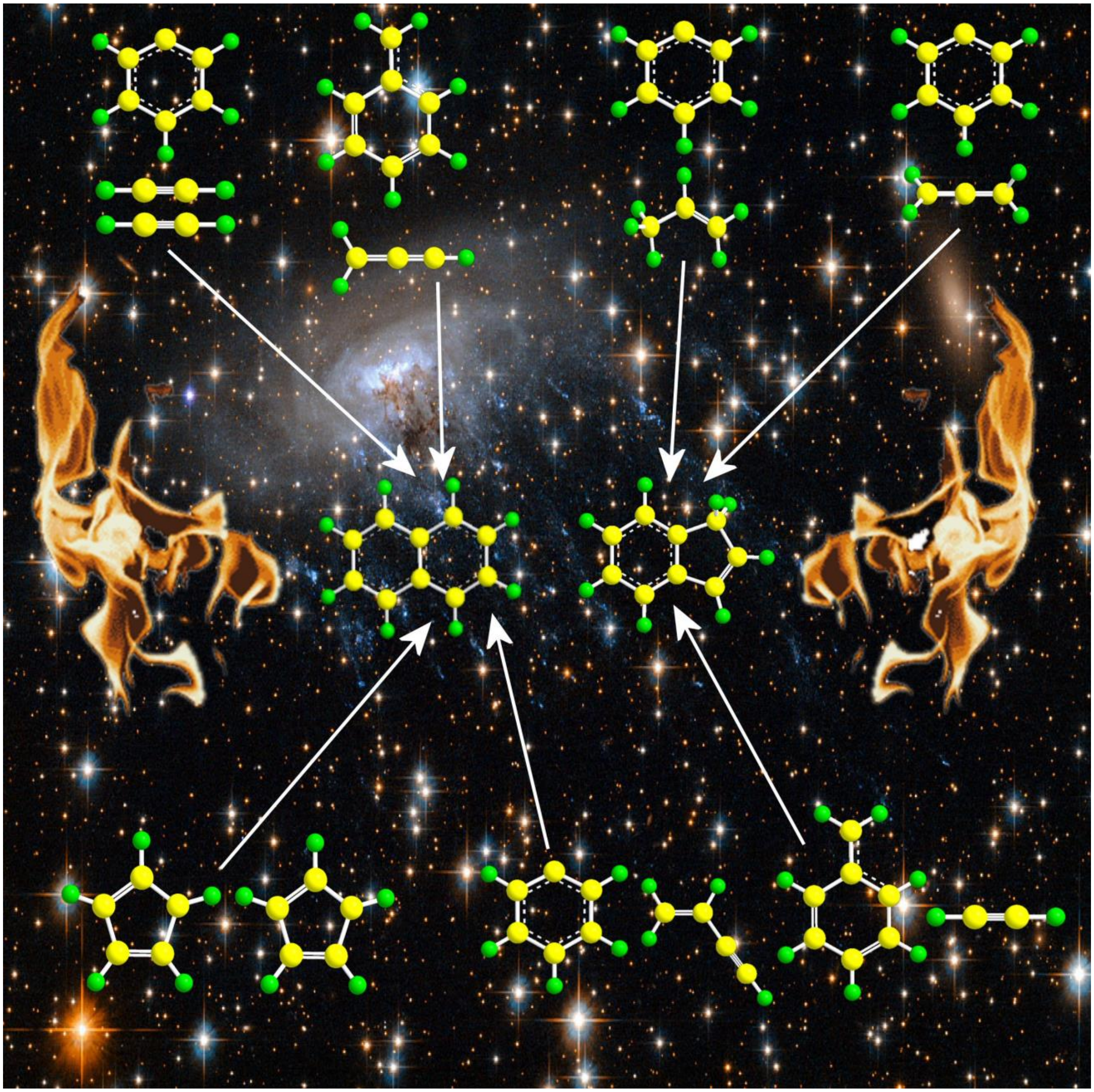


Figure 1. Chemical reactions forming naphthalene and indene in interstellar space and in combustion (cover art from *J. Phys. Chem. A*, volume 121, issue 6, February 16, 2017).

We employed the ab initio RRKM - Master Equation approach to predict the rate constants involved in the formation of indene and its conversion to naphthalene.[7] The reactions eventually leading to indene involve C_9H_x (x = 8-11) potential energy surfaces (PESs) and include C_6H_5 + C_3H_4 (allene and propyne), C_6H_6 + C_3H_3, benzyl + C_2H_2, C_6H_5 + C_3H_6, C_6H_6 + C_3H_5, and C_6H_5 + C_3H_5. These predictions allowed us to make a number of valuable observations on the role of various mechanisms. For instance, we demonstrated that reactions which can significantly contribute to the formation of indene include phenyl + allene and H-assisted isomerization to indene of its major product, 3-phenylpropyne, benzyl + acetylene, and the reactions of the phenyl radical with propene and allyl radical, both proceeding via the 3-phenylpropene intermediate. 3-phenylpropene can be activated to 1-phenylallyl radical, which in turn rapidly decomposes to indene. Next, indene can be converted to benzofulvene or naphthalene under typical combustion conditions via its activation by H atom abstraction and methyl substitution on the five-member ring followed by isomerization and decomposition of the resulting 1-methylindenyl radical, $C_{10}H_9 \rightarrow C_{10}H_8 + H$. Alternatively, the same region of the $C_{10}H_9$ PES can be accessed through the reaction of benzyl with propargyl, $C_7H_7 + C_3H_3 \rightarrow C_{10}H_{10} \rightarrow C_{10}H_9 + H$, which therefore can also contribute to the formation of benzofulvene or naphthalene. Benzofluvene easily transforms to naphthalene by H-assisted isomerization. An analysis of the effect of pressure on the reaction outcome and relative product yields was given and modified Arrhenius fits of the rate constants were reported for the majority of the considered reactions. Ultimately, the implementation of such expressions in detailed kinetic models will help quantify the role of these reactions for PAH growth in various environments.

Combined experimental and theoretical studies of the formation of naphthalene and phenanthrene 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 revealed the fundamental chemistry of the styrenyl and the ortho-vinylphenyl radicals (C_8H_7)—key transient species of the HACA mechanism—with acetylene and provided the first solid experimental evidence on the facile formation of naphthalene in a simulated combustion environment validating the previously theoretically proposed HACA mechanism for these two radicals.[5,8] Our study highlighted, at the molecular level spanning combustion and astrochemistry, the importance of the HACA mechanism to the formation of the prototype PAH naphthalene. In another work, by exploring the previously unknown chemistry of the ortho-biphenylyl radical with acetylene, we demonstrated the efficient synthesis of phenanthrene in carbon-rich circumstellar environments.[10] However, the lack of formation of the anthracene isomer implies that HACA alone cannot be responsible for the formation of PAHs in extreme environments.

Future Plans

The main goal of this project will continue to be unraveling reaction mechanisms and generating reliable temperature- and pressure-dependent rate constants for various processes in PAH formation, growth, and oxidation. To accomplish this goal we will convert PESs of the pertinent reactions into pressure- and temperature-dependent rate constants using the eigenvalue-based RRKM-ME code developed by Klippenstein and co-workers. In the new three-year project period we will focus on the following systems: 1) the remaining reactions and pathways leading to the formation of naphthalene and indene, such as $C_5H_5 + C_5H_5/C_5H_6$, $C_7H_7 + C_3H_3$, and $C_6H_5 + C_3H_5$, the kinetics of which have not yet been explored; 2) reactions producing three-ring PAHs, such as anthracene, phenanthrene, and acenaphthalene, including HACA routes and the reactions of naphthyl and indenyl radicals with C_4H_6, C_3H_4, and C_4H_4; 3) HACA mechanism in larger PAHs via acetylene addition to zigzag and arm-chair edges; 4) oxidation of six- and five-member rings in aromatic and PAH radicals such as phenanthryl, anthracyl, cyclopentadienyl, indenyl, and acenaphthyl. The rate constants will be included in the latest combustion models in collaboration with S. Klippenstein, L. Harding, Y. Georgievskii, R. Sivaramakrishnan, J. Miller, and M. Frenklach. We will continue our collaborations with R. Kaiser's and M. Ahmed's groups on the studies of combustion-relevant bimolecular reactions in crossed beams and in the pyrolytic reactor at LBNL, with A. Suits on photodissociation of pyridine, and with R. Tranter on the roaming dynamics of Cl reactions with hydrocarbons.

Grant Number and Grant Title
DE-FG02-04ER15570 Theoretical studies of chemical reactions related to the formation and growth of polycyclic aromatic hydrocarbons and molecular properties of their key intermediates
Postdoc: None
Students: Joao Marcelo Ribeiro, Daniel Belisario-Lara

DOE/BES sponsored publications (2014-2017)
1. Kislov V.V., Singh R.I., Edwards D.E, Mebel A.M., Frenklach M., "Rate coefficients and product branching ratios for the oxidation of phenyl and naphthyl radicals: A theoretical RRKM-ME study", Proc. Int. Combust. Inst. 2015, 1861-1869.
2. Singh R.I., Mebel A.M., Frenklach M., "Oxidation of graphene-edge six- and five-member rings by molecular oxygen", J. Phys. Chem. A 2015, 119, 7528-7547.
3. Mebel A.M., Kaiser R.I., "Formation of resonantly stabilised free radicals via the reactions of atomic carbon, dicarbon, and tricarbon with unsaturated hydrocarbons: Theory and crossed molecular beams experiments", Int. Rev. Phys. Chem. 2015, 34, 461-514.
4. Ribeiro J.M., Mebel A.M., "Reaction mechanism and product branching ratios of the CH + C_3H_6 reaction: A theoretical study", J. Phys. Chem. A 2016, 120, 1800-1812.
5. Yang T., Troy T.P., Xu B., Kostko O., Ahmed M., Mebel A.M., Kaiser R.I., "Hydrogen-Abstraction/Acetylene-Addition Exposed", Angew. Chem. Int. Ed. 2016, 55, 14983-14987.
6. Thomas A.M., Yang T., Dangi B.B., Kaiser R.I., Kim G.S., Mebel A.M., "Oxidation of the para-Tolyl Radical by Molecular Oxygen under Single-Collision Conditions: Formation of the para-Toloxy Radical", J. Phys. Chem. Lett. 2016, 24, 5121-5127.
7. Mebel A.M., Georgievskii Y., Jasper A.W., Klippenstein S.J., "Pressure-dependent rate constants for PAH growth: formation of indene and its conversion to naphthalene", Faraday Discuss. 2016, 195, 637-670.
8. Mebel A.M., Georgievskii Y., Jasper A.W., Klippenstein S.J., "Temperature- and Pressure-Dependent Rate Coefficients for the HACA Pathways from Benzene to Naphthalene", Proc. Int. Combust. Inst. 2017, 36, 919-926.
9. Mebel A.M., Landera A., Kaiser R.I., "Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames", Feature Article, J. Phys. Chem. A 2017, 121, 901–926.
10. Yang T., Kaiser R.I., Troy T.P., Xu B., Kostko O., Ahmed M., Mebel A.M., Zagidullin M.V., Azyazov V.N., "HACA's Heritage: A Free Radical Pathway to Phenanthrene in Circumstellar Envelopes of Asymptotic Giant Branch Stars", Angew. Chem. Int. Ed. 2017, DOI: 10.1002/ange.201701259.

Intrinsic to collective properties of ions in solution

Christopher J. Mundy
Physical Sciences Division
Pacific Northwest National Laboratory
902 Battelle Blvd, Mail Stop K1-83
Richland, WA 99352
chris.mundy@pnnl.gov

Program Scope

The long-term objective of this research is to develop a fundamental understanding of processes, such as transport mechanisms and chemical transformations, at interfaces of hydrogen-bonded liquids. Liquid surfaces and interfaces play a central role in many chemical, physical, and biological processes. Many important processes occur at the interface between water and a hydrophobic liquid. Separation techniques are possible because of the hydrophobic/hydrophilic properties of liquid/liquid interfaces. Reactions that proceed at interfaces are also highly dependent on the interactions between the interfacial solvent and solute molecules. The interfacial structure and properties of molecules at interfaces are generally very different from those in the bulk liquid. Therefore, an understanding of the chemical and physical properties of these systems is dependent on an understanding of the interfacial molecular structure. The adsorption and speciation of ions at aqueous liquid interfaces are fundamental processes encountered in a wide range of physical systems. In particular, the manner in which solvent molecules solvate ions at the interface is relevant to problems in a variety of areas. Another major focus lies in the development of reduced models of interaction based on the potential of mean force (PMF) that can be used with appropriate simulation techniques for sampling statistical mechanical ensembles to obtain the desired collective properties such as nuleation.

Progress Report

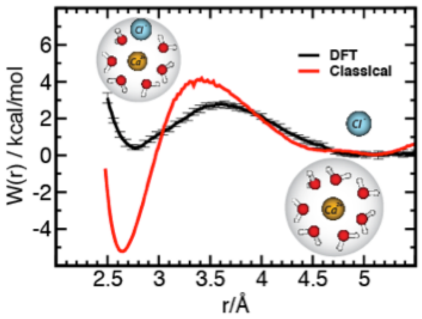


Figure 1: PMF for ion pairing of $CaCl_2$ using different levels of molecular interaction. The DFT is consistent with a picture little ion pairing in agreement with experiment.[1] The classical force field would suggest that $CaCl_2$ forms strong ion pairs.

A microscopic picture of collective properties of ions in solution [1-3]: In current and previous funding periods we have studied both the structure and solvation free energetics of single ions in solution. We have demonstrated that the accuracy of the ion-water and water-water interaction afforded by DFT are good enough to reproduce the local aqueous structure of anions as determined by extended x-ray fine structure spectroscopy (EXAFS). Nevertheless questions pertaining to the collective nature of concentrated electrolyte solutions still remain. Moreover, producing well converged ensembles of trajectories of electrolyte solutions at finite concentrations using DFT based interaction potentials remains a challenge. Questions pertaining to the extent of an accurate representation of the short-ranged structure is necessary to predict the long-range collective response of a concentrated electrolyte solution remains. We have shown that DFT based interaction potentials reproduce the local aqueous solvation structure as determined by by EXAFS of both isolated Ca^{2+} and Cl^{-} ions reproduce.[1] Having established this notionally “intrinsic” measure of accuracy with DFT interaction potentials, we can compute the PMF between two ions in water. **Figure 1** depicts the potential of mean force (PMF) as computed from DFT interaction potentials and classical empirical potential. Also shown in **Figure 1** is the same PMF computed with a classical empirical potential that is known to give good agreement with EXAFS. The PMFs are remarkably different.[1] It is well known in the literature that CaCl$_2$ does not ion-pair until concentrations above 6M.[1] Although data provided in **Figure 1** provides qualitative evidence of how an accurate description of local structure impacts collective properties such as activity and osmotic coefficients, a more rigorous connection is needed.

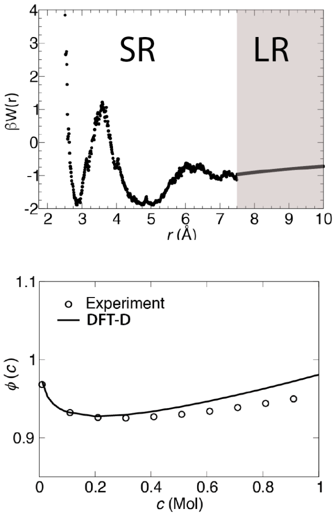


Figure 3: (top) the potential of mean force for an isolated Na^{+}--Cl^{-}. The SR is determined by DFT. The LR is a simple electrostatic term. (bottom) The computed and experimentally determined osmotic coefficients for NaCl as a function of concentration.

Figure 2 demonstrates schematically how our research is making connections between “intrinsic” properties at infinite dilutions and collective properties at finite concentration.[2] To this end we provided a model for ion pairing of NaCl using the short-range (SR) interaction as determined by DFT and the long-range (LR) interaction being determined by simple Coulomb form as shown in **Figure 3.** Using this simple two-body potential for the ion-ion interaction as the input in an integral equations with the hypernetted-chain closure, we can efficiently access the osmotic coefficients at finite concentration.[2] The result, as shown in **Figure 3** shows that the coarse grained two-body interaction potential indeed yields reasonable osmotic coefficients up to concentrations of 1 M. Using the ideas of the intrinsic PMF from accurate representations of interaction based in quantum mechanics to inform our understanding of collective properties such as clustering in solution up to moderate concentrations will be the focus of future studies. Specifically, it will be the differences in the SR component between quantum versus classical empirical interaction potentials that will drive much of the interesting phenomena.[3]

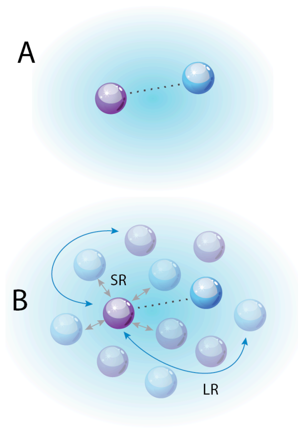


Figure 2: A schematic of a PMF of ion-pairing in the dilute limit (A) that was computed in **Figure 1.** (B) how the dilute limit PMF informs collective behavior. This will require the delicate interplay between the slowly varying long-range (LR) interaction and the complex short-range (SR) interaction.

Acknowledgements. This work was performed with Mirza Galib (PNNL), Santanu Roy (PNNL), Tim Duignan (PNNL), John D. Weeks (U. Maryland), Rick Remsing (Temple), Ilja Siepmann (U. Minn.), Greg Schenter (PNNL), Marcel D. Baer (PNNL), Shawn M. Kathmann (PNNL), Greg Kimmel (PNNL), and John Fulton (PNNL). We also acknowledge computer resources from NERSC. Battelle operates Pacific Northwest National Laboratory for the US Department of Energy. The Molecular Theory and Modeling FWP 16249 is co-managed by CTC and CPIMS programs of DOE Office of Basic Energy Sciences Division of Chemical Sciences, Geosciences, and Biosciences.

Publications with BES support (2016-present):

1. M Galib, MD Baer, LB Skinner, **CJM**, T Huthwelker, GK Schenter, CJ Benmore, N Govind, JL Fulton, "Revisiting the hydration structure of aqueous Na^+" *The Journal of Chemical Physics* **146**, 084504
2. Marcel D. Baer and **CJM,** "Local aqueous solvation structure around Ca^{2+}during Ca^{2+}--Cl^- pair formation" *Journal of Physical Chemistry B* **120**, 1885, (2016)
3. Duignan, T.; Baer, M.D.; **CJM**, "Ions Interacting in Solution: Moving from Intrinsic to Collective Properties" *Current Opinion in Colloid & Interface Science* **23**, 58 (2016)
4. Daily M.; Baer, Marcel, **CJM,** "Divalent Ion Parameterization Strongly Affects Conformation and Interactions of an Anionic Biomimetic Polymer" *The Journal of Physical Chemistry B* **120**, 2198 (2016)
5. L. B. Skinner, L.B.; Galib, M.; Fulton, J.L. **CJM**; Parise, J. B.; Pham, V.-T.; Schenter, G.K. and Benmore, C.J., "The structure of liquid water up to 360 MPa from x-ray diffraction measurements using a high Q-range and from molecular simulation, *The Journal of Chemical Physics* **144**, 134504 (2016)
6. Roy, S; Baer, M.D.; **CJM**; Schenter, G.K., "Reaction Rate Theory in Coordination Number Space: An Application to Ion Solvation" *The Journal of Physical Chemistry C* **120**, 7597 (2016)
7. Lei, H.; Baker, N.A.; Wu, L.; Schenter, G.K.; **CJM**, and Tartakovsky, A, "Smoothed Dissipative Particle Dynamics model for mesoscopic multiphase flows in the presence of thermal fluctuations,"*Physical Review E* **94**, 023304 (2016)

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

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

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

Postdoc: Linda Hung
Student: Bin Shi

PROGRAM SCOPE

The primary goals of our research program are to develop and apply state-of-the-art first-principles methods to predict electronic and optical properties of three systems of significant scientific and technological interest: transition metal clusters, organic dyes, and metal-organic frameworks. These systems offer great opportunities to manipulate light for a wide ranging list of energy-related scientific problems and applications. We focus our investigations on the development, implementation, and benchmarking of many-body Green's function methods (*GW* approximation and the Bethe-Salpeter equation) to examine excited-state properties of transition metal/transition-metal-oxide clusters and organic molecules that comprise the building blocks of dyes and metal-organic frameworks (MOFs).

RECENT PROGRESS

Excitation Spectra of Group IB and IIB Transition Metal Atoms and Monoxides

We benchmarked the impact of various numerical and theoretical approximations on excitations of Group IB and IIB atoms and monoxide molecules. *GW* quasiparticle energies were computed for ground state atoms in three valence electron configurations: d^{10} (Cu^+, Ag^+, Zn^{2+}, and Cd^{2+}), $d^{10}s^1$ (Cu^0, Ag^0, Zn^+, and Cd^+), and $d^{10}s^2$ (Cu^-, Ag^-, Zn^0, and Cd^0). For the same species, we also determined low-lying *GW*-BSE neutral excitation energies. We compared our pseudopotential *GW* calculations performed with our software RGWBS to Gaussian basis-set, all-electron *GW* calculations performed with software MOLGW. For comparison to experimental ionization energies, quasiparticle energies were obtained across six levels of *GW* theory - G_0W_0@LDA, $G_0W_0\Gamma_{\mathrm{LDA}}$@LDA, ev$G_0W_0$@LDA, ev$G_0W_0\Gamma_{\mathrm{LDA}}$@LDA, G_0W_0@PBE, evG_0W_0@PBE – where Γ_{LDA} denotes the inclusion of a 2-point LDA vertex and ev*GW* is eigenvalue self-consistent *GW*.

Taking the Zn atom as a test case, we first showed that the complete basis set limit for *GW* energies can be reached via extrapolation. Improved extrapolations of *d*-state *GW* energies can be obtained using a static remainder closure relation for the quasiparticle summation, but convergence remains slower than for *s* and *p* states, and numerical accuracy is ~0.2 eV. We found that energy differences between G_0W_0 and evGW converge more quickly with basis set size than the energy itself. evGW energies can, therefore, be obtained from a smaller basis set, if the complete basis set limit of the G_0W_0 energy is already known. For the BSE, we showed that transitions between *s* and *p* orbitals were found to be well converged on finite basis sets, while the numerical accuracy associated with d states was again ~0.2 eV.

In benchmarks comparing perturbative and self-consistent GW, accuracies do not improve with eigenvalue self-consistency or the LDA vertex. The effect of $\Gamma_{\rm LDA}$ on the GW calculation is to increase the quasiparticle energies, but in contrast with our work on aromatic molecules, the amount of the shift is not nearly constant, but relates to the localization of the wave function. We showed that GW@PBE energies are very similar to those of GW@LDA for *s* and *p* states, but for *d* states the G_0W_0@PBE is slightly more accurate than any variant of GW that uses a LDA starting point. For two-particle excitations, we obtained excellent agreement between BSE@$G_0W_0\Gamma_{\rm LDA}$@LDA eigenvalues and experimental measurements of absorption, as long as off-diagonal terms are included in the self-energy contributions (Fig. 1). The more computationally expensive BSE@evGW@PBE was found to have comparable high accuracy. We observed that a cancellation of errors occurs for the GW quasiparticles, with these two levels of theory producing mean errors ~0.2 eV. These results suggested that inclusion of off-diagonal elements and further development of vertex corrections may be a route to cheaper yet more accurate GW-BSE computations of optical properties.

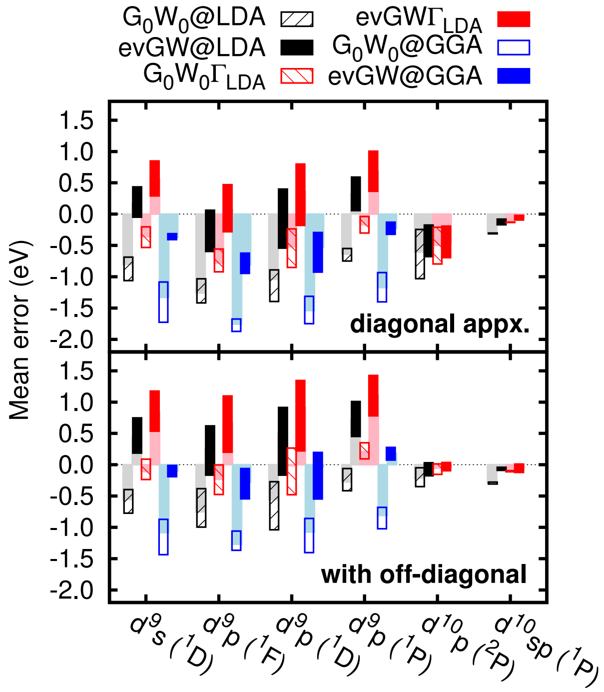


Fig 1: Error of GW-BSE predictions (with and without off-diagonal terms in the self-energy) relative to experimental absorption energies from a d^{10} (first four sets of bars), $d^{10}s$ (fifth set), or $d^{10}s^2$ (sixth set) electron configuration to the configuration listed along the x-axis. Rectangles matching the legend indicate the error range across the Cu, Ag, Zn, and Cd test set, with fainter colored bars providing a guide for the eye.

Photoelectron Spectra of Copper Oxide Cluster Anions

In a collaborative project involving Leeor Kronik and Anna Krylov, we investigated 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 PBE, PBE0, HSE06, and optimally-tuned range separated hybrid (OT-RSH) functionals, many-body perturbation theory within the G_0W_0@PBE approximation, and equation-of-motion coupled-cluster methods. We compared results from these first principles methods with each other and experimental data.

The computed photoelectron spectra of the CuO^- cluster show interesting variations across different levels of theory (Fig. 2). 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. 2(a)] can be interpreted as arising from the removal of $pd\pi^*$ and $pd\sigma^*$ electrons from anti-bonding orbitals of significant O 2*p* 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 3*d* character (bonding $pd\sigma$, $pd\pi$ and non-bonding Cu 3*d*). 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, HSE06, and OT-RSH (with exact exchange fraction $\alpha = 0.2$) predictions are virtually the same, but they significantly underestimate both the ionization potential and the X-Y separation by ~0.5 eV. While G_0W_0 and CCSD(T) predict the position of the first peak quite accurately, they differ in the position of the second peak. 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 G_0W_0 and CCSD(T) levels of theory 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 do slightly better. Overall taking all five peaks (with BEs less than 6 eV) into account, G_0W_0 and CCSD(T) perform moderately well. 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.

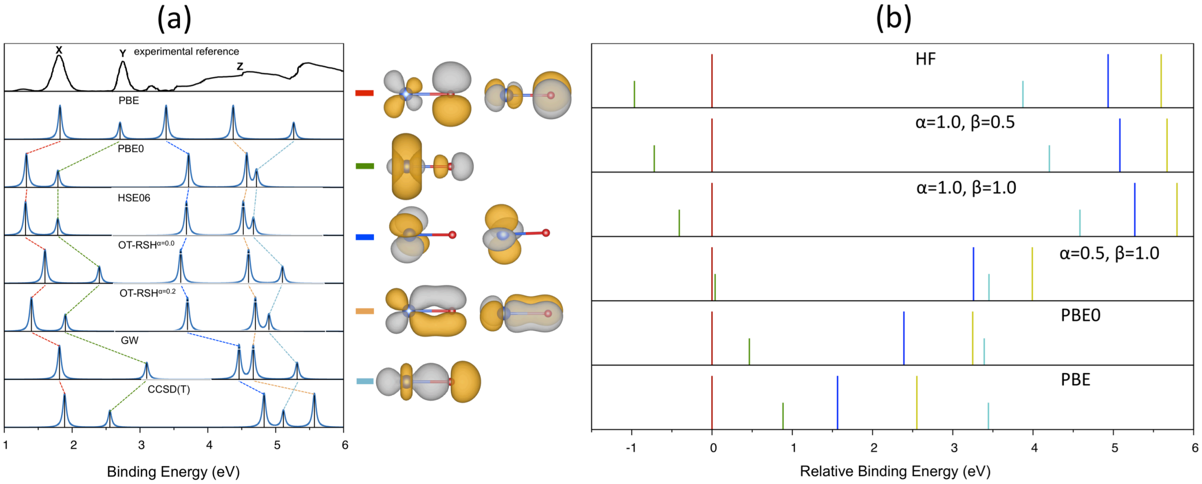


Fig. 2: (a) Computed binding energies at various levels of theory for CuO^- along with experimental data. Isosurfaces for $pd\pi^*$, $pd\sigma^*$, non-bonding Cu 3*d*, $pd\pi$, and $pd\sigma$ orbitals at the PBE level are also shown. (b) Relative binding energies computed with differing amounts of Fock exchange and PBE correlation. The binding energy of the $pd\pi^*$ orbital is set at zero for each case.

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 $E_{xc} = \alpha E_{x,HF} + (1-\alpha)E_{x,PBE} + \beta E_{c,PBE}$ where $E_{x,HF}$ is the Hartree-Fock (HF) exchange, and $E_{x,PBE}$ $E_{c,PBE}$ are semilocal PBE exchange and correlation, respectively, we performed a series of DFT computations varying α and β from 0 to 1 [Fig. 2(b)]. 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 static correlation, we attributed the apparent success of the PBE predictions (for the first two peaks) to a more accurate accounting of static correlation in PBE compared to PBE0.

Similar observations can be made about the predictions of PBE versus hybrid functionals for cluster anions of relatively large O 2*p* character in low-lying orbitals, such as CuO_2^- and CuO_3^-. When the Cu content increases, however, the overall predictions of PBE compared to hybrid functional predictions significantly worsen, *e.g.* for the case of Cu_2O^-, and hybrid functional perform quite well. A detailed understanding of correlation effects in systems in which localized *d* orbitals, less localized *pd* hybrid orbitals, and even less localized O 2*p*-like orbitals coexist simultaneously is, therefore, a challenging and much needed endeavor, which forms the basis for our future studies on 3*d* transition metal oxide and dioxide molecules.

FUTURE PLANS

Our ongoing research and future plans in first-principles investigations into the optical and electronic properties of transition-metal oxide nanostructures include:

- Benchmarking *GW* theories for electronic excitations in 3*d* transition metal oxide and dioxide clusters
- Modeling the optical and electronic properties of CuO_2-based nanocrystals
- Investigations into the optical properties of MOFs building blocks using TDDFT and GW-BSE

PUBLICATIONS ACKNOWLEDGING THIS GRANT

1) Hung, L.; Baishya, K.; Ogut, S. First-principles real-space study of electronic and optical excitations in rutile TiO2 nanocrystals. *Phys. Rev. B* **2014**, *90*, 165424.
2) 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.
3) 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** (**DOI:** 10.1021/acs.jctc.7b00123)

Molecular modeling of multifunctional metal-organic frameworks

C. Huy Pham, Jordi Cirera, Francesco Paesani
University of California, San Diego

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

A remarkable example of SCO behavior in MOFs is provided by the family of Hoffmann-type [Fe(pz)M(CN)4] MOFs (pz = pyrazine, and M = Ni, Pd, Pt). These materials display cooperative thermal- and light-induced spin crossover with transition temperatures (T1/2) close to room temperature. Of particular interest is the [Fe(pz)Pt(CN)4] framework that exhibits bidirectional chemo-switching between low-spin (LS) and high-spin (HS) states upon adsorption of chemically and structurally different guest molecules. Specifically, while the SCO transition for the empty framework occurs at ~290 K, the adsorption of protic solvents (e.g., alcohols and water) and bulky molecules (e.g., benzene and pyridine) stabilizes the HS state, shifting T1/2 to lower values. In contrast, CS2 molecules adsorbed in the MOF pores stabilize the LS state. No effect on the SCO transition is observed upon adsorption of small molecules such as CO2 and N2. Importantly, the [Fe(pz)Pt(CN)4] framework exhibits “memory” response, being able to retain a given spin state upon guest desorption. Although a weak correlation between the SCO transition and the dielectric constant of the guest molecules can be found, the modulation of the SCO behavior of MOFs upon guest adsorption remains poorly understood.

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

We first applied our hybrid MC/MD method to investigate the SCO behavior of the [Fe(pz)Pt(CN)4] MOF upon adsorption of a variable number of water molecules, from Nw = 1 to Nw = 5 molecules per unit cell. The transition temperature $T_{1/2}$ shows a progressive shift to lower values as a function of water loading. A distinct change in the magnetization occurs when two water molecules are adsorbed per unit cell, with $T_{1/2}$ decreasing more rapidly at higher loadings.

In a subsequent study, the spin-crossover behavior of $\{Fe(pz)[Pt(CN)_4]\}$ was investigated upon pyrazine adsorption. In contrast to previous theoretical studies, which reported a transition temperature of ~140 K, our MC/MD simulations predict that the high-spin state is the most stable state at all temperatures, in agreement with the experimental observations (Figure 1). The MC/MD simulations also indicate that the pyrazine molecules adsorbed in the MOF pores lie nearly parallel but staggered by 60° relative to the pyrazine ligands of the framework. The analysis of the magnetization curve as a function of the temperature demonstrates that the staggered configuration assumed by the guest pyrazine molecules within the framework is responsible for the stabilization of the high-spin state. Both the guest pyrazine molecules and the pyrazine ligands of the framework are effectively locked into the minimum- energy configuration and do not display any rotational mobility.

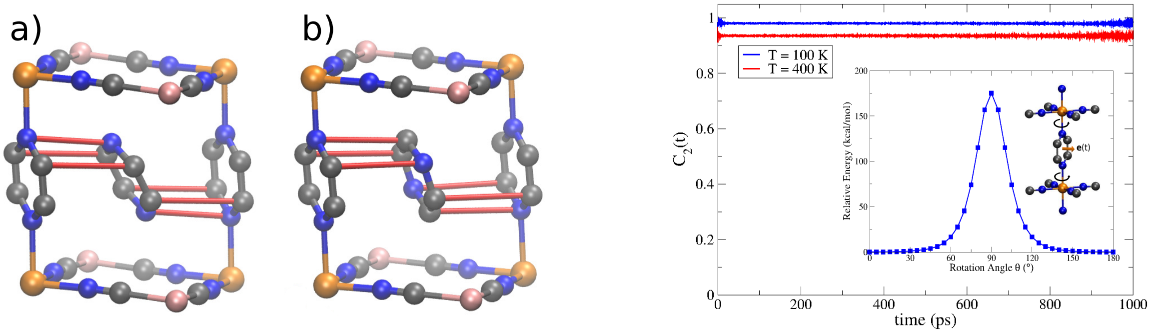


Figure 1. *Left: (a) Structure of pz@{Fe(pz)[Pt(CN)$_4$]} previously predicted by DFT calculations. (b) Structure of pz@{Fe(pz)[Pt(CN)$_4$]} obtained from our MC/MD simulations, which are in agreement with the experimental measurements. Right: Orientational correlation function, $C_2(t)$, describing the rotation of the pyrazine linkers of the framework at 100 and 400 K. The energy profile associated with the rotation of a pyrazine linker is shown in the inset.*

In the future, we will apply our hybrid MC/MD method to the *in silico* design of MOFs that can use the spin-crossover transition to detect and separate different molecular species in gas mixtures. In parallel with these MC/MD applications, we are currently working on the extension of our many-body (MB) potential energy functions to different molecular species of interest for storage and separation in MOFs (e.g., CH_4, CO_2, and H_2). The integration of MB potentials in our hybrid MC/MD approach will enable predictive, molecular-level simulations of adsorption, diffusion, and separation processes in MOFs.

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Theoretical Studies of Spin Crossover Metal-Organic Frameworks

Postdocs: Jordi Cirera, Andreas W. Götz, C. Huy Pham
Students: Pushp Bajaj, Kevin Bao

Publications Acknowledging this Grant in 2013-2016

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

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

Pham, C.H.; Cirera, J.; Paesani, F. Molecular Mechanisms of Spin Crossover in the [Fe(pz)Pt(CN)$_4$] Metal-Organic Framework upon Water Adsorption. *J. Am. Chem. Soc.* **2016**, *138*, 6123-6126.

Pham, C.H.; Paesani, F. Spin Crossover in the [Fe(pz)Pt(CN)$_4$] Metal-Organic Framework upon Pyrazine Adsorption. *J. Phys. Chem. Lett.* **2016**, *7*, 4022-4026.

Computational Methods Based on Density Functional Theory for Reactions and Processes Involving Electronic Spin

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

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

Postdoc: None.
Student: Suresh Thapa (hired September 2016).

Abstract

Recent Progress

Magnetization dynamics: Real-time time-dependent density functional theory (RT-TDDFT) is routinely employed to calculate linear and non-linear optical adsorption spectra, charge transfer dynamics, as well as the simulation of time-dependent phenomena in molecular conductance. Despite this success, not much attention has been given to the dynamics of the spin degrees of freedom that are responsible for a wealth of important chemical and physical phenomena. Two years ago we have developed a computational code based on a time-dependent extension of noncollinear spin density functional theory for the simultaneous simulation of charge and magnetization vector dynamics in molecular systems.[2] Including the spin density in TDDFT simulations necessarily implies dealing with noncollinear magnetization to properly propagate both, charge and magnetization density vector, $n(\mathrm{t})$ and $\boldsymbol{m}(\mathrm{t})$. We have benchmarked the method against the low-frequency spin dynamics of the H–He–H molecule and a bimetallic Mn complex, where the magnetization dynamics can be directly compared to the classical magnetization precession of a Heisenberg-Dirac-van Vleck spin Hamiltonian. We are currently making progress in optimizing the efficiency of the code, including adjusting the time steps and exploring the use of scalar and spin-orbit pseudopotentials to eliminate the high-frequency dynamics that forces the use of small time-steps.

Analysis Tools: These tests showed that RT-TDDFT can successfully capture the low-energy spin dynamics of magnetic systems. However, there are no many available analysis tools to extract and interpret the information provided by the noncollinear magnetization density. In view of this, we generalized the local spin analysis of Clark and Davidson [J. Chem. Phys. 115, 7382 (2001)] for the partitioning of the expectation value of molecular spin square operator into atomic contributions to the noncollinear spin case in the framework of DFT, which provides additional information that complements the standard one-particle spin population analysis (Figure 1 and Table 1). As a proof-of-concept we also employed the local spin analysis to evaluate the spin correlation functions $\langle \mathbf{S}_{\mathrm{A}} \cdot \mathbf{S}_{\mathrm{B}} \rangle$ in terms of the interatomic spin angle. This, combined with the dependence of the electronic energy with that angle, provides an alternative to energy differences based methods for the calculation of magnetic exchange couplings that is independent of *ad-hoc* assumptions about the nominal spin values.[1]

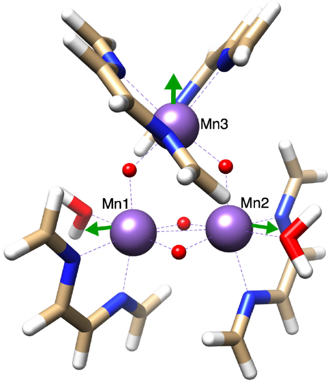


Figure 1: Noncollinear spin structure of a Mn3 complex.[Luo et al., J. Phys. Chem. Lett. 2, 2629 (2011)] The green arrows show the noncollinear atomic magnetization $\langle \mathbf{S}_{\mathrm{Mn}} \rangle$.

Magnetization components in noncollinear spin DFT: Practical generalizations of collinear GGA realizations to the noncollinear spin realm utilize either the longitudinal component of the magnetization gradient, or both, longitudinal and transversal components on an equal footing. It has been pointed out that none of these approaches have a solid physical ground [Eich et al., Phys. Rev. B88, 245102 (2013)]. We are currently working on a generalization that allows to "dial" between both approaches and exploring its effect in both, static and dynamic calculations.

Table 1: Calculated total and local spin expectation values (in a.u.) for the Mn_3 complex for different density functionals (see Figure 1).

	$\langle \boldsymbol{S}^2 \rangle$	$\langle S_1 \rangle$	$\langle S_3 \rangle$	$\langle \mathbf{S}_1^2 \rangle$	$\langle \mathbf{S}_3^2 \rangle$	$\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle$	$\langle \mathbf{S}_1 \cdot \mathbf{S}_3 \rangle$
LSDA	4.85	1.16	0.91	4.32	3.64	-1.28	-0.30
BP86	5.26	1.22	0.95	4.5	3.72	-1.38	-0.34
PBE	5.4	1.25	0.98	4.59	3.79	-1.43	-0.37
B3LYP	7.02	1.5	1.07	5.38	3.95	-0.79	-0.96
PBEh	8.77	1.58	1.14	5.69	4.17	-0.52	-1.17

Future Plans

- Continue the optimization of the time step during the propagation part of the noncollinear spin TD-DFT code to allow for longer time evolutions and larger systems.
- Implement the local spin analysis for the time propagation. This is important to analyze the response of general magnetic systems, including spin-orbit and magnetic perturbations.
- Continue to analyze the impact of longitudinal and transversal gradients of the magnetization in the XC potential in realistic static and dynamical simulations.

Publications Acknowledging this DOE sponsored research (2013-2016)

1. Abate B. A.; Joshi R. P; Peralta J. E. Local Noncollinear Spin Analysis (manuscript in preparation).
2. Peralta, J. E.; Hod, O.; Scuseria, G. E. Magnetization Dynamics from Time-Dependent Noncollinear Spin Density Functional Theory Calculations, *J. Chem. Theory Comput*. **2015**, 11, 3661–3668.

3. Joshi, R. P.; Burak, O.; Barone, V.; Peralta, J. E. Hexagonal BC$_3$: A Robust Electrode Material for Li, Na, and K Ion Batteries, *J. Chem. Phys. Lett.* **2015**, 6, 2728-2732.
4. Williams, B.; Barone, B.; Pate, B.; Peralta J. E. Gradient Copolymers of Thiophene and Pyrrole for Photovoltaics. *Comput. Mater. Sci.* **2015**, *96*, 69-71.
5. Phillips, J. J.; Peralta, J. E. Magnetic Exchange Couplings from Noncollinear Perturbation Theory: Dinuclear Cu$^{\mathrm{II}}$ Complexes. *J. Phys. Chem. A* **2014**, *118*, 5841-5847.
6. Peralta, J. E.; Barone, V.; Jackson K. A. Site-specific Polarizabilities from Analytic Linear-response Theory. *Chem. Phys. Lett.* **2014**, *608*, 24-27.
7. Abate B. A.; Peralta J. E. The Performance of Density Functional Approximations for the Structures and Relative Energies of Minimum Energy Crossing Points. *Chem. Phys. Lett.* **2013**, *590*, 227-230.

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

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

I. Program Scope

This research program focuses on the development, dissemination, and applications of 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 characterized by substantial electronic near-degeneracies, and properties other than energy. The overall goal is to design and apply methods that enable precise modeling of molecular processes and properties relevant to combustion, catalysis, light harvesting, and photochemistry. The emphasis is on approaches that offer high accuracy, ease of use, and lower computational costs compared to other quantum chemistry techniques that aim at similar precision, so that one can study complex molecular problems with dozens or hundreds of non-hydrogen atoms, in addition to smaller systems, in a predictive and systematically improvable manner, supporting ongoing experiments or in the absence of experimental information. Methods pursued in this program can utilize modern multi-node, multi-core computer architectures and are well suited for pursuing novel coding strategies, such as automated and parallel implementations. The most promising electronic structure approaches developed in this program are shared, at no cost, with the community through the GAMESS package. Some methods discovered in this program, in the original or modified form, are also available in the NWChem, Q-Chem, and MRCC codes.

II. Recent Progress (2014 – 2016 and January 1 – April 18, 2017)

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 extended the idea of the active-space equation-of-motion (EOM) CC methods to the doubly electron-attached (DEA) and doubly ionized (DIP) formalisms, which are applicable to open-shell species with two electrons outside the closed-shell cores, particularly to the electronic spectra of biradicals and single bond breaking, without invoking complicated steps of genuine multi-reference CC theories. In particular, following our initial work published in 2013 (J. Shen and P. Piecuch, *J. Chem. Phys.* **138**, 194102 (2013)), we reported the development of the state-of-the-art, full and active-space, DEA- and DIP-EOMCC methods with up to 4-particle–2-hole (4*p*-2*h*) and 4-hole–2-particle (4*h*-2*p*) excitations [1,10], which are capable of providing virtually exact results for the electronic spectra of biradicals, while preserving the symmetries of the Hamiltonian that traditional particle-conserving CC and EOMCC models often break. In the case of the DEA-EOMCC methodology, we have further simplified the active-space DEA-EOMCC(4*p*-2*h*) approach discussed in Ref. [1] to a more cost-effective model at the 3*p*-1*h* level, where both 3*p*-1*h* and 4*p*-2*h* terms, not just the latter ones, are selected using active orbitals [10]. By examining the low-lying singlet and triplet states of the methylene, $(HFH)^-$, and trimethylenemethane biradicals and bond breaking in the F_2 molecule, we demonstrated that the DEA- and DIP-EOMCC methods with the active-space treatment of 4*p*-2*h* and 4*h*-2*p* excitations reproduce the results of the analogous full calculations at the small fraction of the computer effort, while considerably improving the DEA/DIP-EOMCC theories truncated at 3*p*-1*h*/3*h*-1*p* excitations and making the DEA/DIP-EOMCC results almost insensitive to the type of molecular orbitals (MOs) used in the calculations [1,10]. 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 the underlying MO basis [1,10]. Using the above and several additional examples, including singlet-triplet gaps in a series of antiaromatic molecules, such as cyclopropenyl anion (in preparation), cyclobutadiene [10], cyclobutadiene derivatives (in preparation), and cyclopentadienyl cation [10], we showed that our newest DEA-EOMCC method with the active-space treatment of both 3*p*-1*h* and 4*p*-2*h* excitations and its lower-level counterpart neglecting 4*p*-2*h* contributions are capable of accurately reproducing the results obtained using their parent counterparts with a full treatment of 3*p*-1*h* and full or active-space treatment of 4*p*-2*h* excitations at the small fraction of the computer effort.

We have also continued working on the previously developed EA- and IP-EOMCC methodologies. For example, we used the scalar relativistic IP-EOMCC approaches, correlating valence and semi-core electrons and including up to 3*h*-2*p* terms in the ionizing operator, to provide an accurate and complete assignment of peaks and other key features in the experimental photoelectron spectra of Ag_3^- and Au_3^- nanoparticles, including electron binding energies as high as about 6–6.5 eV, for the first time [3,8]. 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 showed that geometry relaxation during electron ejection from Ag_3^- and Au_3^- contributes to the peak widths, in addition to multiple electronic states behind a given spectral feature.

We have made significant progress in the development and utilization of the biorthogonal moment energy expansions, which in the past resulted in the left-eigenstate completely renormalized (CR) CC and EOMCC approaches, such as CR-CC(2,3) and CR-EOMCC(2,3), exploited, for example, in Refs. [2,4,5-7], by focusing on the CC(*P*;*Q*) formalism, originally proposed in 2012 (J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012)). The CC(*P*;*Q*) theory and the generalized moment energy expansions that define it enable one to consider a wide variety of novel, computationally efficient, *ab initio* schemes for rapidly converging high accuracy calculations of ground- and excited-state potential energy surfaces along bond breaking coordinates within a formally single-reference framework. Among the various CC(*P*;*Q*) methods one can contemplate is the CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy, in which energies obtained in the active-space CC/EOMCC calculations, such as CCSDt/EOMCCSDt or CCSDtq/EOMCCSDtq, which recover much of the non-dynamical and some dynamical electron correlation effects, are corrected for the higher-order, primarily dynamical, correlations, such as certain classes of triples ('3') or triples and quadruples ('3,4') missing in the active-space CC/EOMCC considerations. In the reporting period, we extended the previously developed CC(t;3) approach (J. Shen and P. Piecuch, *Chem. Phys.* **401**, 180 (2012), *J. Chem. Phys.* **136**, 144104 (2012), *J. Chem. Theory Comput.* **8**, 4968 (2012)), which provides ground-state potential energy surfaces, reaction profiles involving biradical transition states, and singlet-triplet gaps in biradical systems that agree with the parent full CCSDT data to within small fractions of a millihartree for total as well as relative energies at a fraction of the computer cost, to the virtually exact CC(t,q;3) and CC(t,q;3,4) models including connected quadruple excitations. By examining the double dissociation of water, the insertion of Be into H_2, and the singlet-triplet gap in the strongly correlated $(HFH)^-$ system, we demonstrated that the CC(t,q;3) and CC(t,q;3,4) methods, especially the latter one, offer significant improvements in the active-space CCSDtq results, reproducing the exact (full CI) or virtually exact (CCSDTQ) total energies to within small fractions of a millihartree at a tiny fraction of the computer effort involved in the CCSDTQ calculations, even when the electronic quasi-degeneracies become substantial. Our paper reporting these findings, N.P. Bauman, J. Shen, and P. Piecuch, "Combining Active-Space Coupled-Cluster Approaches with Moment Energy Corrections via the CC(*P*;*Q*) Methodology: Connected Quadruple Excitations," has been submitted to *Mol. Phys*. and is presently under revision. We are preparing new papers discussing the excited-state CC(*P*;*Q*) approaches and testing the CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy on the challenging beryllium dimer.

We have already taken advantage of the CC(*P*;*Q*)-based CC(t;3) methodology in a few application projects, such as our recent collaborative study with Professor Donald Truhlar of the structural and electronic properties of the neutral and singly charged magnesium clusters [7]. In this study, 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 and several CC methods with single, double, and triple excitations, 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. We have found that the geometry and binding energy of the weakly bound Mg_2 dimer requires a robust treatment of connected triple excitations, represented by full CCSDT and the CR-CC(2,3) and CC(t;3) methods developed in this program, which are considerably more accurate than the popular CCSD(T) approximation, but CCSD(T) is sufficiently accurate when larger Mg clusters are considered. We have also demonstrated that hybrid functionals have higher accuracy than local ones, with PW6B95, SOGGA11-X, M11, and PWB6K being the most accurate, both for the geometries and for the binding energies, ionization potentials, and electron-detachment energies.

We have also 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 CR-EOMCCSD(T) method, abbreviated as δ-CR-EOMCCSD(T), and the analogous two variants of the newer, rigorously size-intensive, δ-CR-EOMCC(2,3) approach based on the biorthogonal moment energy expansions against the previously published CASPT2, CC3, and EOMCCSDT-3 results as well as the suggested theoretical best estimate (TBE) values [5]. We demonstrated that the non-iterative triples corrections to the EOMCCSD excitation energies defining the relatively inexpensive, single-reference, black-box δ-CR-EOMCC approaches provide significant improvements in the EOMCCSD data, while closely matching the results of the iterative and considerably more expensive CC3 and EOMCCSDT-3 calculations and their CASPT2 and TBE counterparts, demonstrating the utility of the cost effective δ-CR-EOMCC methods in applications involving molecular electronic spectra [5]. 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 previous work on the same molecules and which can be used in future benchmark studies [5]. We uncovered a simple relationship between the reduced excitation level diagnostic obtained in EOMCCSD calculations, introduced by our group in 2005, and the magnitude of the triples δ-CR-EOMCC corrections to the EOMCCSD excitation energies [5]. This may allow us to estimate the effect of triples on the EOMCCSD results solely on the basis of relatively inexpensive EOMCCSD calculations. We also applied the CR-EOMCC(2,3) approach and its ground-state CR-CC(2,3) counterpart to several singlet and triplet potential energy surfaces corresponding to the dissociation of the water molecule into OH and H, showing that the black-box CR-CC(2,3) and CR-EOMCC(2,3) methods are as accurate as or even more accurate than the most sophisticated, expert, multi-reference CC approaches with singles and doubles augmented with triples and quadruples extracted from multi-reference CI [2]. We are preparing a paper, which shows that further (in fact, spectacular) improvements in the CR-EOMCC(2,3) excited-state data for the water molecule can be made if we replace the CR-EOMCC corrections by their aforementioned CC(t;3) extensions. We also performed the unprecedented active-space CCSDt/EOMCCSDt and CR-CC(2,3)/CR-EOMCC(2,3) computations for the low-lying singlet and triplet states of the challenging organic biradical, 1,2,3,4-cyclobutanetetraone, which present substantial problems to the existing single- and multi-reference wave function and DFT approaches [6]. 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. [9], 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 [9].

III. Future plans

Our future method development effort will focus on **(i)** continuation of our work on the CC(P;Q) formalism, which allows one to combine the CC and EOMCC approaches with non-traditional choices of cluster and excitation operators with the moment expansions used in the completely renormalized CC/EOMCC computations, to accurately describe ground- and excited-state potential energy surfaces along bond breaking coordinates, **(ii)** investigation of novel classes of single-reference CC methods for strongly correlated electronic systems by extending the approximate coupled-pair (ACP/ACC) theories, co-pioneered by the PI with Professor Josef Paldus about 25 years ago, to higher-order dynamical correlation effects the ACP/ACC approaches have difficulty with, such as connected triples, **(iii)** extension of the previously developed active-space variants of the electron-attached (EA) and ionized (IP) EOMCC methodologies, already in GAMESS, and their recently developed doubly electron attached (DEA) and doubly ionized (DIP) analogs, which enable precise determination of ground and excited states of open-shell species that differ by one or two electrons from the related closed-shell systems, to the triply electron attached (TEA) and triply ionized (TIP) cases, and **(iv)** work toward implementation of highly parallel, linear scaling, local correlation CC codes exploiting the previously developed cluster-in-molecule (CIM) ideas and their multi-level extensions allowing one to mix different electronic structure theory levels in a single computation (see our various CIM-CC and CIM-MP2 codes, and their multi-level extensions in the GAMESS package), which can take full advantage of modern massively parallel, multi-node computer platforms, where each node has multiple cores. As in the past, all of the proposed methodological and algorithmic advances will be accompanied by benchmark and realistic computations, especially those that can be tied to the ongoing experimental work in areas of small molecule spectroscopy and dynamics, elementary chemical reactions, catalysis, photoelectron spectroscopy, and photochemistry.

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

[1] J. Shen and P. Piecuch, "Doubly Electron-Attached and Doubly Ionised Equation-of-Motion Coupled-Cluster Methods with Full and Active-Space Treatments of 4-particle-2-hole and 4-hole-2-particle Excitations: The Role of Orbital Choices," *Mol. Phys.* **112**, 868-885 (2014).

[2] J.J.Lutz and P.Piecuch, "Performance of the Completely Renormalized Equation-of-Motion Coupled-Cluster Method in Calculations of Excited-State Potential Cuts of Water," *Comput. Theor. Chem.* **1040-1041**, 20-34 (2014).

[3] N.P. Bauman, J.A. Hansen, M. Ehara, and P. Piecuch, "Communication: Coupled-Cluster Interpretation of the Photoelectron Spectrum of Au_3^-," *J. Chem. Phys.* **141**, 101102-1 – 101102-5 (2014).

[4] P. Piecuch, M. Włoch, J.R. Gour, W. Li, and J.J. Lutz, "Dealing with Chemical Reaction Pathways and Electronic Excitations in Molecular Systems via Renormalized and Active-Space Coupled-Cluster Methods," *AIP Conf. Proc.* **1642**, 172-175 (2015).

[5] P. Piecuch, J.A. Hansen, and A.O. Ajala, "Benchmarking the Completely Renormalised Equation-of-Motion Coupled-Cluster Approaches for Vertical Excitation Energies," *Mol. Phys.* **113**, 3085-3127 (2015).

[6] J.A. Hansen, N.P. Bauman, J. Shen, W.T. Borden, and P. Piecuch, "*Ab Initio* Coupled-Cluster and Multi-Reference Configuration Interaction Studies of the Low-Lying Electronic States of 1,2,3,4-Cyclobutanetetraone," *Mol. Phys.* **114**, 695-708 (2016) [published online: 9 December 2015].

[7] K. Duanmu, O. Roberto-Neto, F.B.C. Machado, J.A. Hansen, J. Shen, P. Piecuch, and 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).

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

[9] G. Rasskazov, M. Nairat, I. Magoulas, V.V. Lozovoy, P. Piecuch, and M. Dantus, "Femtosecond Real-Time Probing of Reactions MMXVII: The Predissociation of Sodium Iodide in the A 0^+ State," *Chem. Phys. Lett.* **XXX**, XXX-XXX (2017), in press; corrected proof, available online: 9 February 2017.

[10] A.O. Ajala, J. Shen, and P. Piecuch, "Economical Doubly Electron-Attached Equation-of-Motion Coupled-Cluster Methods with an Active-Space Treatment of 3-particle–1-hole and 4-particle–2-hole Excitations," *J. Phys. Chem. A* **XXX**, XXX-XXX (2017), in press; just accepted manuscript, publication date (web): 14 April 2017.

Department of Energy, Basic Energy Sciences, Chemical Theory and Computation
Principal Investigator (PI): Adrienn Ruzsinszky
PI's Institution: Temple University
Street Address/City/State/Zip: 1925 N.12th Street, Philadelphia, PA 19122
PI Postal Address: Department of Physics
PI Email: aruzsinszky@temple.edu

Department of Energy under Grant No. DE- SC0010499
Previous Project title: Exploring the Random Phase Approximation for Materials and Chemical Physics

Postdocs: Savio Laricchia**,** Jefferson Bates
Graduate student: Niladri Sengupta

The Renormalized Random Phase Approximation with Kernel Correction for Materials Science

Scope of the work

In this work we test the performance of the fully nonlocal random phase approximation (RPA) for challenging problems in materials chemistry and physics.

The Random Phase Approximation (RPA) will soon be a standard method beyond semi-local Density Functional Theory (DFT0 that naturally incorporates weak interactions and eliminates self- interaction error in the exchange energy. RPA is not perfect, however, and suffers from self- correlation error as well as an incorrect description of short-ranged correlation. To improve upon RPA, an exchange(-correlation) kernel can be included in the calculation of the correlation energy, which typically requires a numerical integration over the coupling strength. Exchange-correlation kernels can be approached in various ways. In this work we utilize nonempirical kernels based on exact constraints. Model kernels can introduce electronic instabilities when inverting the response function with the kernel. To eliminate the additional cost in comparison to RPA and avoid inversion involving the kernel, the response function can be approximated through a low-order expansion using RPA renormalization. The first-order contribution can be integrated analytically over the coupling strength, while the second- and higher-order corrections must be approximated.

In this project we reveal the strengths and limitations of some model kernels through some materials problems focusing on structural phase transitions and surface energies (work in progress). In addition we demonstrate the accuracy of the Renormalized RPA for total correlation energies of simple solids, and the pressure-induced phase transitions.

Recent progress:

Transition Pressures from renormalized RPA with kernel corrections:

Phase transition pressures of materials can be difficult to describe with semi-local DFT. Previous works have shown that the RPA is more accurate than most semilocal approximations for the insulator-metal transition of Silicon diamond to beta-tin. RPA's accuracy is difficult to benchmark, however, as reported DMC results predict a slightly larger transition pressure and energy difference between phases. Within this project we tested the renormalized PBE kernel (rAPBE) as a correction to RPA to various semiconducting/metallic systems. In order to reduce the computational cost of the kernel correction we tested first order RPA renormalization (RPAr1). The GPAW code was used to compute the RPA and rAPBE results.

Recently we have extended the application of our method to the structural phase transitions of different materials, including metal to metal, metal to semiconductor, semiconductor to semiconductor transitions. Transition pressures of Pb(fcc-hcp), BN(cubic-hexagonal), GaAs(zns -cmcm), SiC(zns-nacl), Ge(diamond-Sn) and Si(diamond- beta-Sn) have been calculated using GGA exchange correlation (PBE) from semilocal DFT, exact exchange (EXX), EXX plus nonlocal correlation (RPA) from adiabatic connection fluctuation dissipation DFT and RPA plus kernel corrected correlation from ACFD DFT at zero temperature. We also computed temperature correction with the inclusion of zero point energy (ZPE) contribution from phonon spectra to find the correct phase ordering for all the calculated methods. We have found that temperature correction and kernel correction are very important to get the correct phase ordering and accurate transition pressure in accordance with the experiment, especially for a material possesing energetically nearly degenerate phases.

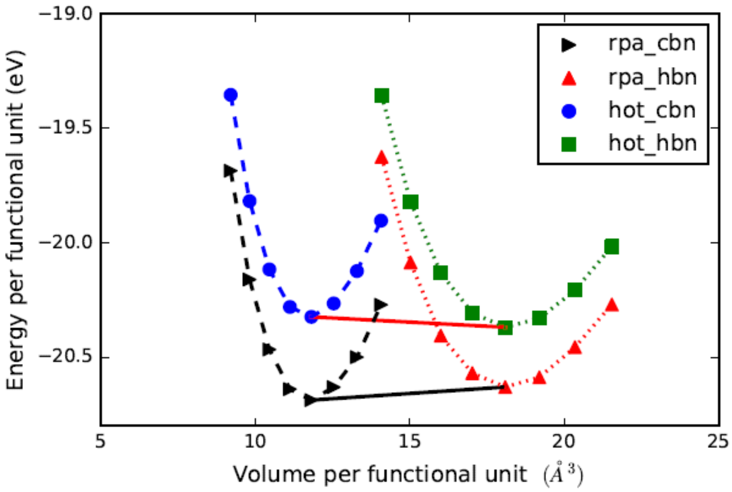
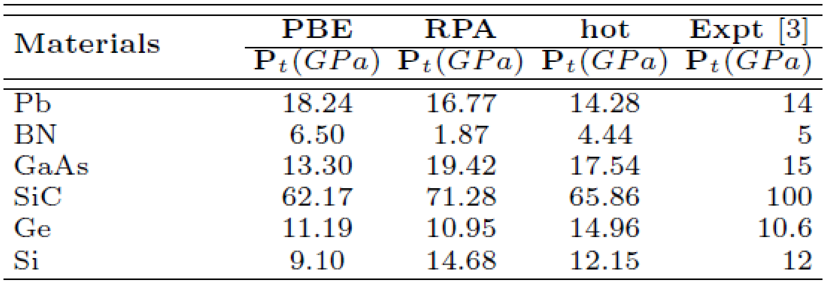


Figure 1. Energy-volume curve of the cubic and hexagonal phases of BN computed with RPA and kernel-corrected RPA including the HOT terms. (HOT refers to higher-order terms in RPA Renormalized Perturbation Theory)

RPA Renormalized Perturbation Theory replaces the infinite-order response function by a lower-order approximation which includes the kernel. RPA renormalization enables the simultaneous calculation of RPA and beyond-RPA correlation energies since the total correlation energy is the sum of a series of independent contributions. The first order approximation (RPAr1) yields the dominant beyond-RPA contribution to the correlation energy for a given exchange-correlation kernel, but systematically underestimates the total beyond-RPA correction. For very delicate energy differences the treatment of the higher-order terms (HOT) is necessary.

Table I. Transition pressures computed with RPA and kernel-corrected RPA including the HOT terms.



Materials	PBE	RPA	hot	Expt [3]
	$\mathbf{P}_t(GPa)$	$\mathbf{P}_t(GPa)$	$\mathbf{P}_t(GPa)$	$\mathbf{P}_t(GPa)$
Pb	18.24	16.77	14.28	14
BN	6.50	1.87	4.44	5
GaAs	13.30	19.42	17.54	15
SiC	62.17	71.28	65.86	100
Ge	11.19	10.95	14.96	10.6
Si	9.10	14.68	12.15	12

For most of the materials (other than Ge and SiC) included in our assessment, the mean relative error of kernel- corrected RPA with HOT corrections is smallest among all the applied methods for calculating the transition pressures. Moreover, the experimental value for SiC is highly uncertain. Beyond RPA (bRPA) approaches are not significantly more expensive than RPA itself and deliver high accuracy, so they should become a benchmark method in this area.

Publications acknowledging this Grant in 2013-2016

[1] Xiao, B., Sun, J., Ruzsinszky, A., and Perdew, J.P., Testing the Jacob's ladder of density functionals for electronic structure and magnetism of rutile VO_2, *Phys. Rev. B,* **2014,** 90, 085134.

[2] Xiao, B., Sun, J., Ruzsinszky, A., J. Feng, and Perdew, J.P., Structural phase transitions in Si and SiO_2 crystals via the random phase approximation, *Phys. Rev. B* **2012**, 86, 094109.

[3] Xiao, B., Sun, J., Ruzsinszky, A., J. Feng, Haunschield, R. Scuseria, G.E. and Perdew, J.P.,Testing New Meta-GGA Density Functionals for Structural Phase Transitions of Solids Under Pressure: Si, SiO_2 and Zr**,** *Phys. Rev. B,* **2013**, 88, 184103.

[4] Ruzsinszky, A., Zhang, I.Y., and Scheffler, M., Insight into Organic Reaction from Many-Body Approximations, *J. Chem. Phys.* **2015**, 143, 14411.

[5] Mezei, P.D, Csonka, G.I, Ruzsinszky, A. Accurate Complete Basis Set Extrapolation of Direct Random Phase Correlation Energies, *J. Chem. Theory Comput.* **2015**, 11, 3961.

[6] Mezei, P.D. Csonka, G.I. and Ruzsinszky, A., Accurate, Precise and Efficient Theoretical Methods to Calculate Anion-pi Interaction Energies in Model Structures, *J. Chem. Theory Comput.*, **2015**, 11, 360.

[7] Mezei, P.D, Csonka, G.I., Ruzsinszky, A. and Kállay, M. Construction and Application of a New Dual-Hybrid Random Phase Approximation, *J. Chem. Theory Comput.* **2015**, *11*, 4615.

[8] Bates, J.E, Laricchia, S. and Ruzsinszky, A. A Non-Local, Energy-Optimized Kernel: Recovering Second-Order Exchange in the Homogeneous Electron Gas, *Phys.Rev. B*, **2016**, 93, 045119.

[9] Mezei, P.D, Csonka, G.I, Ruzsinszky, A. Application of an Efficient Dual-Hybrid Random Phase Approximation to Water Clusters, *J. Chem. Theory Comput.* **2016,** 12, 4222.

[10] Bates, J.E, Mezei P.D., Sun, J., Csonka, G.I., and Ruzsinszky, A. Reference determinant dependence of the random phase approximation in 3d transition metal chemistry, *J. Chem. Theory Comput*, **2017**, *13*, 100.

Future plans

The research performed in the previous grant period was based upon interacting response functions and exchange-correlation kernels for the calculation of ground-state properties. The research proposed for the next grant period is based upon similar ingredients for time-dependent phenomena and excited-state energies.

An accurate theoretical treatment of the charge-transfer (CT) process has always raised difficulties. Time- dependent density functional theory (TDDFT) offers an efficient procedure to compute optical properties for large systems, but fails to yield accurate CT excitation energies. Alternatively, one can always resort to many-body techniques, at the price of computational complexity. Many-body treatment or at least some exact exchange mixing in semilocal density functionals can to some extent solve the failure of TDDFT for CT excitations.

TDDFT inherits the self-interaction error (SIE) from ground-state DFT. Due to the SIE and the derivative discontinuity, the CT excitation energies remain too low within TDDFT. Self-interaction corrections (SIC's) have been known for a long time within ground-state DFT. Some of these SIC schemes are accurate enough to describe stretched systems. A significant requirement of SIC is the localization of the orbitals, as required by size-consistency. But the localization procedure can make SIC computationally infeasible for large systems. In 2014, Pederson and collaborators recommended a computationally much more attractive version of the earlier Perdew-Zunger (PZ) SIC. This SIC utilizes Fermi orbitals, greatly restricting the number of possible unitary transformations of the occupied Kohn-Sham orbitals. The result of this specific construction of the localized orbitals is a computationally feasible SIC for the ground state energy.

Within this proposal the PI offers an extension of this scheme toward excited systems within the linear response region of TDDFT. The proposal is a straightforward continuation of the Fermi orbital PZ-SIC to a self-consistent version with a model potential. This step provides a simplified OEP scheme with an accurate Kohn-Sham potential. The next step extends the SIC to TDDFT with a one-electron self-interaction free model kernel to treat exchange-correlation effects. The proposed method will be extensively tested and applied to various CT problems such as polymer-fullerene donor-acceptor systems.

Molecular Theory and Modeling

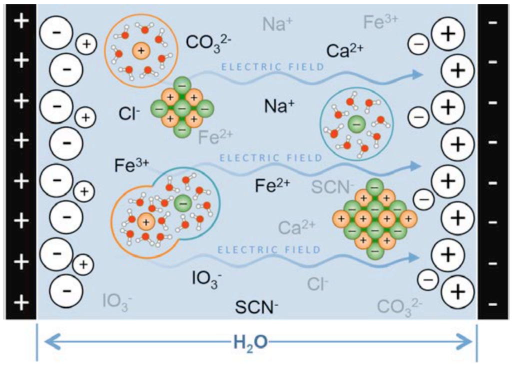
Gregory K. Schenter, Liem X. Dang, Shawn M. Kathmann, Chris J. Mundy, Sotiris S. Xantheas, and Marat Valiev

Pacific Northwest National Laboratory
PO Box 999

Richland WA 99352

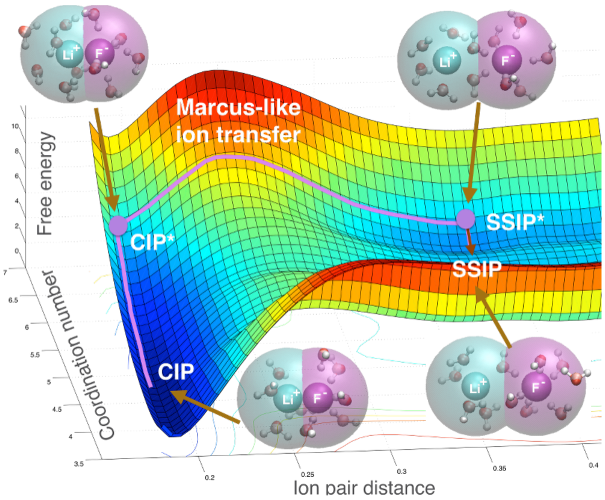
Abstract

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



In current work, 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. We have established that a Density Functional Theory (DFT) description of molecular interaction provides a quantitative representation of the short-range interaction and structure when compared to Extended X-ray Absorption Fine Structure (EXAFS) measurements. To do this we continue to develop our MD-EXAFS approach. [1] This direct comparison to experimental measurement gives us the confidence that the short range molecular phenomena are effectively and accurately described by DFT electronic structure coupled to statistical mechanical sampling. Much of our future efforts will concentrate on characterizing fluctuations, taking advantage of effective potentials of mean force and linear response kernels from density, charge and electromagnetic fluctuations.

In Ref. [5] we explored the dynamics of Li^+ - F^- ion pairing in aqueous solvent, focusing on the transition from a contact ion-pair to a solvent separated ion pair. We constructed a generalized Langevin equation framework to compare DFT and empirical potential descriptions of molecular interaction. A key result of this study was the identification of high frequency coupling associated with "geometrically-frustrated charge pairing" that occurs in the empirical potential but not in the DFT description of molecular interaction. In Ref. [4] we explored the use of the coordination number as a reaction coordinate to describe water exchange rates about solvated ions. We developed a consistent transition state theory (TST) in this coordinate. This allows us to more effectively characterize the important collective motions that lead to the rare event processes. Currently we are considering the two-dimension potential of mean force consisting of both distance based reaction coordinates (distance between ions)



and coordination number. [See Figure] We are exploring how this energy landscape changes with the nature of the ions and the controlling factors that determine the transition thermodynamics and rates between the contact ion pair (CIP) and the solvent separated ion pair (SSIP). In doing so, we discovered a natural separation of motions. First involves restructuring of the solvent environment, characterized by the coordination number reaction coordinate. Next, the final stage of motion corresponds to ion separation. This separation of motions has allowed us to construct a "Marcus Theory of Ion-Pairing" [Santanu Roy], involving parabolic free energies and inverted regions of behavior.

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

Publications Acknowledging this Grant

Publications of GK Schenter. For other Molecular Theory and Modeling efforts, see contributions from Chris Mundy, Marat Valiev and Sotiris Xantheas in this Abstract book.

1. Schenter GK, and JL Fulton. 2017. "Molecular Dynamics Simulations and XAFS (MD-XAFS)." Chapter 18 in *XAFS Techniques for Catalysts, Nanomaterials, and Surfaces*, ed. Y Iwasawa, K Asakura and M Tada, pp. 251-270. Springer International Publishing, Cham, Switzerland. doi:10.1007/978-3-319-43866-5_18
2. Galib M, MD Baer, LB Skinner, CJ Mundy, T Huthwelker, GK Schenter, CJ Benmore, N Govind, and JL Fulton. 2017. "Revisiting the hydration structure of aqueous Na^+." *Journal of Chemical Physics* 146(8):084504. doi:10.1063/1.4975608
3. Dang LX, and GK Schenter. 2016. "Solvent Exchange in Liquid Methanol and Rate Theory." *Chemical Physics Letters* 643:142-148. doi:10.1016/j.cplett.2015.10.045
4. Roy S, MD Baer, CJ Mundy, and GK Schenter. 2016. "Reaction Rate Theory in Coordination Number Space: An Application to Ion Solvation." *Journal of Physical Chemistry C* 120(14):7597-7605. doi:10.1021/acs.jpcc.6b00443
5. Pluharova E, MD Baer, GK Schenter, P Jungwirth, and CJ Mundy. 2016. "Dependence of the rate of LiF ion pairing on the description of molecular interaction." *Journal of Physical Chemistry B* 120(8):1749-1758. doi:10.1021/acs.jpcb.5b09344
6. Skinner LB, M Galib, JL Fulton, CJ Mundy, JB Parise, VT Pham, GK Schenter, and CJ Benmore. 2016. "The structure of liquid water up to 360 MPa from x-ray diffraction measurements using a high Q-range and from molecular simulation ." *Journal of Chemical Physics* 144(13):134504. doi:10.1063/1.4944935
7. Chun J, CJ Mundy, and GK Schenter. 2015. "The Role of Solvent Heterogeneity in Determining the Dispersion Interaction Between Nanoassemblies ." *Journal of Physical Chemistry B* 119(18):5873-5881. doi:10.1021/jp512550c

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

Mary Van Vleet, Tingting Weng, Xinyi Li, Jesse G. McDaniel, J.R. Schmidt

Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison,

1101 University Ave, Madison, WI 53706

Abstract

Metal-organic frameworks (MOFs) represent an incredibly diverse class of materials with equally diverse applications in catalysis, separations, and gas storage. Tremendous amounts of human effort have been dedicated to the synthesis and characterization of various functionalized MOF structures with the aim of designing and realizing tailored / optimized materials for specific applications. 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. Successful syntheses often require a delicate balance of reaction conditions (temperature, reactant concentrations, solvent / solvent mixtures…), typically discovered empirically by time consuming screenings over reaction conditions. Our present work aims to enable targeted MOF synthesis by developing a comprehensive and predictive models of the fundamental processes occurring at the MOF-solution interface under synthetically-relevant conditions, including MOF interfacial structure and stability, crystal growth, nucleation, and post-synthetic modification. Modeling MOF nucleation and growth requires overcoming a number of challenges, including (i) development of simulation approaches for modeling the nucleation of low-solubility crystals; (ii) development of MOF intra-molecular force fields that capture the correct relative stability of various crystalline/amorphous phases; and (iii) accurate force fields for the MOF-solvent interaction. We are making rapid recent progress in each of these areas.

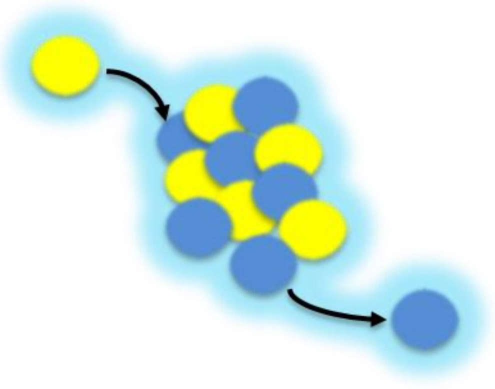


Figure 1. Schematic illustration of GCMC-based particle growth in explicit solvent. Cations/ions can be inserted or deleted based on their bulk concentration/chemical potential.

Nucleation of low-solubility crystals. Simulations of the nucleation of low-solubility crystals represents an important challenge in our understanding of the growth of many important crystalline materials (e.g. $CaCO_3$, oxalates, MOFs). Existing simulation methodologies are either infeasibly slow (due to system sizes necessary for simulating reasonable supersaturation, and diffusive mass transport) or incapable of modeling the *thermodynamics* of growth (e.g. ad hoc "grafting" based methods). 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. Briefly, we utilize particle addition/deletion moves to the growing crystal nucleus while carefully maintaining detailed balance. Such a framework allows us to rigorously estimate the equilibrium particle size distribution (and thus nucleation free energy barrier) as a function of synthetically controllable parameters. The presence of explicit solvent (which is essential for the stability of porous materials during nucleation) presents a number of additional challenges. As such, we have also implemented an expanded ensemble

GCMC (EE-GCMC) approach in conjunction with GPU acceleration that yields orders-of-magnitude increase in computational efficiency. We are currently testing this novel methodology on simple low-solubility crystals (NaF) prior to applications to MOFs and other materials of significant interest (e.g. $CaCO_3$).

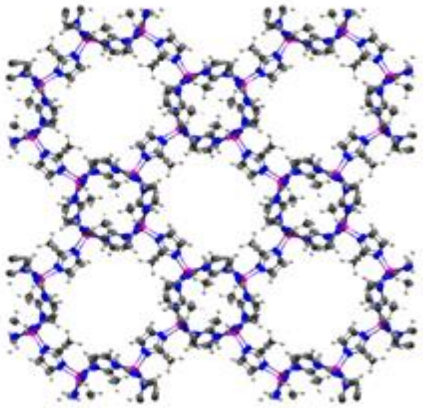


Figure 2. Comparison of DFT-calculated structure (grey) with that of ZIF force fields (colored).

*Force fields for Zeolitic Imidazolate Frameworks (ZIFs).*We are initially focusing on ZIF nucleation and growth. Since ZIFs can be synthesized into a variety of topologies (for a single chemical composition), it is crucial to utilize 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. These classical force fields are parameterized against dispersion-corrected DFT, which itself is in good agreement with experimentally measured ZIF structures. An example of the characteristic force field quality is shown in Figure 2, which shows an overlay of the force field- and DFT-calculated ZIF geometries. We have developed models consistent with our own symmetry-adapted perturbation theory (SAPT) inter-molecular force fields, as well as with "standard" Generalized Amber force fields. As such, the resulting force fields should be of widespread interest and applicability for ZIF simulations.

Accurate force fields for MOF-solvent interactions. We have also continued development of methodologies for generating accurate first-principles *inter*-molecular force fields, which is of widespread fundamental interest, including for the development of accurate MOF-solvent interactions. Our approach uses the SAPT energy decomposition to parametrize force fields on a term-by-term basis, thus yielding high accuracy and transferability. Recent advances include: (i) the development of an Iterated Stockholder Analysis-based approach for estimating exchange interaction parameters; (ii) development of a novel functional form to far more accurately describe short-range exchange repulsion and other density-overlap mediated terms (e.g. electrostatic charge penetration). The combination of these two advances in our Slater-ISA type force fields yielded an impressive (~x2) reduction in the characteristic errors for a large test case of fitted intermolecular interactions, and corresponding improvements in the accuracy and robustness of the resulting force and

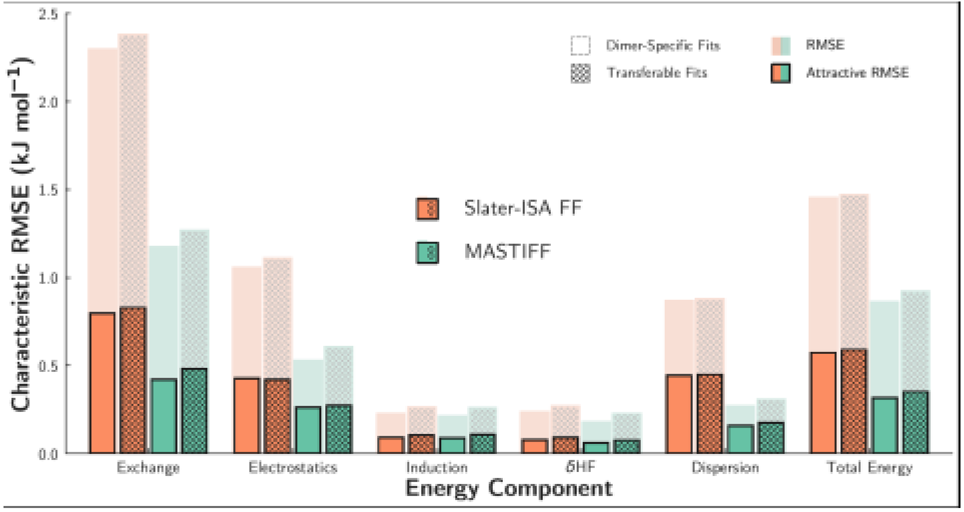


Figure 3. Comparison of isotropic Slater-ISA and simple anisotropic MASITFF models. The latter yields significant decreases in the characteristic errors, at minimal additional computational expense.

calculated bulk properties. More recently, we have extended this approach to incorporate the influence of "atomic anisotropy", which is essential for an accurate treatment of molecules containing "lone pairs" or π electrons. The resulting "MASTIFF" model yields an additional factor of ~x2 error reduction, while maintain conceptual simplicity and high computational efficiency (see Figure 3).

Grant Numbers and Grant Titles

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

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

Student(s):

- Mary Van Vleet (Partial support: NSF Graduate Fellowship)
- Tingting Weng
- Xinyi Li
- Dr. Jesse G. McDaniel

Recent Publications

1. Van Vleet, M. J.; Misquitta, A. J.; Stone, A. J.; Schmidt, J. R., Beyond Born–Mayer: Improved Models for Short-Range Repulsion in ab Initio Force Fields. *J. Chem. Theory Comput.* **2016,** 12, 3851-3870.
2. Son, C. Y.; McDaniel, J. G.; Schmidt, J. R.; Cui, Q.; Yethiraj, A., First Principles United Atom Force Field for the Ionic Liquid [BMIM][BF_4] : An Alternative to Charge Scaling. *J. Phys. Chem. B* **2016**.
3. McDaniel, J. G.; Schmidt, J. R., Next-Generation Force Fields from Symmetry-Adapted Perturbation Theory. *Annu. Rev. Phys. Chem.* **2016,** 67, 467-88.
4. McDaniel, J. G.; Choi, E.; Son, C.-Y.; Schmidt, J. R.; Yethiraj, A., Conformational and Dynamic Properties of Poly(ethylene oxide) in an Ionic Liquid: Development and Implementation of a First-Principles Force Field. *J. Phys. Chem. B* **2016,** 120, 231-243.
5. McDaniel, J. G.; Choi, E.; Son, C. Y.; Schmidt, J. R.; Yethiraj, A., Ab Initio Force Fields for Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2016,** 120, 7024-7036.
6. Schmidt, J. R.; Yu, K.; McDaniel, J. G., Transferable Next-Generation Force Fields from Simple Liquids to Complex Materials. *Acc. Chem. Res.* **2015,** 48, 548-556.
7. McDaniel, J. G.; Li, S.; Tylianakis, E.; Snurr, R. Q.; Schmidt, J. R., Evaluation of Force Field Performance for High-Throughput Screening of Gas Uptake in Metal–Organic Frameworks. *J. Phys. Chem. C* **2015,** 119, 3143-3152.
8. McDaniel, J. G.; Choi, E.; Son, C.-Y.; Schmidt, J. R.; Yethiraj, A., Conformational and Dynamic Properties of Poly(ethylene oxide) in an Ionic Liquid: Development and Implementation of a First-Principles Force Field. *J. Phys. Chem. B* **2015**.
9. FitzGerald, S. A.; Schloss, J. M.; Pierce, C. J.; Thompson, B.; Rowsell, J. L. C.; Yu, K.; Schmidt, J. R., Insights into the Anomalous Vibrational Frequency Shifts of CO2 Adsorbed to Metal Sites in Microporous Frameworks. *J. Phys. Chem. C* **2015,** 119, 5293-5300.
10. McDaniel, J.; Schmidt, J. R., First-principles many-body force fields from the gas-phase to the liquid: A "universal" approach. *J. Phys. Chem. B.* **2014,** 118, 8042-8053.
11. Choi, E.; McDaniel, J.; Schmidt, J. R.; Yethiraj, A., First-Principles, Physically Motivated Force Field for the Ionic Liquid [BMIM][BF4]. *J. Phys. Chem. Lett.* **2014,** 5, 2670–2674.

Advanced Molecular Electronic Structure Methods for Exciton and Spin Dynamics

Toru Shiozaki
Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208
shiozaki@northwestern.edu

Program Scope and Definition: The goal of our research program is to develop new accurate electronic structure methods to treat exciton dynamics in organic semiconductors and strongly correlated spin structures in inorganic complexes. The relevant electronic structures involved in these processes are often described using so-called (quasi)diabatic model Hamiltonians. The site energies are obtained from the diagonal elements of the model Hamiltonians, and the off-diagonal elements (together with bath parameters) are used to determine the rate of the dynamics. However, most of the methods in quantum chemistry are tailored to computing the adiabatic states. In this research, we aim to establish our new methodology, called the **active space decomposition** (ASD) method, that enables the computation from first principles of model Hamiltonians for exciton and spin dynamics. This research will bring together advanced concepts in quantum chemistry, condensed matter physics, and energy sciences. All of the computer programs are implemented in the BAGEL package and are available to the public under the GNU General Public License.

Recent Progress: Active Space Decomposition: During the previous funding period, we have developed so-called active space decomposition (ASD) methods. ASD is an efficient active-space solver applicable to problems that are intractable using conventional active FCI approaches. The wave functions are decomposed in our ASD method using molecular geometries as $\Psi = \sum_{IJ} C^{IJ} \Phi_I^A \Phi_J^B$. It has been shown that the Hamiltonian matrix elements between the product basis $\Phi_I^A \Phi_J^B$ can be efficiently computed using a technique similar to the approach taken in density matrix renormalization group (DMRG). This decomposition of the wave function can be thought of as a singular value decomposition (SVD) of the total wave function. Additionally, it has been numerically demonstrated that the rank of SVD is small when the subsystems A and B are chosen based on molecular geometries (or based on chemical intuition).

Furthermore, we have shown that these product basis functions are related to the diabatic picture, since each of the product basis functions have well-defined local quantum numbers. Therefore, the model Hamiltonians for exciton and charge dynamics can be easily extracted by diagonalizing each diagonal block of the dimer Hamiltonian and retaining only the low-energy part. Furthermore, this ansatz has been extended to multiple active subspaces using the DMRG algorithm, demonstrating the relationship between ASD and tensor-network states. Note that ASD-based model Hamiltonians for singlet fission processes in pentacene and tetracene crystals have been used as reference data by other computational chemists studying these processes.

Finally, we are exploring the inverse problem of the theory described above. The ASD method utilizes the chemical picture to compress the wave function. Is it possible to do the reverse: to optimize the compression to derive the chemical picture? To date we have shown that for continuous variables (e.g., orbital rotations and configuration interaction coefficients) this appears to be the case and the optimization of wave functions does lead to chemically interpretable pictures. On the other hand, the optimization of integer parameters (such as the number of active orbitals in each subspace) is more challenging, and will be investigated in the coming funding period.

Recent Progress: Analytic Nuclear Energy Gradients for CASPT2. In order to understand photodynamics, the important nuclear degrees of freedom, those that are strongly coupled to the electronic degrees of freedom, must be identified. Toward this end, one often locates conical intersection seams on the potential energy surface. This requires computing the nuclear energy gradients and the derivative coupling using the underlying electronic structure theories. In the previous funding period, we developed nuclear energy gradients for CASPT2 for the first time; moreover, the code can also calculate CASPT2 derivative couplings. The program is efficient: the computational cost of calculating nuclear energy gradients is a few times that of the energy evaluation.

Program development: Supported by this funding, we have developed the software infrastructure within the BAGEL package, as well as the automatic code generator SMITH3. Both BAGEL and SMITH3 are licensed under the GNU General Public License Version 3+. All of the ASD programs are implemented in the BAGEL program, which is available at http://www.nubakery.org and can be freely downloaded by end users and theory developers.

On-going efforts: The ASD-DMRG method is currently being extended to higher-dimensional tensor networks (beyond one dimension). Under the support by this grant, the fermionic PEPS solver for finite Hubbard models has been implemented, which itself is an important contribution in condensed matter physics (unpublished). The combination of the new PEPS solver with the ASD machinery should be completed in the near future. We are also developing a new algorithm to define the ASD subspaces in a manner that allows ASD to be applied to the spin structures of multi-nuclear transition metal complexes. The applications of this work will include the spin structures of porous magnets. Another important challenge is to include dynamical correlation in ASD methods.

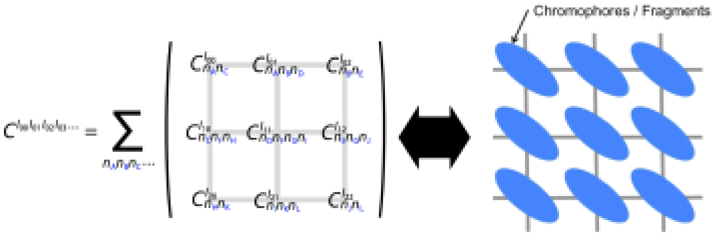


Figure 1: Graphical representation of the PEPS wave function for two-dimensional network of chromophores.

Grant Number and Grant Title

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

Postdoc(s) currently supported: n/a
Student(s) currently supported: Jheng-Wei Li, Yiqun Wang

Publications Acknowledging these Grant:

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

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Advanced Molecular Electronic Structure Methods for Exciton and Spin Dynamics

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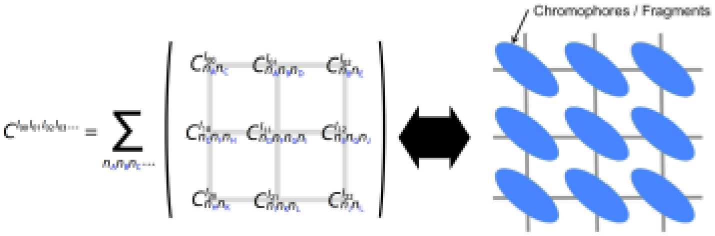

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Molecular Level Understanding of Solvation Processes

Marat Valiev

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P. O. Box 999,
Richland, Washington 993521

Abstract

The main focus of our project is to provide fundamental molecular level understanding of solvation processes that take place in clusters, interfacial and bulk systems. This is accomplished by using advanced ab-initio simulation methods performed in close collaboration with experimental spectroscopy measurements. Our main objective is to identify common mechanisms and collective variables that account for electronic structure information and go beyond simple classical models. At the same time we would like to retain simple physically motivated driven description to allow insight into the overall behavior and properties of the complex solution system.

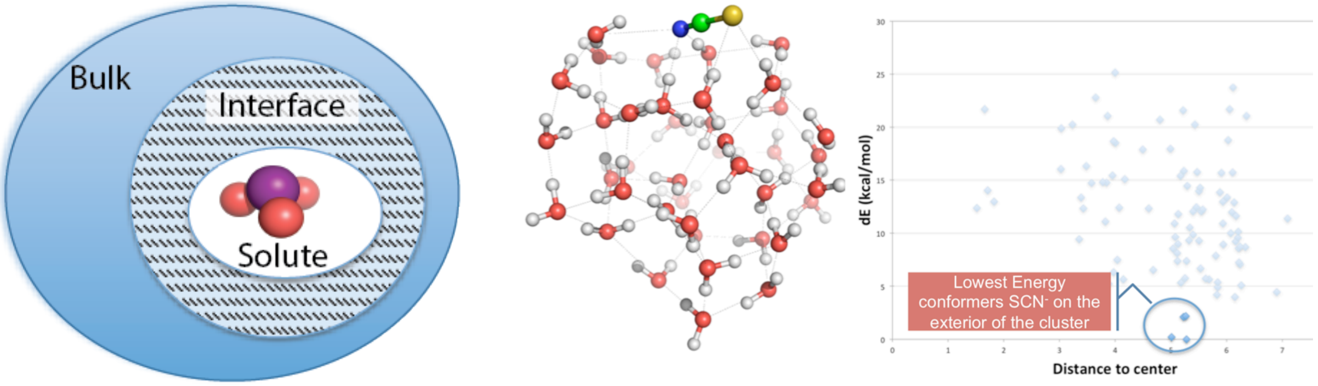

Figure 1: Solvation process as interaction between solute, interface, and bulk components (left); Evidence for surface solvation of SCN- from large cluster systems(right)

The underlying model that guides and defines our research activities is the view on solvation process as an interaction between three distinct components or subsystems - solute, interfacial region, and bulk phase (see Figure 1). Each of the components plays its own role in the solvation process and has unique requirements for its description. We believe such view provides good starting point to manage the inevitable complexity of our theoretical description.

For example, in the analysis solute part of the system we place a heavy emphasis on high-level electronic structure calculations. Solute, almost by construction, contains the least understood part of the system that often undergoes reactive changes, and whose description is particularly important to capture at highest levels to fidelity to insure reliable comparative analysis within a given class of solutes. The key component of our research efforts in this area is collaboration with experimental photoelectron spectroscopy efforts of Xuebin Wang’s group at PNNL. Photoelectron spectroscopy provides a sensitive probe into electronic properties of the molecules and naturally integrates with ab-initio simulations as a required means to analyze and interpret the data. Our recent work in this area includes investigation of iodine sulfur oxide compounds, long chain dicarboxylate molecules, and pinonic anion systems.

Photoelectron spectroscopy also provides an excellent tool for the analysis of probing local solvation environment. Through the analysis of increasingly larger solvated clusters with a specific solute, we gain insight into properties of interfacial region and its impact on the overall solvation process. For example, such application in the case of SCN- solute allowed us to gain unique insight into chaotropic nature of this system. Following our initial results on small solvated clusters (up to 12 waters), we are now investigating large systems containing up to 40 water molecules (see Figure 1). To expedite the search for lowest energy conformers, our calculations utilize quantum-mechanical molecular mechanics (QM/MM) module that we implemented in NWChem computational chemistry package. The new version allows the use of AMBER molecular dynamics code and have been successfully applied to the analysis of excited state properties of green fluorescent chromophore.

QM/MM based methods can also be used to study properties of the bulk component in the solvation process, as we have done in the past. However, our ongoing efforts in this areas are now concentrated on developing coarse-grained models using classical density-functional approaches as underlying framework. Our current focus is on developing systematic theoretical approach using effective field theory. Using molecular liquids as a main target system we are developing a framework that can merge strong local interactions with weak long-range interactions.

Acknowledgement

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Project Publications: (2016-present)

Valiev, M.; Deng, S. H. M.; Wang, X. B., How Anion Chaotrope Changes the Local Structure of Water: Insights from Photoelectron Spectroscopy and Theoretical Modeling of SCN- Water Clusters. *J Phys Chem B* **2016,** *120* (8), 1518-1525.

Hou, G. L.; Valiev, M.; Wang, X. B., Deprotonated Dicarboxylic Acid Homodimers: Hydrogen Bonds and Atmospheric Implications. *J Phys Chem A* **2016,** *120* (15), 2342-2349.

Qin, Z. B.; Hou, G. L.; Yang, Z.; Valiev, M.; Wang, X. B., Negative ion photoelectron spectra of ISO3-, IS2O3-, and IS2O4- intermediates formed in interfacial reactions of ozone and iodide/sulfite aqueous microdroplets. *J Chem Phys* **2016,** *145* (21).

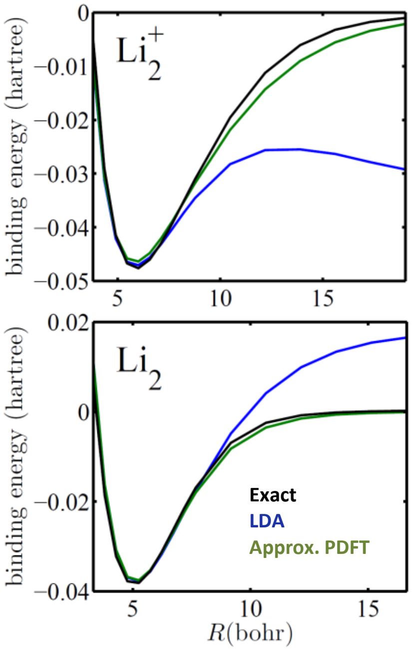
T. Pirojsirikul, M. Valiev, A. W. Götz, J. Weare, R. Walker, K. Kowalski,
Combined Quantum-Mechanical Molecular Mechanics Calculations with NWChem and AMBER: Excited State Properties of Green Fluorescent Protein Chromophore Analogue in Aqueous Solution. Journal of Computational Chemistry, (in press), **2017** DOI:10.1002/jcc.24804

Hou, G.-L.; Zhang, J.; Valiev, M.; Wang, X.-B., Structures and energetics of hydrated deprotonated cis-pinonic acid anion clusters and their atmospheric relevance. Physical Chemistry Chemical Physics, **2017**.

Partition Energy Functionals: Theory and Applications

Adam Wasserman[*]
Department of Chemistry
Purdue University
560 Oval Dr.,West Lafayette, IN 47907
[*]awasser@purdue.edu

Program scope: The main objective of this project is to improve the accuracy and efficiency of density-based fragmentation methods for the calculation of ground-state molecular properties. We are developing Partition Density Functional Theory (PDFT) and working toward linear-scaling implementations based on physically-motivated approximations to the partition energy functional. We will apply the new methods to systems of increasing complexity where calculations are presently not feasible, such as those needed to elucidate the molecular interactions at the interface between ionic liquids and nano-porous carbon materials in electrochemical capacitors.



Recent progress: **(1)** ***Benchmark calculations*****:** We carried out benchmark PDFT calculations on homonuclear diatomic molecules. We derived various exact conditions that guide the construction of approximate partition potentials, established the connection between charge-transfer and electronegativity equalization between fragments, and tested alternative ways for dealing with fractional charges and spins within PDFT. We also calculated extremely accurate non-additive non-interacting kinetic energies of covalently-bonded diatomic molecules to use as reference data for the construction of approximate partition energy functionals; **(2)** ***Correct description of bond breaking:*** We have demonstrated how PDFT fixes the delocalization and static-correlation errors that plague density-functional calculations of stretched molecules. For example, the figure shows the cases of stretched Li_2 and Li_2^+. No existing approximation to the XC-functional yields both of these correctly within standard KS-DFT. The local-density approximation (LDA, in blue) underestimates the binding energy of the ion due to delocalization error and overestimates it in the neutral dimer due to static-correlation. PDFT (in green), with a simple overlap approximation for the partition energy and LDA for the fragments, almost entirely corrects both. We have explained why, emphasizing the importance of the ensemble treatment of fragment energies*;* **(3)** ***Partitioning the current density:*** We showed the existence of one-to-one mappings between the total current density of a molecule, a sharply-defined set of fragment current densities, and an auxiliary vector-scalar partition-potential pair. Thus, regarding a molecule as a set of non-interacting subsystems that individually evolve under the influence of the corresponding partition potential, PDFT can be generalized to use the fragment current densities as the main variables. We proved the zero-force theorem for the fragmented systems, established a variational formulation in terms of action functionals, and worked out in detail a simple example for a charged particle in a ring; **(4)** ***Initial applications and error analysis:*** We analyzed how various approximate functionals and charge-distribution schemes describe ground-state atomic-charge distributions in a model system of relevance to carbon-based super-capacitors. Among other findings, we observed that for semilocal functionals, natural-bond orbital and Mulliken schemes yield opposite pictures of how charge transfer occurs. Our initial implementation into *NWChem* was tested on small water clusters. We analyzed the errors of our PDFT calculations to distinguish between errors in approximate functionals versus errors in the self-consistent density, yielding insight into the origins of many errors, especially those often attributed to self-interaction or delocalization.

Future plans: In the next 3 years we will continue developing physically-motivated approximations for both the exchange-correlation and the kinetic contributions to the partition energy of PDFT; *Q*-functions measuring how fragment densities respond to changes in the total molecular density will be systematically studied, leading to new algorithms for efficiently solving the PDFT equations; the conditions will be determined under which charge transfer between fragments leads to fractional electronic occupations. In parallel with these formal developments, a robust implementation of PDFT will be completed in the embedded-Quantum ESPRESSO program (in collaboration with M. Pavanello) and applied to systems of increasing complexity. The practical goal is to calculate the permittivity of confined ionic liquids as a function of pore-size distributions of carbon-based electrodes, which is critical in determining the overall capacitance of these materials.

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Students:

Kaili Jiang, Martin Mosquera, Jonathan Nafziger.

Publications Acknowledging this Grant in 2014-2017:

(1) A. Wasserman, J. Nafziger, K. Jiang, M.C. Kim, E. Sim, and K. Burke, “*The importance of being inconsistent”*, Annu. Rev. Phys. Chem. DOI:10.1146/annurev-physchem-052516-044957, *in press* (2017).

(2) J. Nafziger, K. Jiang, and A. Wasserman, “*Accurate Reference Data for the Non-Additive Non-Interacting Kinetic Energy in Covalent Bonds*”, J. Chem. Theory Comput. **13**, 577 (2017).

(3) S. Gomez, J. Nafziger, A. Restrepo, and A. Wasserman, “*Partition-DFT on the water dimer*”, J. Chem. Phys. **146**, 074106 (2017).

(4) C.H. Borca, L.V. Slipchenko, and A. Wasserman, “*Ground-state Charge Transfer: Lithium-Benzene and the Role of Hartree-Fock Exchange*”, J. Phys. Chem. A **120**, 8190 (2016).

(5) J. Nafziger and A. Wasserman, “*Fragment-based treatment of delocalization and static-correlation errors in density functional theory*”, J. Chem. Phys. **143**, 234105 (2015).

(6) J. Nafziger and A. Wasserman, “*Density-based Partitioning Methods for Ground-State Molecular Calculations*”, J. Phys. Chem. A **118**, 7623 (2014).

(7) M. Mosquera and A. Wasserman, “*Integer Discontinuity in Density Functional Theory*”, Phys. Rev. A **89**, 052506 (2014).

(8) M. Mosquera and A. Wasserman, “*Current Density Partitioning in Time-dependent Current Density Functional Theory*”, J. Chem. Phys. **140**, 18A525 (2014).

(9) P. Elliott, D. Jensen, A. Wasserman, and K. Burke, “*Comment: Application of Partition Density Functional Theory to One-dimensional Models*”, Phys. Rev. A **89**, 026501 (2014).

Intermolecular Interactions in the Gas and the Condensed Phases

Sotiris S. Xantheas

Pacific Northwest National Laboratory, PO Box 999, MS K1-83, Richland WA 99352
sotiris.xantheas@pnnl.gov

Abstract

The overarching themes of this research component of the Molecular Theory & Modeling Program are:

- establish accurate benchmarks for archetypal intermolecular interactions, aqueous clusters and guest – host interactions relevant to energy applications,
- incorporate the appropriate physics into models (classical or quantum) that explicitly account for the desired behavior,
- elucidate the molecular level factors that control complex behavior,
- understand the interplay between the molecular level information and the macroscopic properties of complex aqueous environments.

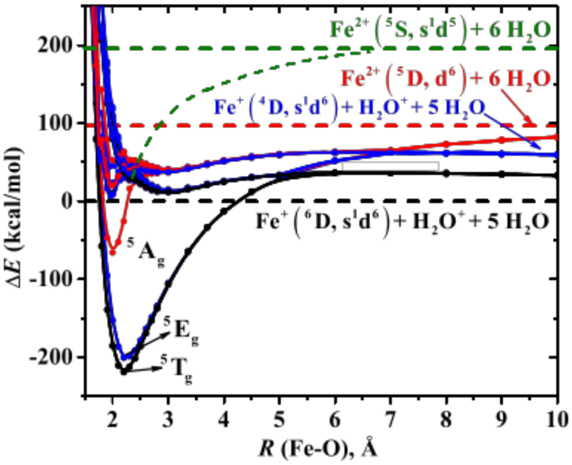
The ultimate goal of the program is *to develop accurate descriptions of intermolecular interactions for complex environments that include molecular level detail*.

In current work, we have focused on the aqueous solvation of multi-valent metal ions by explicitly considering the low-lying electronic states and the reaction channels leading to water hydrolysis that they induce. These channels arise from the fact that the second ionization potential (I.P.) of most metals is larger than the ionization potential of water (12.62 eV). In particular, we considered the various electronic states arising from the sequential hydration of the Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+} and Fe^{3+} ions with up to six water molecules. Our results offer insight into the shifting of electronic states and dissociation asymptotes with the degree of solvation, identify their complex interaction with other states arising from different dissociation channels, and shed light on the mechanism behind the energetic stabilization of the multi-charged hydrated $M^{+q}(H_2O)_n$ moieties observed in solution with respect to the water ionization products. A critical number of water molecules is necessary to create a stable $M^{+k}(H_2O)_n$ complex; for Mg this number is at least two, while for Al at least four.

A more complex system (see Figure) deals with the ground and low-lying electronically excited states of the $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ clusters as well as their aggregate. Both the second and third ionization potentials of Fe are larger than the one for water, so the ground-state products asymptotically correlate with dissociation channels that are repulsive in nature at large separations containing at least one H_2O^+ fragment and a single positively charged structures emanate from the channels consisting of the lowest electronic states of Fe^{2+} (^{5}D; 3d^6) or Fe^{3+} (^{6}S; 3d^5) and six neutral water molecules. Upon hydration, the ground state of $Fe^{2+}(H_2O)_6$ is a triply (^5T_g) degenerate state, with the doubly (^5E_g) degenerate state lying ~20 kcal/mol higher in energy, while the $[Fe(H_2O)_6]^{3+}$ cluster has a ground state of ^6A_g symmetry under T_h symmetry, which is well separated from the first excited state. Regarding their gas-phase interaction, for R(Fe-Fe) < 6.0 Å, the water molecules in the respective first solvation shells located between the two

metal centers were found to interact via weak hydrogen bonds. We examined a total of 10 electronic states for this complex, including those corresponding to the electron transfer (ET) channel. A possible path via a quasi-symmetric transition state is suggested.

In future work we will investigate the interactions associated with the process of CO_2/CH_4 exchange in a hydrate lattice, as well as the barrier and molecular mechanism corresponding to the diffusion of the guest species from one cage to the neighboring one. The latter must occur via the temporary breaking and reforming of hydrogen bonds in the lattice. We will attempt the first CCSD(T) calculation for the interaction of H_2, N_2, CH_4, and CO_2 inside hollow $(H_2O)_{20}$ and $(H_2O)_{24}$ cages with a triple zeta quality set. Preliminary calculations at the MP2 and B3LYP+D levels will be performed. It should be remembered that at the DFT level the guest [H_2, CH_4] + host [$(H_2O)_{20}$] system lies *above* the asymptote of the empty cage + the gas-phase molecule, whereas at the MP2 or CCSD(T) level it lies *below* the asymptote, i.e., it is more stable than the two isolated fragments. This finding further justifies the necessity of using high-level electronic structure calculations in order to quantify the relevant interactions in those systems. Additional calculations for the accommodation of CO_2 and CH_4 inside the small and large cages of the structure I (sI) hydrate lattice will focus on understanding their exchange mechanism between adjacent cages in the hydrate lattice by computing the barrier for that exchange between adjacent cages in the lattice.



Potential energy curves of the quintet electronic states of $[Fe(H_2O_6)]^{2+}$. Different colors correspond to different adiabatic fragments. The dashed green line traces the expected diabatic curve for the ^5A_g state.

Furthermore, we will extend our previous studies of weak π-π interactions in an attempt to establish an accurate interaction energy for the Coronene dimer, a polyaromatic hydrocarbon (PAH) with 7 perifused benzene rings that has been used as a molecular model for the interactions between graphene sheets, at the MP2 and CCSD(T) levels of theory. Due to the technological applications of the electrical properties of grapheme sheets and associated carbon-based functionalized nanomaterials, the magnitude of the interaction in the Coronene dimer has recently received a lot of attention. Most calculations have been performed to date using various density functionals, the accuracy of which is difficult to assess, since an accurate benchmark is currently not available. Following the same protocol we have established earlier for the benzene dimer, we expect that CCSD(T) single-point energy calculations with the cc- pVDZ and cc-pVTZ basis sets (1,775 basis functions) will provide an accurate binding energy for the Coronene dimer.

We will finally extend our work on weak intermolecular interactions to the C_{60} dimers and trimers. To date, the interaction between two C_{60} molecules as well as the simulation of their phase diagram has been reported using either classical potentials or various Density Functional Theory approaches and their variants. We will compute the interaction between two and three carbon nanoparticles up to C_{60} at the MP2 and CCSD(T) levels of theory in order to obtain accurate dimer potential energy curves as well as the magnitude of the respective 3-body term. Of particular importance is the investigation of the long-range part of the interaction potential and the ability of MP2 to provide accurate $1/R$ behavior when compared to CCSD(T). For this purpose we will also consider corrections to the c_6 coefficient at long range proposed by Head-Gordon. The ab initio potentials will be fitted to the simple PEFs developed during the past award period and will provide accurate pairwise additive and 3-body potentials that can be used to model the aggregation and phase diagram of those carbon nanoparticles. The nature of bonding both in and between those nanoparticles will be investigated using a recent analysis based on molecule-intrinsic quasi-atomic, bonding, and correlating orbitals. Subsequent studies will be extended to the interaction between carbon nanoparticles, starting from C_{24} and extending all the way to C_{60}.

Molecular Theory and Modeling FWP 16249

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

Publications Acknowledging this Grant in the last 2 years

1. J. C. Werhahn, E. Miliordos and S. S. Xantheas, "A new variation of the Buckingham exponential-6 potential with a tunable, singularity-free short-range repulsion and an adjustable long-range attraction", *Chemical Physics Letters* **619**, 133 (2015)
2. E. Miliordos and S. S. Xantheas, "Ground and excited states of the $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ clusters: Insights into the electronic structure of the $[Fe(H_2O)_6]^{2+}$ – $[Fe(H_2O)_6]^{3+}$ complex", *Journal of Chemical Theory and Computation* **11**, 1549 (2015)
3. E. Miliordos and S. S. Xantheas, "An accurate and efficient computational protocol for obtaining the Complete Basis Set (CBS) limits of the binding energies of water clusters at the MP2 and CCSD(T) levels of theory: Application to $(H_2O)_m$, $m = 2 - 6, 8, 11, 16$ and 17", *Journal of Chemical Physics* **142**, 234303 (2015)
4. J. A. Fournier, C. T. Wolke, and M. A. Johnson, T. T. Odbadrakh and K. D. Jordan, S. M. Kathmann and S. S. Xantheas, "Snapshots of Proton Accommodation at a Microscopic Water Surface: Vibrational Spectral Signatures of the Charge Defect in Cryogenically Cooled $H^+(H_2O)_{n=2-28}$ Clusters", Feature Article (invited), *Journal of Physical Chemistry A* **119**, 9425 (2015). Journal cover
5. S. Yoo Willow, X. Cheng Zeng, S. S. Xantheas, K. S. Kim and S. Hirata, "Why is MP2-Water 'Cooler' and 'Denser' than DFT-Water?", *Journal of Physical Chemistry Letters* **7**, 680 (2016)
6. S. Iwata, D. Akase, M. Aida and S. S. Xantheas, "Hydrogen-Bonded Networks in Polyhedral Water Clusters $(H_2O)_n$, $n = 8$, 20 and 24" *Physical Chemistry Chemical Physics* **18**, 19746 (2016)
7. E. Miliordos, E. Aprà and S. S. Xantheas, "A New, Dispersion - Driven Intermolecular Arrangement for the Benzene – Water Octamer Complex: Isomers and Analysis of their Vibrational Spectra", *Journal of Chemical Theory and Computation* **12**, 4004 (2016)
8. S. S. Xantheas, "Spying on the neighbors' pool: Spectral signatures are obtained for the movement of protons in cold water clusters", invited Perspective, *Science* **354**, 1101 (2016)
9. G. E. Douberly, R. E. Miller and S. S. Xantheas, "Formation of Exotic Networks of Water Clusters in Liquid Heium Droplets Facilitated by the Presence of Neon Atoms", *Journal of the American Chemical Society* **139**, 4152 (2017)
10. S. Yoo Willow and S. S. Xantheas, "A Molecular Level Insight of the Effect of Hofmeister Anions on the Interfacial Surface Tension of a Model Protein", *Journal of Physical Chemistry Letters* **8**, 1574 (2017)