

**SETCA 2022 Program**  
**May 19-21<sup>st</sup>, Atlanta GA**

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**Invited Lectures**

**IL1 : Three methods for 'dark' doubly excited states in the Equation-of-Motion  
Coupled-Cluster theory**

Rodney Bartlett  
University of Florida

Doubly excited states have always been more difficult for EOM-CCSD than normal, excited states dominated by single excitations. The average error for those is  $\sim 0.2$  eV with the addition of triples in EOM-CCSD(T) reducing that error by an order of magnitude. But for double excited states, the errors at EOM-CCSD can range from  $\sim 1-6$  eV. Once triple excitations are added, EOM-CCSDT, those errors can be eliminated. But putting in triples is at least an  $\sim m^7$  procedure ( $\sim m^*$  for full triples), while CCSD is only  $\sim m^6$ . This talk will present three ways to address this error at the EOM-CCSD level to provide a seamless treatment of all electronic excited states: (1) intermediate state approach; (2) using simplified CCSD as in 'Distinguished Cluster' theory; and (3) via the pair CCD (pCCD) method that reduces CCD to just pair excitation terms.

**IL2 : Bridging the pressure gap in theoretical models of gas-solid adsorption**

Sharani Roy  
University of Tennessee

Akin to the pressure gap between laboratory surface-science experiments performed under ultrahigh vacuum and industrial surface chemistry conducted under high gas pressures, theoretical models of gas-solid interfacial chemistry are often developed for low gas concentrations yet applied to surface phenomena that occur under high gas concentrations. The primary reason for this discrepancy is the steep cost of computing chemical properties at high surface concentrations (or coverages) of the gas using electronic structure methods. To address this challenge and to study the percolation of gases just beneath the surface, i.e.,

into the subsurface, at high coverages, we have developed lattice-gas adsorption models that include surface as well as subsurface sites in a crystalline solid and are fully parameterized using density functional theory (DFT). We have applied the models to study the adsorption of atomic oxygen on the Ag(111) surface, first as functions of coverage and temperature using canonical Monte Carlo simulations, and next as functions of pressure and temperature using grand-canonical Monte Carlo simulations. The simulations show the conditions under which subsurface adsorption occurs and provide insight into how subsurface adsorbates might participate in catalytic partial oxidation on silver surfaces. The symbiotic relationship between DFT and the lattice-gas model initially helps to develop the model and later helps to compute the electronic differences between surface and subsurface adsorbates using structures predicted by the model. Overall, the lattice-gas adsorption model provides a simple and transferable theoretical framework to explore the competition between surface and subsurface adsorption in gas-surface systems.

### **IL3 : Perturbative density-functional-based approaches for simulating resonant-inelastic x-ray scattering maps in transition-metal complexes**

Daniel Nascimento  
University of Memphis

Resonant inelastic x-ray scattering (RIXS) is a two-photon process that provides valuable information on the electronic structure of molecules and materials that, due to selection rule restrictions, is not easily accessible by one-photon spectroscopies. With the continuing development of light source technologies, RIXS is rapidly becoming an important technique for the study of gas- and solution-phase molecular systems, and the need for reliable yet inexpensive electronic structure methods to aid in the prediction and interpretation of complicated spectral features is becoming apparent. In this talk, I will present simplified approaches based on linear-response time-dependent density functional theory and perturbative treatments of excited-state transition moments and spin-orbit couplings. I will demonstrate that an approach based on linear-response time-dependent density functional theory and the zeroth-order regular approximation, is able to describe the RIXS maps of ruthenium complexes with sufficiently good accuracy without the need to solve expensive quadratic-response or fully relativistic equations.

### **IL4 : Excited-state energy transport under strong light-matter interactions**

Raphael Ribeiro  
Emory University

Molecular polaritons are hybrid quasiparticles emergent from strong interactions between optical microcavities and bright molecular excitations. Recent observations of ultrafast long-range polariton propagation and distance-independent intermolecular energy transfer

in microcavities suggest transport phenomena can be significantly enhanced in these devices despite the presence of considerable energetic disorder in typical molecular materials. However, the operating mechanism and parameters controlling the efficiency and speed of energy transport in polaritonic materials remain unknown especially under usual conditions where the molecular density of states is orders of magnitude greater than the photonic.

In this talk, I will explain the methodology and key results of our recent studies of energy transport in polaritonic wires. Focus will be given to the i) connections of our results to puzzling experimental observations and to ii) the identification of photonic and molecular parameters controlling the efficiency and speed of polariton and weakly coupled molecular excited-state transport in optical cavities. Throughout the talk, we will also reveal several qualitative inadequacies of minimal models of polariton chemistry.

### **IL5 : Molecular Modeling of Ring Polymer Mechanics – Expanding Applicability of Topological Polymer Chemistry**

Ting Ge

University of South Carolina

Recent advances in chemical synthesis have enabled precise control of polymer topology. In the past several decades, non-concatenated ring polymers have received particular interest due to the topology distinctive from that of conventional linear polymers and their derivatives. Although many aspects of the conformation and dynamics of non-concatenated ring polymers have been elucidated, the transformation of the ring polymers into practically useful materials has remained less explored. Using molecular simulations with perfect control of polymer topology, we make elastomers and thermoplastics out of non-concatenated ring polymers and study their mechanical properties in large deformation and failure. The ring elastomers exhibit superior stretchability and softness with respect to their linear counterparts at the same cross-linking density. The ring thermoplastics under tension fail through a mechanism similar to the crazing in their linear counterparts but with a diluted entanglement network. For both ring elastomers and thermoplastics, we develop a microscopic theory to relate the mechanics to the underlying polymer topology and validate the theory using the simulation results. This work demonstrates tuning polymer topology as a pathway to design the mechanics of polymeric materials, creating a new paradigm of topological polymer chemistry entering materials science.

### **IL6 : Computing optimal real-space orbitals for correlated methods**

Edward Valeev

Virginia Tech

Real-space representations are attractive alternatives to the traditional preoptimized atomic orbital (Gaussian, Slater, and numerical) representations due to their ability to converge to the numerical (basis set limit) systematically. Until recently real space representations have been only deployed for 1-particle methods (Hartree-Fock, density functional theory). Here we demonstrate how to compute optimal orbitals for correlated methods using adaptive spectral-element representation first introduced by Harrison and Beylkin. Orbitals are optimized by minimizing the 2-RDM energy lagrangian via an integral (Lippmann-Schwinger) update. Natural orbitals appear as the natural (no pun intended) targets for the optimization due to their unique ability to uncouple the kinematic contributions to the orbital gradient. Surprisingly, even very weakly-occupied natural orbitals (with occupancies of  $1E-6$  or less, thus purely describing dynamical correlation effects) can be computed very robustly. The presented solver is generally applicable not only to atoms (where we find superior convergence relative to existing numerical solvers) but also to general polyatomic molecules.

### **IL7 : Real-time TDDFT Study of Nonadiabatic Thouless Pumping of Electrons**

Yosuke Kanai

University of North Carolina at Chapel Hill

We demonstrate nonadiabatic Thouless pumping of electrons in trans-polyacetylene and related systems in the framework of topological Floquet engineering using first-principles theory. By employing maximally localized Wannier functions in real-time time-dependent density functional theory, we connect the winding number, a topological invariant, to a molecular-level understanding of the quantized pumping. Using a gauge-invariant transformation called dynamical transition orbitals, an alternative viewpoint on the nonequilibrium dynamics is obtained in terms of the particle-hole excitation. The pumping dynamics manifests itself in the dynamics of this single orbital as it undergoes changes from its  $\pi$  bonding orbital character at equilibrium to acquiring resonance and anti-bonding characters in the driving cycle. Floquet engineering of the nonadiabatic topological state in driven systems is demonstrated and future directions are discussed.

### **IL8 : Quantum algorithms for the non-unitary time evolution of quantum systems**

Kade Head-Marsden

Washington University in St. Louis

Open quantum system evolution in the presence of an environment is crucial to understanding and improving many processes including the communication of quantum information and the transfer of energy. Quantum computing platforms have emerged as a promising route to modelling and predicting the behaviour of such systems. However, mapping inherently non-unitary dynamics into the unitary framework of gate-based

quantum algorithms is a challenging task. Here, I will discuss density matrix gate-based quantum algorithms to predict the dynamics of open quantum systems, their applications, and potential extensions.

## IL9 : Spectroscopy in the Condensed Phase: Connecting Theory and Experiments

Samer Gozem  
Georgia State University

UV-visible and photoelectron spectroscopy are powerful tools for probing the structure of matter from the subatomic to the bulk scale. The experimental spectra are generally plotted using two quantities: energies and absorption strengths (the latter typically reported as molar attenuation coefficients or cross sections). Energies and transition strengths could also be predicted from first principles with quantum chemical methods. However, connecting the computed and experimental quantities is not always straightforward, especially for experiments in the condensed phase where the spectra are shifted and broadened by intermolecular interactions. A few examples of this are discussed in the introductory part of the talk.

In UV-visible spectroscopy, experiments provide a plot of wavelength-dependent molar extinction/attenuation coefficients ( $\epsilon$ ). The corresponding electronic structure computations typically provide single-valued excitation energies and oscillator strengths ( $f$ ) for each band.  $\epsilon$  and  $f$  are related, but this relation is complicated by various factors. To make the comparison easier, we derive 164 experimental oscillator strengths from the UV-visible spectra of 100 organic molecules in solution, allowing for a direct comparison of experimental and computed oscillator strengths. The preparation and results of this benchmark study will be presented.

### References

Gozem S, Krylov AI. The ezSpectra suite: An easy-to-use toolkit for spectroscopy modeling. WIREs Comput Mol Sci. 2021, 12, e1546.

DOI: <https://doi.org/10.1002/wcms.1546>

Tarleton AS, Garcia-Alvarez JC, Wynn A, Awbrey CM, Roberts TP, Gozem S. OS100: A Benchmark Set of 100 Digitized UV-Visible Spectra and Derived Experimental Oscillator Strengths.

J. Phys. Chem. A, 2022, 126 (3), 435-443

DOI: [10.1021/acs.jpca.1c08988](https://doi.org/10.1021/acs.jpca.1c08988)

## **IL10 : Coupling of electrostatic preorganization and structural dynamics in enzymes: insights from electric field calculations**

Valerie Welborn  
Virginia Tech

Enzymes remain the most efficient catalysts to date, accelerating reactions in complex environments by several orders of magnitude. Two main protein properties have been attributed to this remarkable catalytic efficiency: electrostatic preorganization of protein structure, including the scaffold, and structural and dynamic heterogeneity. However, these two aspects of enzymatic machinery are often seen as incompatible because, intuitively, permanent electrostatic effects are stronger in stiff, rigid, structures. Here, I will present a series of computational experiments that shows that electrostatic preorganization of proteins and dynamics effects are intimately coupled. We use a metric, electric fields, that can treat electrostatic contributions and dynamics effects on equal footing, for a unique perspective on enzymatic catalysis. I will use the example of Adenylate Kinase, a paradigm in protein flexibility and decouple various time and length scales to reveal the fundamental principles behind enzymatic rate accelerations. I will demonstrate that the residues that contribute the most to strong electrostatic interaction between the protein and the substrate are also the most flexible residues, coupling dynamic allostery to electrostatic preorganization. Detailed analysis of AdK mutants with single entropy-tuning mutations reveals that flexibility is raised at the picosecond timescale where more conformations can be visited on short time periods, softening the sharp heterogeneity normally visible at the microsecond timescale. This work sheds light on the molecular origin of enzymatic catalysis, reconciling two seemingly contradictory experimental observations, with direct application in synthetic enzyme design and rational drug design.

M. M. Lawal and V. Vaissier Welborn, ChemBioChem, 2022, DOI: 10.1002/cbic.202200097

## **IL11 : Systematically improvable first-principles force fields: Case studies on water and benzene**

Mary VanVleet  
Spelman College

Molecular simulation is an essential tool for chemical prediction and analysis, with the caveat that the accuracy of such simulations can only be as good as the quality of the underlying mathematical model (termed force field) used to calculate molecular energies and forces. While traditional force fields have had remarkable success, they also rely heavily on error cancellation and empiricism. Consequently, for systems where these force fields have known issues (such as with mixtures, hydrogen-bonded molecules, and pi interactions), it can be extremely difficult and laborious to make improvements. This talk will introduce MASTIFF (a Multipolar, Anisotropic Slater-Type Intermolecular Force Field), an alternate approach to force field development that eliminates empiricism and greatly

reduces the need for error cancellation. By using first-principles functional forms and gold-standard ab initio calculations, MASTIFF force fields are systematically improvable and can be used transferably across phases and chemical compositions. Water and benzene will be discussed as case studies for how the methodology can accurately treat both hydrogen-bonding systems and pi-pi stacking.

## **IL12 : Modeling excitation energy transfer in photosynthesis with polarizable QM/MM**

Lyudmila Slipchenko  
Purdue University

Photosynthetic pigment-protein complexes in plants and bacteria have been optimized by evolution for reliable capture and conversion of solar energy. However, while general mechanisms of energy flow in photosynthetic complexes are well recognized, mechanistic details of how a particular molecular system controls energy and charge transfer are barely available. Recently we have shown that describing protein environment with the polarizable effective fragment potential (EFP) method provides realistic description of excitonic interactions in one of the most studied photosynthetic systems, the Fenna-Matthews-Olson (FMO) pigment-protein complex. We decompose protein effects on electronic excitation energies of the FMO pigments into contributions of individual amino acids and leading short- and long-range electrostatic and polarization effects. We also decipher specific mechanisms of how excitonic interactions in FMO are affected by point mutations. Thus, our simulations, supported by experimental data, provide structure-function relations for excitonic interactions and energy transfer in FMO, and pave the way for predictive modeling of electronic properties and spectroscopy in other photosynthetic complexes.

## **Contributed Lectures**

### **CL1 : Ab initio cavity quantum electrodynamics**

Eugene DePrince  
Florida State University

Strong coupling of photonic and molecular degrees of freedom can lead to the formation of hybrid light-matter states known as polaritons that can exhibit dramatically different properties relative to the original uncoupled states. A fundamental understanding of the principles that govern polariton formation and manipulation is desirable, as such knowledge can facilitate light-mediated control over chemical transformations. Cavity quantum electrodynamics (QED) generalizations of density functional theory (DFT) and coupled-cluster (CC) theory have emerged as powerful approaches for the description of cavity-induced effects in many-electron systems. I will discuss applications of time-dependent QED-DFT and equation-of-motion QED-CC to cavity-bound molecular systems.

### **CL2 : Machine learning aided quantum chemical discovery in realistic environments**

Fang Liu  
Emory University

Modeling the complex environments involving solvent or pressure in quantum chemical calculations is of great importance to understanding chemistry at real-world experimental conditions. We combine quantum chemistry calculations and machine learning (ML) models to enable fast and accurate prediction of molecular properties in real experimental environment to accelerate chemical discovery.

The availability of large, high-quality data sets is the foundation for artificial intelligence design and discovery in chemistry. However, rapid computational data set generation of solution-phase molecular properties at the quantum mechanical level of theory was previously hampered by the complicated simulation procedure. We developed AutoSolvate, an open-source toolkit to streamline the workflow for QC calculation of explicitly solvated molecules. Another major challenge in solution-phase computational discovery is the discrepancy between computationally predicted molecular properties and experimental measurements. Specifically, prominent errors persist in redox potential calculations compared to experimental measurements. We develop ML models to reduce the errors of redox potential calculations in both implicit and explicit solvent models.

Pressure also plays essential roles in chemistry by altering structures and controlling chemical reactions. The extreme-pressure polarizable continuum model (XP-PCM) is an

emerging method with an efficient quantum mechanical description of molecules at high pressure (on the order of GPa). However, its application to large molecular systems was previously hampered by the computational overhead to describe the pressure. We exploit advances in graphical processing units (GPUs) to accelerate XP-PCM and have enabled high-pressure quantum chemistry simulation of proteins that used to be computationally intractable.

### **CL3 : Residue Interaction Networks and the Cheminformatics of Atomic-Level**

#### **Enzyme Models**

Nathan DeYonker  
University of Memphis

Enzyme simulations are notoriously challenging as their large size prevents modeling the whole enzyme with highly accurate but computationally expensive quantum mechanical (QM) methods. Currently, only the chemically important “active site” residues/substrates/cofactors are modeled with QM-methods. However, determining which biological sub-units necessarily should be included in the QM-model remains ambiguous, and current practices for model construction typically suffer from human bias and unclear methodology. My lab has been developing software called RINRUS (Residue Interaction Network Residue Selector) designed to use protein topology to construct residue interaction networks for the prediction of appropriate QM-only models of enzyme active sites. As the RINRUS workflow becomes more sophisticated and flexible, I hope to address reproducibility and throughput / data velocity issues that arise in atomic-level enzyme modeling. First, molecular dynamics (MD) simulations are sampled and refined with QM-cluster models to study the enzyme mechanism of chorismate mutase. The evolution and visualization of Residue Interaction Networks through the course of an MD simulation will also be discussed. In tandem with RINRUS development, we have applied computational enzymology to study fascinating proposed mechanisms of snake venom metalloproteinases, catechol-O-methyltransferase, and cytochrome P450 proteins involved in lignin valorization.

### **CL4 : Analytic Solution to a previously unintegrable rate law governing autocatalysis and epidemiology**

James Baird  
University of Alabama in Huntsville

The most elementary autocatalytic reaction mechanism consists of an initial bimolecular step in which a molecule of the substrate,  $A$ , reacts with a molecule of the catalyst,  $B$ , to produce another molecule of  $B$ , followed by a unimolecular step in which  $B$  decomposes to form a molecule of the product,  $C$ . [1] This autocatalysis mechanism is isomorphic to the

Kermack – McKendrick mechanism [2] of epidemiology where in the first step a susceptible individual, A , catches the disease from an infected individual, B , and then in the second step, the infected individuals recover and assume the non-infectious state, C. Since its introduction in 1927 , the rate law for this mechanism has proved to be unintegrable in closed form.[2] In the chemical context, however, the formation of the product, C , is optimized if the rate of the first reaction is faster than the rate of the second reaction. We have integrated the rate equation for this case and have obtained a closed form analytical solution whose predictions are indistinguishable from the numerical integration of the same rate equation.

1. Bissette, A. J.; Fletcher, S. P. Mechanisms of autocatalysis, *Angewandte Chemie Int. Ed.* 2013, 52, 12800 – 12826
2. Kermack, W. O., McKendrick, A contribution to the mathematical theory of epidemics. *Proc. Roy. Soc. of London Series A* 1927, 115, 700 -721.

## CL5 : Atomic structure generation from structural fingerprints

Victor Fung

Oak Ridge National Laboratory

Data-driven machine learning methods have the potential to dramatically accelerate the rate materials design over conventional human-guided approaches. These methods would help identify or, in the case of generative models, even create novel crystal structures of materials with a set of specified functional properties to then be synthesized or isolated in the laboratory. For crystal structure generation, a key bottleneck lies in developing suitable atomic structure fingerprints or representations for the machine learning model, analogous to the graph-based or SMILES representations used in molecular generation. However, finding data-efficient representations invariant to translations, rotations, and permutations, while remaining invertible to the Cartesian atomic coordinates remains an ongoing challenge. Here, we propose an alternative approach to this problem by taking existing non-invertible representations with the desired invariances and developing a method to reconstruct the atomic coordinates through gradient-based optimization using automatic differentiation. This can then be coupled to a generative machine learning model which generates new materials within the representation space, rather than in the data-inefficient Cartesian space. In this work, we demonstrate our approach by using invertible neural networks to generate representations from atom-centered symmetry functions, which are then reconstructed to their corresponding atomic positions using our optimization algorithm. We are able to successfully generate novel and valid atomic structures of sub-nanometer Pt nanoparticles as a proof of concept. Furthermore, this method can be extended to any suitable structural representation, thereby providing a powerful, generalizable approach towards structure-based generation.

## **Poster Session 1 (Thursday, May 19<sup>th</sup>)**

### **P1-1 : Investigation of Carbene Formation in Ionic Media with Physics-based, Neural Network Force Fields**

John Stoppelman  
Georgia Institute of Technology

N-heterocyclic carbenes (NHCs) are among the most powerful catalysts in organic chemistry. While steric and electronic modulation of carbene formation has been extensively characterized, quantitative investigation of the (de)stabilization of NHCs in ionic media has not been performed. We have developed physics-based, neural network force fields to perform reactive molecular dynamics simulations of NHC formation from [EMIM+][OAc-] in ionic media, allowing for the analysis of solvent effects on carbene stability. Our approach utilizes neural networks to model short-range interactions of the reacting complex, while physics-based force fields are used to describe the interactions between the reacting complex with the surrounding solvent. We show how our approach allows for the computation of reaction free energies with chemical accuracy in comparison to ab initio results, while allowing for efficient simulation of reactions in bulk liquids.

### **P1-2 : Influence of an Ar Atom on the Structures, Energetics and Vibrational Frequencies of the Water Hexamer**

Mikhayla Clothier  
Erskine College

This work locates the preferred binding sites of a single Ar atom around eight, well-characterized water hexamer structures (i.e., prism, ring, cage, bag, boat1, boat2, book1 and book2) using the MP2, CCSD(T) and 2-body:Many-body (2b:Mb) CCSD(T):MP2 methods in conjunction with robust correlation consistent basis sets. The Ar atom was placed at the vertex, edge or face of each examined (H<sub>2</sub>O)<sub>6</sub> structure before undergoing full geometry optimizations with the MP2 and 2b:Mb methods. Harmonic vibrational frequencies have been computed to further characterize the optimized Ar(H<sub>2</sub>O)<sub>6</sub> geometries and examine spectroscopic perturbations induced by the Ar atom. CCSD(T) single point computations will be carried out to probe changes to the energetics of the water hexamers.

### **P1-3 : DFT-based QM/MM with Particle-Mesh Ewald for Direct, Long-Range Electrostatic Embedding**

John Pederson  
Georgia Institute of Technology

We present a DFT-based, QM/MM implementation with long-range electrostatic embedding achieved by direct real-space integration of the particle mesh Ewald (PME) computed electrostatic potential. The key transformation is the interpolation of the electrostatic potential from the PME grid to the DFT quadrature grid, from which integrals are easily evaluated utilizing standard DFT machinery. We provide benchmarks of the numerical accuracy with choice of grid size and real-space corrections, and demonstrate that good convergence is achieved while introducing nominal computational overhead. Furthermore, the approach requires only small modification to existing software packages, as is demonstrated with our implementation in the OpenMM and Psi4 software. After presenting convergence benchmarks, we evaluate the importance of long-range electrostatic embedding in three solute/solvent systems modeled with QM/MM. Water and BMIM/BF<sub>4</sub> ionic liquid were considered as “simple” and “complex” solvents respectively, with water and p-phenylenediamine (PPD) solute molecules treated at QM level of theory. While electrostatic embedding with standard real-space truncation may introduce negligible error for simple systems such as water solute in water solvent, errors become more significant when QM/MM is applied to complex solvents such as ionic liquids. An extreme example is the electrostatic embedding energy for oxidized PPD in BMIM/BF<sub>4</sub> for which real-space truncation produces severe error even at 2-3 nm cutoff distances. This latter example illustrates that utilization of QM/MM to compute redox potentials within concentrated electrolytes/ionic media requires carefully chosen long-range electrostatic embedding algorithms, with our presented algorithm providing a general and robust approach.

### **P1-4 : Investigation of the Non-Covalent Interactions Between Carbon Dioxide and Pyridine Using Data-Driven Coupled-Cluster Singles and Doubles**

Justin Phillips  
University of Tennessee, Knoxville

A CO<sub>2</sub>-pyridine supersystem was investigated to better understand various aspects of the performance of the Data-Driven Coupled-Cluster Singles and Doubles (DDCCSD) model on systems that contain non-covalent interactions. The DDCCSD model was trained and tested using coplanar CO<sub>2</sub>-pyridine configurations in which the distance between the carbon of the CO<sub>2</sub> and the nitrogen of the pyridine was varied. Initial DDCCSD calculations were completed, revealing a large mean absolute error between DDCCSD and conventional CCSD calculations. A novel algorithm which eliminates excess coupled-cluster amplitudes, responsible for biasing machine learning algorithms, was developed. The algorithm was implemented into the DDCCSD model and tested on the CO<sub>2</sub>-pyridine supersystem. The resulting mean absolute error of the DDCCSD calculations was reduced. A set of novel

algorithms which rank amplitudes based on the uniqueness of their corresponding features was developed, allowing for the reverse bias of overpopulated regions of feature space, thusly ensuring the trained DDCCSD model contained a robust feature-space. The set of algorithms were implemented into the DDCCSD model and tested on the CO<sub>2</sub>-pyridine supersystem. The resulting mean absolute error of the DDCCSD calculations was reduced. The frozen core approximation was implemented to eliminate two-electron excitations that provide a small amount of correlation energy. In comparison to the model containing all electron excitations, the mean absolute error of the DDCCSD calculations of the CO<sub>2</sub>-pyridine supersystem was reduced. The transferability of the trained DDCCSD model was determined by performing calculations with CO<sub>2</sub>-pyridine systems with orientations not introduced during the training of the model.

### **P1-5 : Real-time density matrix embedding theory: Electron dynamics for strongly correlated extended systems**

Dariia Yehorova  
Georgia Institute of Technology

The simulation of electron dynamics in strongly correlated systems presents a great challenge because it requires accurate calculation of electron-electron correlation across the entirety of the system. In this work, we have successfully developed a time-dependent extension of the wavefunction based method projected density matrix embedding theory (pDMET), which was originally designed to treat strong correlation in static systems. As in the previously developed static pDMET, in real time pDMET the system is partitioned into fragments; the interactions between a chosen fragment and the rest of the system are treated through a compact representation of the environment obtained using the Schmidt decomposition (1). We have derived and implemented dynamical equations of motion that describe the time dependence of the system within this framework. We applied the method to a multi-impurity Anderson model with various distributions of impurities and showed the convergence to the exact dynamics with an increase in the fragment size. Since the calculations for each fragment of the system are performed independently, the method allows for an efficient treatment of extended and disordered systems without the need to invoke periodicity.

#### References:

[1] Wu, X., Cui, Z. H., Tong, Y., Lindsey, M., Chan, G. K. L., & Lin, L. (2019). Projected density matrix embedding theory with applications to the two-dimensional Hubbard model. *The Journal of Chemical Physics*, 151(6), 064108.

## **P1-6 : Data-driven coupled-cluster singles and doubles localized orbital implementation and investigation of the amplitude space**

Perera Don Varuna Pathirage  
University of Tennessee, Knoxville

Coupled-cluster singles and doubles with perturbative triples (CCSD(T)) is the gold standard for quantum chemical calculations. Recently, machine learning (ML) has been introduced in as a tool to reduce the computational cost of CCSD(T) calculations. Data-driven coupled-cluster (DDCCSD) scheme is using electronic structure data at MP2 level to predict the coupled-cluster two electron excitation amplitudes (t2 amplitudes).<sup>1</sup> We have extended the applicability of the DDCCSD scheme by introducing localized orbitals and we have demonstrated its applicability of a small set of five small molecules. Currently, we are working on the exploration of the amplitude space and the effective elimination of datapoints that share similarities from the data used for DDCCSD model training. For example, a larger molecular database that includes 100 molecules containing 10 non-hydrogen atoms generates 77.6 million amplitudes, which lead to overfitted models. A 10-fold reduction in mean average error was achieved when selection techniques that reduce the overfitting of the ML model applied prior to model training.

(1) Townsend, J.; Vogiatzis, Journal of Physical Chemistry Letters 2019, 10 (14), 4129–4135.

## **P1-7 : Water contribution to Helmholtz capacitance of aqueous solutions at Au(100) electrode**

Sue Park  
Georgia Institute of Technology

Electrochemical interfaces of aqueous solutions and metal electrodes have fundamental importance due to the influence on electrochemical reactivity at the electrode surface. A detailed understanding of the interfaces is necessary to control electrochemical and electrocatalytic processes; especially, the structural changes of electrolytes at the electrode surface affect the electron transfer which is required for redox reactions. In order to understand the interfacial structure, electrochemists have characterized the capacitance of the interface between aqueous solutions and metal electrodes. The capacitance can be divided into two contributions of water and metal, yet how much capacitance comes from each contribution is not understood well. However, separating two contributions from each other is challenging due to their complexity and technical difficulties. In this work, we isolate water contribution to the capacitance by performing molecular dynamics simulations and investigate Helmholtz capacitance of water and [Na+][Cl-] solutions at Au(100) electrode under applied voltage. We find that water contribution to Helmholtz

capacitance only depends on the perpendicular dielectric constant of water in Stern layer, which supports Helmholtz theory. We show that the capacitance trend consistent with the dielectric constant is induced by the fluctuation of water dipoles in response to the potential. We further investigate the influence of the polarization of electrolytes. We show that the capacitance isn't sufficiently sensitive enough to detect the polarization effect, but the dielectric response is considerably disrupted.

### **P1-8 : Ligand field effect on the ground and redox states of MoN<sub>2</sub> species**

Maria V. White

University of Tennessee, Knoxville

Dinitrogen functionalization under ambient conditions remains a challenge in the field of catalysis. Structures bearing transitional metal center(s) have displayed interesting reactivities and have been suggested for the catalytic conversion of dinitrogen to ammonia. Using molybdenum, one of the most azophilic metals of the transitional metal series, moderate ammonia yields have been attained experimentally. Although much effort has been expended in the topic of N<sub>2</sub> fixation, relevant questions still require addressing with regards to the chemical activity that takes place during the nitrogen reduction process under a ligand field environment. We previously demonstrated that the reduced states of bare MoN<sub>2</sub> clusters lead to a greater degree of N<sub>2</sub> activation [1]. Here we further expand these findings by exploring the ligand field effects on the ground and redox states of Mo-N<sub>2</sub> species. Molecular structures of molybdenum complexes bearing ligands of varying strength were optimized with density functional theory (DFT). Multiconfigurational Complete-active space self-consistent field (CASSCF) method and its second-order perturbative complement (CASPT2) methodologies were applied to enhance the accuracy of the study. This study will shed light on the electronic structure and binding properties of molybdenum based molecular systems. In addition, the understanding of the reactivity of known catalytically active complexes will provide insight into the development and improvement of novel synthetic catalysts.

[1] Maria V. White, Justin K. Kirkland, Konstantinos D. Vogiatzis. J. Chem. Phys. 154, 224308 (2021).

## **P1-9 : Dynamical models of molecular junctions using density functional theory and ab initio molecular dynamics**

Matthew Curry  
University Of Tennessee

Ever since Aviram and Ratner theoretically proposed that rectifiers could be constructed from single molecules, great interest has been expressed in the development of molecular junctions as nano-electronic devices. To this end, a large body of experimental and theoretical work has been done to elucidate the properties of such devices. Sophisticated break-junction experiments typically report a conductance distribution collected over many single measurements, portraying the changes in conductance as the molecule adopts different geometries and occupies different electrode sites in the junction. To understand the molecular and dynamical mechanisms underlying the observed variations in conductance, we have studied the internal motion of molecular junctions and the effects of motion on conductance using a combination of atomistic electrode-molecule-electrode models, density functional theory, and ab initio molecular dynamics simulations. The dynamics is performed within the microcanonical ensemble and conductance is computed along a trajectory to construct conductance histograms. In our current approach, conductance is calculated from tunneling coefficients of electrons or holes across the orbitals of the bridging molecule. We have applied this approach to junctions consisting of sulphur or nitrogen-terminated aromatic molecules embedded between gold electrodes, and investigated the influence of molecular nature, electrode binding sites, and temperature on conductance distributions. Our results highlight chemical and dynamical properties that control the locations and widths of conductance peaks, and provide insight into why sulphur-termination leads to much wider distributions than nitrogen-termination.

## **P1-10 : Insight into Subsurface Adsorption and Its Effects on Surface Phenomena Deduced from a Lattice-Gas Model and Monte Carlo Simulations**

Carson Mize  
University of Tennessee, Knoxville

Gas-phase adsorption models are a beneficial tool for studying elementary steps of surface chemistry, like adsorption. While many previously developed models exist, most models are limited to low adsorbate coverages due to the computational cost required to produce high coverage models. To investigate adsorption over a broad range of adsorbate coverages on a crystalline solid, we have developed a hierarchy of lattice-gas adsorption models that includes surface and subsurface adsorption, tunable interaction parameters calculated with density functional theory, and larger scale modeling with Monte Carlo (MC) simulations. We have applied the models to study oxygen adsorption on a Ag(111) surface due to experimental findings suggesting the possibility of subsurface-adsorbed oxygen species. The first construction of the model includes a reduced-site model using pairwise interactions between oxygen atoms adsorbed to the surface and subsurface of Ag(111).

Canonical MC simulations show the saturation of surface-adsorbed oxygen at 0.375 monolayer (ML) and larger oxygen accumulation in the second subsurface than the first. The second model construction includes all high-symmetry adsorption sites in the surface and subsurface. Canonical MC simulations show qualitatively similar oxygen distributions to the first-generation model, while grand canonical MC simulations show subsurface oxygen is not formed in Ag(111) at ultrahigh vacuum but is formed at high pressures like those used in industrial catalytic epoxidation. We are currently developing a third-generation model that includes O-O, Ag-Ag, and Ag-O pairwise interactions to enable us to study the role of surface and subsurface oxygen in inducing surface reconstructions of Ag(111).

### **P1-11 : Quantum Chemical Study on the Interactions between CO<sub>2</sub> and Amino Acids**

Amarachi Sylvanus  
University of Tennessee, Knoxville

Globally, there has been a continued effort to reduce the volume of carbon dioxide (CO<sub>2</sub>) in the atmosphere, as this is the main component that contributes to climate change. Conventional carbon capture and separation methods are grouped into absorption, adsorption, membrane separation, and cryogenic separation techniques. However, the challenge remains in developing a technique that is simultaneously cost efficient and environmentally friendly. Absorption solvents, for instance, are characterized by high-temperature requirements for breaking the solvent-CO<sub>2</sub> covalent bond and solvent regeneration. In this study, the proposed solution is the selective separation of CO<sub>2</sub>, using bio-inspired materials. This would be biomimicry of the weak attractive interactions between CO<sub>2</sub> and amino acids, the building blocks of enzymes. Here, we have carried out a highly accurate quantum chemical study of the non-covalent interactions between CO<sub>2</sub> and the 20 natural amino acids. A benchmarking study with different density functionals and basis sets was completed, and results were compared with highly accurate CCSD(F12)(T) reference values. The reliable energies have revealed the tendencies and strengths of the non-covalent interactions between CO<sub>2</sub> and these amino acids in the gas phase towards physisorption. The benchmarking results show the density functionals together with corrections to the use of minimal basis sets and dispersion effects align closely with our CCSD(F12)(T) reference values.

## **P1-12 : Ion-pairing effects on the absolute oxidation potential of the Fc/Fc<sup>+</sup> redox couple in complex nonaqueous environments**

John Hymel  
Georgia Institute of Technology

Ferrocene (Fc) is commonly used as an internal redox couple in electrochemical measurements. Therefore, understanding how the absolute oxidation potential of Fc is modulated by different solvents and ion concentrations is important for facilitating the comparison between different experimental measurements. Standard implicit solvation models are unable to examine these systems since they lack atomistic detail of the solvent structure and ion coordination. Using polarizable forcefields fit to ab initio quantum chemistry calculations, we have computed the absolute oxidation potential of the Fc/Fc<sup>+</sup> redox couple in acetonitrile and 1,2-dichloroethane. In order to elucidate the effect ion-pairing has on the thermodynamics of this redox process, we have computed the absolute oxidation potential of Fc in mixtures of these solvents with an ionic liquid (IL), [BMIM<sup>+</sup>][BF<sub>4</sub><sup>-</sup>]. Physical insight is gained by analyzing the correlation between the differential solvation free energy of Fc/Fc<sup>+</sup> and average anion coordination number in solvent mixtures with varying mole fractions of IL. Quantification of these solvation/environmental effects has important implications in how the thermodynamics of electron transfer processes are modulated by ion concentration fluctuations in the electrical double layer at electrode interfaces.

## **P1-13 : Effect of Vibrational Strong Coupling on Isomerization Equilibria**

Kaihong Sun  
Emory University

It has been shown experimentally that chemical equilibria can be shifted via vibrational strong coupling (VSC). However, the mechanism has not been unveiled. In this poster, we will report our recent progress on the identification of key factors controlling the effects of optical cavities on the chemical equilibrium of a simple isomerization reaction. We employed a prototype model Hamiltonian including a single cavity mode under collective strong coupling with bright reactant vibrational modes. By minimizing the Helmholtz free energy, we obtained the isomerization equilibrium constant in different scenarios. High and low temperature limits were explored, and the effect of light-matter coupling was also quantitatively studied. The obtained results are interpreted with Le Chatelier's principle along with the decomposition of free energy variation into entropic and energetic components.

## **P1-14 : Controlling molecular electronic properties with topological phases of matter**

Luis Martinez-Gomez  
Emory University

The exotic new topological phases of matter promise a technological revolution due to their novel and unique electronic properties. However, surface interactions of topological insulators and molecules have yet to be harnessed for chemical catalysis, and the underlying question of whether these new phases of matter can be employed to achieve high-efficiency and selective synthesis remains open. In the present work, we employed the Fano-Anderson model Hamiltonian to compute the electron occupancy of the LUMO orbital of a molecule adsorbed near the edges and on the bulk of a polyacetylene chain in the trivial, metallic, and topological phases. We find characteristic signatures of the topological phase transition and demonstrate numerically and analytically that the topological material has a significant advantage and robustness over the metallic phase for electron donation into the molecular system.

## **P1-15 : Leveraging near-term quantum computers with unitarily downfolded Hamiltonians**

Renke Huang  
Emory University

Simulating strongly correlated molecules and materials is one promising application for quantum computers. However, the resource requirements of quantum algorithms for molecular simulations are not amenable for current quantum devices. To address this, we utilize a quantum-classical hybrid strategy that combines an active space computation using the variational quantum eigensolver (VQE) to treat static correlation and a downfolding of Hamiltonian based on the multireference driven similarity renormalization group (MR-DSRG), to treat dynamical correlation. We compute the potential energy curves of H<sub>2</sub> in the cc-pV5Z basis, atomization energy of H<sub>4</sub>, and the adiabatic singlet-triplet splitting of para-benzyne diradical. We benchmark the results on both the simulator and IBMQ quantum devices.

## **P1-16 : Low-Order Scaling Electronic Structure Methods for Non-Covalent Interactions in Psi4**

Zachary Glick  
Georgia Institute of Technology

Many methods in electronic structure theory (EST) are limited in application by their high asymptotic scaling. This is particularly unfortunate for investigations of non-covalent

interactions, which are often long-range in nature and therefore require computations on large chemical systems. We developed and implemented a number of approximate, reduced-cost EST methods in the Psi4 software package which exhibit better scaling properties than their conventional counterparts. These low-order scaling methods extend the range of chemical systems that can be studied with EST.

### **P1-17 : Range-dependence of two-body intermolecular interactions and their energy components in molecular crystals**

Derek Metcalf  
Georgia Institute of Technology

Routinely assessing the stability of molecular crystals with high accuracy remains an open challenge in the computational sciences. The many-body expansion (MBE) decomposes computation of the crystal lattice energy (CLE) into an embarrassingly parallel collection of computations over molecular dimers, trimers, and so forth, making quantum chemistry techniques tractable for many crystals of small organic molecules. By examining the range-dependence of different types of energetic contributions to the CLE, we can glean qualitative understanding of solid-state intermolecular interactions as well as practical, exploitable reductions in the number of computations required for accurate energies. Here, we assess the range-dependent character of two-body interactions of 24 small organic molecular crystals using the physically interpretable components from symmetry-adapted perturbation theory. We also examine correlations between the convergence rates of electrostatics and London dispersion terms with molecular dipole moments and polarizabilities, to provide guidance for estimating convergence rates in other molecular crystals.

### **P1-18 : Accurate Anharmonic Vibrational Frequencies with Focal-Point Coupled Cluster**

Philip Nelson  
Georgia Institute of Technology

Focal-point coupled cluster methods have been demonstrated to have excellent agreement with large basis set coupled cluster for energies and geometries. Here we examine the performance of focal-point methods combining MP2 at the complete basis set limit with CCSD(T) at cc-pVDZ and cc-pVTZ basis sets for the calculation of anharmonic vibrational frequencies using vibrational perturbation theory (VPT2). The focal-point CCSD(T) anharmonic frequencies are shown match experimental frequencies for a set of small molecules at a similar accuracy to complete basis set CCSD(T).

## **P1-19 : Application of non-adiabatic ring-polymer molecular dynamics to strongly coupled systems**

Ziying Cao

Georgia Institute of Technology

We extend the non-adiabatic ring-polymer molecular dynamics (nRPMD) method to simulate excited-state non-adiabatic dynamics. The nRPMD method combines the semi-classical Meyer-Miller-Stock-Thoss (MMST) mapping technique with path-integrals to obtain a classically isomorphic representation for both nuclear and electronic degrees of freedom. The nuclear quantum information provided by nRPMD shows advantages over linear semiclassical methods. Here we numerically test the performance of nRPMD in strongly coupled systems including the linear vibronic coupling model of conical intersections and isomerization dynamics under the strong light-matter coupling. We show that the nRPMD method is capable of accurately simulating complicated non-adiabatic systems with little increase in computational complexity.

## **P1-20 : Conducting Electronic Excitation Simulation of Rare Gas-Ethane Dimer Applying Non-Hermitian Real-Time Time-Dependent Density Functional Theory**

Yi-Siang Wang

Georgia Institute of Technology

The impact of photons or energetic particles, such as electrons, introduce non-equilibrium conditions in which many-body interactions can affect and determine the subsequent energy exchange pathways. These processes play an important role in surface-science fragmentation. However, the majority of theoretical descriptions of such processes are limited to static density of states analysis. In this study, we go beyond a static picture by simulating near-resonant Auger processes using real-time time-dependent density functional theory (RT-TDDFT). We examine an ethane-rare gas (Eth-RG) dimer, in which initial deep-core ionization of the RG initializes an Auger process that can further ionize the ethane molecule leading to fragmentation of the molecular species. The RT-TDDFT dynamics are analyzed to differentiate between competing Auger processes that lead to differences in experimentally measured fragmentation ion yields.

## **P1-21 : Elucidating the Electron-Nuclear Dynamics in Halide Perovskites via Ring-Polymer Molecular Dynamics.**

Jordan Hale

Georgia Institute of Technology

For the past decade, halide perovskites (HaPs) have been at the center of solar cell research with power conversion efficiencies consistently reaching 20% and beyond,

competing with current silicon solar cells. However, not everything is clear about their charge transport dynamics. HaPs have long carrier diffusion lengths and lifetimes, yet their charge carrier mobilities remain relatively low when compared to most inorganic semiconductors, contradicting conventional scattering theories. The main physical difference between HaPs and most inorganic semiconductors is their soft lattice resulting in large dynamical disorder. Therefore, it becomes necessary to consider how nuclear motions couple to charge carrier motion to understand charge transport in HaPs. Towards this goal, we use the Ring Polymer Molecular Dynamics (RPMD) method to model the dynamics of a free electron diffusing through a fluctuating perovskite lattice.

The RPMD formulation describes quantum objects as purely classical objects through a classical-quantum isomorphism of the partition function derived by Feynman path integrals. Thereby providing a computationally efficient methodology. Our RPMD calculations are able to capture the correct experimental magnitude and temperature dependence of the electron mobilities in Methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ), a result that has alluded previous computational studies.

## **P1-22 : Computed vs. experimentally derived oscillator strengths: A benchmark study of excited-state quantum chemical methods**

Jorge Garcia-Alvarez  
Department of Chemistry, Georgia State University

Excited-state quantum chemical methods (ESQCM) can reproduce with high accuracy photoabsorption energies associated with electronic transitions, often within a few kcal/mol from experimentally determined absorption maxima. However, the accuracy of ESQCM computed absorption intensities has not been extensively investigated. A difficulty such a study faces is that it is not straightforward to establish a quantitative equivalence between computed transition probabilities (often reported as oscillator strengths or transition dipole moments) and the wavenumber-dependent attenuation coefficients reported in experimental spectra. The present work employs a set of 164 (experimental) transition oscillator strengths derived from the UV-visible spectra of a hundred small organic molecules to benchmark different ESQCM. Widely used TD-DFT methods are the focus of the study: six hybrid and three pure functionals are presented. The accuracy of different solvation models and basis sets is explored, as well as the effect of the Tamm-Dancoff approximation.

## **P1-23 : How Does the Multireference Character of Benzyne Reflect on Their X-ray Absorption Spectra?**

Kevin Marin

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X-ray absorption spectroscopy (XAS) enables the characterization of reaction dynamics and chemical structure in an element-specific way. Theoretical simulations are of critical support in the analysis of XAS spectra, hence a significant endeavor has been made to develop new methods to compute core-excited states. There are several established methods that accurately simulate XAS, however, most are based on a single-reference formalism and may fail to describe molecular systems with open-shell character. Our recently proposed GASSCF-MR-DSRG method combines a generalized-active-space self-consistent-field (GASSCF) treatment of static correlation with dynamical correlation corrections from the driven similarity renormalization group (DSRG). In this study we compute the core-excited states of benzyne diradicals, and discuss how the multireference character of these molecules is reflected in their XAS spectra.

## **P1-24 : Cumulant approximations in second-order driven similarity renormalization group perturbation theory**

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Accurate multireference electronic structure calculations are important for potential energy surface (PES) construction but limitations prevent their routine use. One of the most severe limitations is the high computational cost of post-CASSCF methods as the active space grows, especially due to the use of high-order density matrices. Two cumulant based approximations to high-order density matrices were investigated in strongly contracted second-order  $n$ -electron valence perturbation theory (SC-NEVPT2) [D. Zgid, D. Ghosh, E. Neuscamman, and G. K.-L. Chan, *J. Chem. Phys.* 130, 194107 (2009)]. However, approximated forms of SC-NEVPT2 exhibit intruder state problems and are less accurate than the parent theory. Our group proposed the second-order multireference driven similarity renormalization group perturbation theory (DSRG-MRPT2). DSRG-MRPT2 only requires the three-body reduced density cumulant and, therefore, has a memory cost proportional to the six power of the number of active orbitals ( $n_{\text{act}}^6$ ). To investigate reductions of the memory requirement of DSRG-MRPT2, we test four different levels of three-body reduced density cumulant approximations which set different classes of cumulant elements to zero. Our test cases show that additional error introduced by approximation can be made as small as 1 kcal/mol or less while the amount of memory required is reduced by one-tenth relative to the full DSRG-MRPT2.

## **P1-25 : Data-Driven Exploration of Fe(IV)-oxo Sites for C-H Activation**

Grier Jones

University of Tennessee, Knoxville

Biomimetic design approaches have attempted to mimic the catalytic properties of high-valent iron(IV)-oxo intermediates, found in enzyme active sites, for C-H bond activation. C-H bonds in inert hydrocarbons, such as methane, possess strong bonds that are resistant to chemical functionalization. To aid in the screening of potential catalysts for C-H bond activation, computational methods, such as density functional theory (DFT) and machine learning (ML), are valuable tools for performing high-throughput searches of the vast chemical compound space. In this study, we have built a database of 51 iron(IV)-oxo species with varying coordination environments which are further functionalized for a total of 200k+ structures. DFT calculations are then performed on a subset of the total chemical space to determine spin states, quintet ( $S = 2$ ) or triplet ( $S = 1$ ), and activation energies. The data is then curated by removing structures from both sets of data based on various screening criteria. To avoid performing DFT calculations on the total chemical compound space, we utilize a novel molecular representation based on persistence homology, called persistence images (PIs), to train and test a regression model to predict C-H activation energies and a classification model to predict the spin states. After this screening is performed, we then expand our search to zeolites due to the high-selectivity of methane, for C-H bond activation via iron(IV)-oxo sites, in iron containing zeolite systems.

## **P1-26 : Ligand Field Effects on N<sub>2</sub>O Activation Via Iron(II) Complexes**

Tobias Robertson

University of Tennessee Knoxville

Nitrous oxide (N<sub>2</sub>O) can undergo an oxygen atom transfer (OAT) reaction resulting in inert nitrogen gas (N<sub>2</sub>) while transferring an oxygen atom to a molecular complex or material. This process can be of catalytic importance since this OAT reaction can be leveraged to form iron(IV)-oxo sites, which are known to be catalytic intermediates. Here, an investigation of the ligand field effects on primarily iron(II) complexes for the formation of iron(IV)-oxo sites using nitrous oxide as the oxygen source is presented. A database of sixty-five initial ligand environments varying in field strength and coordination geometry was studied using density functional theory (DFT) calculations. Additional structures were also studied to specifically interrogate a trend observed in the initial database while investigating potential predictive descriptors for the OAT reaction barrier. Generalized design principles rooted in the performance of the varied ligand fields are discussed and have potential applications in catalyst design for both molecular complexes and metal organic frameworks (MOFs).

## **P1-27 : Growth of CaCO<sub>3</sub> Nanoparticles: Formation Energies in Aqueous Solution**

Amanda Duplain  
The University of Alabama

In nature, calcium carbonate (CaCO<sub>3</sub>) serves as a fundamental structural material, for example in biomineralization, leading to three major anhydrous polymorphs, calcite, aragonite and vaterite. In addition, amorphous calcium carbonate plays an important role in many natural systems including the growth processes leading to mineral formation. We have previously studied CaCO<sub>3</sub> nanoparticle growth in vacuo. The current work extends this study to calcium carbonate (CaCO<sub>3</sub>)<sub>n</sub> cluster formation in water. The geometries were optimized at the density functional theory (DFT)  $\omega$ B97XD//cc-pVDZ/DZVP2 level. Additional calculations of gas phase and solution energies at the COSMO level were done with the same basis set and the B3LYP, BLYP, M06, PBE0, and TPSS exchange-correlation functionals. Normalized clustering energies have been calculated for (CaCO<sub>3</sub>)<sub>n</sub> (n = 1-16). The normalized clustering energies are being used to elucidate the particularly small K<sub>sp</sub> value for calcium carbonate dissolution in water. This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, Geochemistry Program on a subcontract from Pacific Northwest National Laboratory.

## **P1-28 : Analysis of Born-Oppenheimer and Factorized Approximations in Electron-Nuclear Systems Using an Exactly Solvable Model**

Julian Stetzler  
University of South Carolina

The accurate and efficient description of electron correlation is one of the key issues in developing electronic structure theory methods. The related problem of electron-nuclear correlation is relevant in methods attempting to account for nuclear motion. In both cases, the correlation is from the Coulomb interaction between the particles but with opposite signs. In this work, we aim to provide an accurate solution in the simple model of a 3-dimensional hydrogen atom with the nucleus in a harmonic well and the electron and nucleus interacting via a Coulomb potential. We then assess the accuracy of the commonly used Born-Oppenheimer (BO) approximation and a factorized solution by comparing them to an exact solution over a range of spring constant (k) values. We find our exact result using a coordinate transformation to center of mass and relative coordinates and using the BO form of the wave function in the full Hamiltonian. In these methods, we find the electron nuclear correlation as new coupling terms in either the harmonic potential or kinetic energy operators. These new coupling terms can be accurately treated as perturbations, unlike the Coulomb interaction of the original problem. We obtain numerical results for the approximations and exact methods in the range of [0.01,100] and obtain analytic expressions for the exact solution at the limits of k=0 and k approaching infinity.

## **P1-29 : Benchmarking Dimer Contributions to Crystal Lattice Energies in Small Organic Crystals**

Caroline Sargent  
Georgia Institute of Technology

Using the many-body expansion to predict crystal lattice energies, an embarrassingly parallel process, allows for flexibility in the choice of theoretical methods. Partial crystal lattice energies of a number of molecules -- including ammonia, water, carbon dioxide, cyanamide, and benzene -- have been calculated using energies of the dimers, with a minimum monomer separation of up to 20 Angstroms, present in the molecular crystal. In an effort to reduce the computational expense of predicting accurate crystal lattice energies, we have calculated this dimer contribution with 15 different levels of theory and compared these energies to those at the coupled-cluster (CCSD(T)) level with the complete basis set limit. For each molecule, we compare the errors of the methods studied for the cases of calculating the energy with all dimers at the proposed method, as well as a subset of dimers, which excludes those with the smallest minimum monomer separation.

## **P1-30 : Theoretical Spectroscopic and Thermodynamic Properties of the Uranium Hydrides UH, UH<sup>-</sup> and UH<sup>+</sup>.**

Gabriel F. de Melo  
The University of Alabama

The interaction of actinides and the hydrogen atom (H<sup>0/-/+</sup>) is of great interest due to its potential to give insights on the atomic states of the metal. To obtain a reliable description of the resulting electronic states, calculations were carried out using the Feller-Peterson-Dixon (FPD) and multireference CASPT2 methods combined with spin-orbit effects. At the FPD level, the adiabatic electron affinity and ionization energy (IE) of UH are predicted to be 0.44 eV and 6.00 eV, respectively. For UH, the spin-orbit calculations resulted in 62  $\Omega$  states below  $\sim 2.5$  eV and the lowest vertical detachment energy (VDE) was 0.48 eV. The bond dissociation energy (BDE) of UH (217.5 kJ/mol), calculated from its IE, is expected to be  $\sim 20\%$  weaker than that of ThH. This value is essentially the same as the one obtained from the isodesmic reaction  $\text{UH} + \text{WF}_6 \rightarrow \text{UF}_6 + \text{WH}$  at the CCSD(T)/aug-cc-pVQZ-PP level. For UH<sup>+</sup>, the calculated BDE is 238.4 kJ/mol in good agreement with available experimental values and for UH<sup>-</sup> a BDE of 217.5 kJ/mol was obtained. Heats of formation ( $\Delta H_{\text{fo}}$ ) at 0K are predicted to be 531.5 (UH), 488.7 (UH<sup>-</sup>) and 1110.7 kJ/mol (UH<sup>+</sup>) for the three species, respectively. The natural bond analysis (NBO) for the ground state of UH (4f<sup>9</sup>/2) shows a 5f<sup>3</sup> sub-configuration and a significant ionic character for the U<sup>+</sup>-H<sup>-</sup> bond. This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Heavy Element Chemistry program through Grant No. DE-SC0018921.

### **P1-31 : Unraveling the mechanism of the hydroxide transport between the cobaltocenium groups in poly-electrolytes**

Sachith Wickramasinghe  
University of South Carolina

Development of anion-exchange membranes (AEMs) with high ionic conductivity and sufficient chemical stability for the fuel cells is an outstanding scientific and technological challenge. A promising type of AEM materials are copolymers containing cationic cobaltocenium, mechanically stabilized by the hydrophobic polyethylene backbone, which exhibit rapid hydroxide transport. Fundamental insight into the pathways of ion transport inside poly-electrolyte membranes, if available, would accelerate the development of efficient AEMs. This work is a theoretical investigation of the hydroxide diffusion mechanisms in cobaltocenium-based poly-electrolytes. The system parameters improving the hydroxide diffusion are obtained from the MD simulations with the forces computed on-the-fly employing the Density Functional Tight Binding (DFTB) theory. Within the simulation cell, the hydrophobic polymeric main chains are mimicked by the graphene sheets, while the hydrophilic domain within these sheets consists of the cobaltocenium cation, water and hydroxide ion. We find that the hydroxide diffusion proceeds via both, the structural diffusion (proton hopping) and the vehicular diffusion. The diffusion coefficient depends on the channel size and the electrostatic interactions, including the rearrangement ability of the solvation shell consisting for the hydroxide of 7-8 water molecules. Separation, cation orientation, and substituents define the channels. The highest diffusion coefficient is observed under moderate water densities (about 50% of the bulk water density) which strikes a balance of forming a full solvation shell, reducing the electrostatic interactions between the ions, and sufficient space for the water rearrangement during the structural diffusion.

### **P1-32 : Comparative Analysis of the Conformations of Human-TFIIH**

Jina Yu  
Georgia State University

Transcription factor IIH (TFIIH), is indispensable for vital cell processes such as transcription and nucleotide excision repair. To uncover the multifaceted involvement of TFIIH in these processes, we built a suitably complete model of the TFIIH-XPA-DNA representative of TFIIH during lesion scanning in nucleotide excision repair. We then carried out extensive molecular dynamics simulations, which revealed the global motions of this assembly. To compare the conformational ensemble of TFIIH in NER to apo-TFIIH and as a constituent of the transcription preinitiation complex (holo-PIC), we performed difference contact network analysis, which defined a partitioning of these complexes into consensus dynamic communities and computed the change in contact probabilities between

communities. This allowed us to quantify dynamic contact rearrangement that accompany TFIIH conformational switching between apo-TFIIH to the holo-PIC and NER-TFIIH conformers. We also used principal component analysis to describe the large-scale motions of the TFIIH XPB and XPD helicase subunits. Our comparative analyses contribute to a more complete mechanistic understanding of how TFIIH dynamically reshapes itself and self-regulates depending on functional context. Mapping of xeroderma pigmentosum, Cockayne syndrome, and trichothiodystrophy patient derived disease mutations to our TFIIH-XPA-DNA model reveals that protein/DNA, protein/protein, and community/community interfaces are important for proper NER function.

### **P1-33 : Performance Analysis of Diverse Coulomb and Exchange Matrix Algorithms**

David Poole

Georgia Institute of Technology

Coulomb (J) and Exchange (K) matrices are some of the most fundamental computational quantities in electronic structure theory, being utilized in a variety of methods including Hartree-Fock (HF) and Density Functional Theory (DFT). Due to their status, many high-performance algorithms exist for constructing the J and K matrices; and it is imperative that electronic structure theory codes utilize these algorithms to achieve optimal performance. Multiple novel J and K build algorithms, including the Linear Exchange (LinK) algorithm, the Continuous Fast Multipole Method (CFMM), and an integral-direct implementation of Density-Fitted HF (DF-HF) for the J matrix, have recently been implemented into the popular Psi4 code. These new algorithms, as well as the integral-direct JK build algorithm, were analyzed for performance and compared against each other. Specifically, timings were recorded for these algorithms for a variety of molecular systems of varying sizes. The scaling order and prefactor were determined for each algorithm, along with the multi-core parallel efficiency. These results provide notable insight into the performance characteristics of each J/K algorithm, as well as the efficacy of the new J/K algorithms implemented recently.

### **P1-34 : Hydrolysis Reactions of the Highest Oxidation State Dimers Pa<sub>2</sub>O<sub>5</sub> and U<sub>2</sub>O<sub>6</sub>. A Computational Study**

Eddy Lontchi

The University of Alabama

Hydrolysis reactions play an important role in the behavior of actinides, their environmental impact, and the use in the nuclear industry. Computational studies on the hydrolysis of high oxidation state oxo/hydroxo dimeric early actinide species Pa<sub>2</sub>(V)O<sub>5</sub> and U<sub>2</sub>(VI)O<sub>6</sub> were performed at the DFT and CCSD(T) levels. Mono-, di-, and tri-bridge

isomeric structures were optimized for both metal oxide molecules. The hydrolysis proceeds by physisorption of H<sub>2</sub>O, forming a Lewis acid/base adduct, followed by a proton transfer to form hydroxides. The process is repeated until all oxo groups are hydrolyzed. Hydrolyzed products are predicted to be energetically preferred over the physisorbed products. The fully hydrolyzed Pa<sub>2</sub>(OH)<sub>10</sub> was predicted as the most stable species in the reaction coordinate with an energy of -145.9 kcal/mol relative to reactants. The hydrated, (H<sub>2</sub>O)U<sub>2</sub>(OH)<sub>6</sub>O<sub>3</sub>, was predicted as the most stable molecule in the reaction coordinate, with an energy of -90.1 kcal/mol relative to reactants, instead of the fully hydrolyzed U<sub>2</sub>(OH)<sub>12</sub> with an energy of -52.2 kcal/mol relative to reactants. Reaction coordinates were generated to show the calculated physisorption energies, reaction barriers, and hydrolysis energies. This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Heavy Element Chemistry program at The University of Alabama through Grant No. DE-SC0018921.

### **P1-35 : Electron tunneling models of junctions containing aromatic heterocyclic molecules with gold or silver electrodes**

Dakota Landrie

University of Tennessee, Knoxville

Theoretical work in molecular electronics looks to produce a model that can accurately describe experimental data for unimolecular rectifiers. Factors that influence the conductance of these metal-molecule-metal motifs include binding site, tunneling height, applied bias voltage, intertip distance and orbital energies. In this work, we seek to gain an inherent understanding of how these factors influence conductance. This was done using density functional theory (DFT) and tunnelling based models. Conductance varied linearly with intertip distance; the general trend shows conductance increasing as the junction is compressed from the DFT calculated optimized geometry. All molecules were placed in face centered cubic (FCC) and on-top sites between both Ag and Au electrodes, respectively. As expected, regardless of junction all molecules showed an increase in conductance as the intertip distance was decreased. Though still in its nascent stages similar work is being conducted with Ag electrodes and the general trends from Au are manifested in Ag junctions. Namely, a linear relationship between intertip distance and conductance. Conductance increases as intertip distance decreases, but the orbital energies increase as intertip distance decreases, and the junction becomes less stable. This indicates the subtle interplay between intertip distance, conductance and stability in Au and Ag junctions containing sulphur or nitrogen terminated aromatic molecules and heterocycles.

## **P1-36 : Electronic Structure Investigation of NO<sub>2</sub> Binding on Vanadium Oxides**

Marcos Mason  
The University of Alabama

The interaction and conversion of acid gases on transition metal oxides is important for the sequestration and conversion of these atmospheric pollutants. Structures and energies of the adsorption of NO<sub>2</sub> on vanadium oxide nanoparticles and TiO<sub>2</sub> supported vanadium oxide Selective Catalytic Reduction (SCR) of NO with NH<sub>3</sub> catalyst models have been calculated at the CCSD(T)//B3LYP level. Good agreement is seen between B3LYP reaction energies and CCSD(T) energies with the B3LYP determined geometries. NO<sub>2</sub> adsorption on dimeric V<sub>2</sub>O<sub>5</sub> behaves like NO<sub>2</sub> binding to Group 4 MO<sub>2</sub> nanoclusters, where strong chemisorption is predicted. This is contrasted to the predicted behavior on larger tetrameric species as well as on SCR catalyst models. In these species, NO<sub>2</sub> binding behaves like binding to Group 6 MO<sub>3</sub> clusters and like NO binding on SCR catalysts with weak physisorption. This work was supported by UNCAGE-ME, an Energy Frontier Research Center led by the Georgia Institute of Technology funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

## **P1-37 : The Study of Spin Polarizability as a measure of chemical reactivity**

Shehani Wetthasinghe  
Department of Chemistry and Biochemistry, University of South Carolina

The substitution reactions between aromatic systems and radicals are common in organic chemistry and biochemistry, and many theoretical models have been developed to explain the relative reactivities of different sites on the aromatic rings. The commonly used models are based on the differences in distributions of the observable properties such as electron density, or on the localization of the frontier orbitals across the aromatic system. In radiation chemistry, the spin density distribution in the radical form of the aromatic system is often used to understand its reactivity. These models work well in simple aromatic systems but fail to explain the reactions with complex molecules. Therefore, we have speculated that the spin polarizability of the aromatic system can explain differential reactivity of aromatic systems with free radicals.

In spin polarizability model is based on the change in spin density in response to the local spin perturbation of the aromatic system. To consider both perturbation and the coupling between molecular orbitals, the model is built based on the Coupled Perturbed Hartree-Fock (CPHF) formalism.

We have considered both the delta-function and Gaussian-based theoretical perturbations and have extended the CPHF equations to be used with the Density Functional Theory.

We apply the spin polarizability model to study the relative product yields in aqueous

radiation experiments using such aromatic systems as naphthols, bisphenols and cresols. The model is successful when applied to naphthols and cresols but disagrees with recent experimental yields of reactions with bisphenols. We speculate that non-planarity of bisphenols complicates the reaction mechanism.

### **P1-38 : Computational Analysis of MOF-based Photoswitch Linkers**

Austin Hill  
University of South Carolina

The implementation of photochromic moieties as metal organic framework (MOF) linkers allows for the remote modulation of metal oxidation states. This modulation is key to modifying several material properties, such as catalytic activity, stability, and charge/energy transport. Spiropyran (SP) and merocyanine (MC) are photoswitches of particular interest because of their photochromic characteristics and the marked change in physical properties as a result of the reversible isomerization between the two forms. While the mechanism of isomerization is generally understood, knowledge surrounding the integrity of the mechanism in a MOF environment and the electronic effects on the MOF properties is lacking. In this work we investigate the electronic contributions of SP and MC and their role in oxidation state tuning in both Zn- and Cu-based MOFs. To this end, we have designed representative models and rigorously analyzed the ground and excited state electronic structures of each isomer using multiple DFT functionals in gas phase and in solution. Additionally, oxidation state and electron coupling calculations, as well as an exciton analysis have been performed on the systems. Our results suggest that changes in the oxidation state of Cu under UV irradiation, observed in experiments, are due to the excited-electronic states of the charge-separated character of the MC.

### **P1-39 : Phosphine Binding Energies to Transition Metals and Lewis Acid: Stronger or Weaker Than NHC Carbenes?**

Damian Duda  
The University of Alabama

Phosphine-based ligands play an important role in the organometallic catalytic chemistry of transition metals. Understanding the reactivity of transition metal complexes with tertiary phosphorus ligands is crucial to improving the activity and selectivity of phosphorus-based catalysts. The nature of the binding of different phosphines (PH<sub>3</sub>, PMe<sub>3</sub>, PPh<sub>3</sub>) with alkali, alkaline earth, transition metals, and selected Lewis acids was calculated to provide a thermochemical data set of the P-M species. The calculations were done using density functional theory (DFT) and high-level electronic structure calculations at the CCSD(T)/CBS level. The binding energies for different metals were compared with each other and with the corresponding nucleophilic carbene (NHC) binding energies. This work was supported

by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, and Catalysis Program on a subcontract from Pacific Northwest National Laboratory.

### **P1-40 : Binding of SO<sub>3</sub> to Group Transition Metal Oxide Nanoclusters**

Nickolas Joyner  
University of Alabama

Transition metal oxide (TMO) clusters have been studied for their ability to absorb acid gases. The current work predicts the interaction of Group 4 metal (Ti, Zr, and Hf) oxide nanoclusters with SO<sub>3</sub>, a byproduct of common industrial processes. The calculations were done using both density functional theory (DFT) and high-level electronic structure calculations at the correlated molecular theory CCSD(T) level. There is reasonable agreement of the WB97xD energies with the CCSD(T) results. SO<sub>3</sub> is predicted to strongly chemisorb like NO<sub>2</sub>, and CO<sub>2</sub>. For SO<sub>3</sub>, these chemisorption processes tend to favor binding to TMO clusters as SO<sub>4</sub>-2 sulfate in both in the terminal and bridging configurations. Physisorption is not common in these clusters because of the favorability of the SO<sub>4</sub>-2 sulfate structure, and optimizations tend to converge to a terminal sulfate. Furthermore, the energy environment shows a positive correlation between the metal atom size, and the enthalpy/free energy of binding. This work was supported by UNCAGE-ME, an Energy Frontier Research Center led by the Georgia Institute of Technology funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences

### **P1-41 : Quantum-Mechanical Analysis of the Interaction Energy Contributions of H-bonded Biomolecules.**

Rameshwar Lal Kumawat  
School of Chemistry and Biochemistry, Georgia Institute of Technology

Understanding the function of bio-macro-molecules such as DNA or RNA and proteins requires a deep knowledge of non-covalent interactions (NCIs). In this respect, quantum chemical studies of non-covalent complexes provide key steps in this direction. Herein, we report a quantum-mechanical analysis of the interaction energy contributions of H-bonded biomolecules. Coupled-cluster theory through perturbative triples [CCSD(T)] extrapolated to the complete basis set (CBS) limit and SAPT2+(3)(CCD)δMP2/aug-cc-pVXZ (X=D, T) level of theory are considered to estimate very accurately (the so-called "gold-standard" of quantum chemistry) NCI energies. Investigated biomolecules with the SAPT variant of intermolecular perturbation theory, yielding a rigorous decomposition of the interaction energy into electrostatic, dispersion, induction, and exchange contributions. Total interaction energies extrapolated to the CBS limit are compared with corresponding MP2 and CBS and estimated CCSD theory results. Further, a comparison of the NCI energy

contribution of H-bonded biomolecules is done. This study could significantly change the present view on the importance of specific non-covalent H-bonding interactions, for instance, in DNA. Present stabilization energies for H-bonding energies represent the most accurate and reliable values and can be considered as new reference data for future studies.

### **P1-42 : Understanding and Tuning the Spectroscopic and Photophysical Properties of the Flavin Cofactor**

Mohammad Pabel Kabir  
Georgia State University

Flavin is the cofactor for the large and diverse family of proteins called flavoproteins. Upon absorption of blue light, the flavin cofactor excites to the first singlet excited state (S1), and the excited flavin can go back to the ground state (S0) and emit light (fluorescence), intersystem cross to a long-lived triplet state (T1) or can form a radical (D1). However, the kinetics of those processes depends on the surrounding environment. Our long-term goal is to understand why flavin chromophore follows different photochemical processes in different proteins and learn how to tune flavoprotein's photophysical properties through mutagenesis. Therefore, we have developed an automated QM/MM protocol for all redox and protonation states of flavoproteins. However, the QM/MM calculation requires a QM method that will accurately describe the relative energies between ground and excited states of flavin. We performed a benchmark study with different multi-reference methods, active space, and states used in state averaging. We also have generated electrostatic spectral tuning maps (ESTMs) of all redox and protonation states of flavin. The ESTMs will tell us where the positive or negative charge containing amino acid residue should be placed around the flavin cofactor to get a significant change in spectral properties. With the guide of ESTMs, we propose mutations for the spectral tuning of a flavoprotein fluorescent protein (iLOV). We also simulated UV-vis and FT-IR spectra of flavin in a different polar environment. The spectra help us understand how the hydrogen bonding interaction influences absorption energy and the vibrational motion of flavin.

### **P1-43 : CNOT-Efficient Selected Projective Quantum Eigensolver**

Ilias Magoulas  
Emory University

Efficient quantum circuits are necessary for realizing quantum algorithms on noisy intermediate-scale quantum (NISQ) devices. Fermionic excitations defining unitary coupled-cluster (UCC) ansätze give rise to quantum circuits containing CNOT “staircases” whose number scales exponentially with the excitation rank. Given that two-qubit gates dominate gate errors in current NISQ devices, minimizing the number of CNOTs is crucial. Recently, Yordanov et al. constructed CNOT-efficient quantum circuits for both fermionic-(FEB) and qubit-excitation-based (QEB) singles and doubles and illustrated their usefulness

in adaptive derivative-assembled pseudo-Trotterized variational quantum eigensolver (ADAPT-VQE) simulations [Y.S. Yordanov et al., Phys. Rev. A 102, 062612 (2020); Y.S. Yordanov et al., Commun. Phys. 4, 228 (2021)]. In this work, we extend these CNOT-efficient quantum circuits to arbitrary excitation ranks. To illustrate the benefits of these compact FEB and QEB quantum circuits, I will present results of numerical simulations using the recently developed selected projective quantum eigensolver (SPQE), which relies on an adaptive UCC ansatz built from arbitrary-order particle-hole excitation operators. I will show that both FEB- and QEB-SPQE decrease the number of CNOT gates compared to traditional SPQE by factors as large as 15. At the same time, QEB-SPQE requires in general more ansatz parameters, in particular those corresponding to higher than double excitations, than FEB-SPQE, resulting in quantum circuits with larger CNOT counts. Finally, I will show that, although ADAPT-VQE generates quantum circuits with fewer CNOTs than SPQE, SPQE requires orders of magnitude less residual element evaluations than gradient element evaluations in ADAPT-VQE.

### **P1-44 : Transition Metal Hydride Reactivity: Hydride Transfer to Ketones and the Hydricity Scale**

Yiqin Hu

The University of Alabama

Transition metal hydrides play an important role as catalysts. The hydricity of a molecule is defined as the energy needed to break a bond to generate naked hydride. The hydricity of transition metal complexes and ketones have been predicted using density functional theory (DFT) with the B3LYP functional in MeCN using the self-consistent reaction field COSMO model. The cc-pVDZ-PP basis set was used for the transition metals and the DZVP2 basis set for the remaining elements. Proper reference molecules were necessary to obtain reasonable hydricities to avoid issue with predicting the energies of H-. W(CO)<sub>5</sub> and BH<sub>3</sub> were as model compounds to connect with the experimental scale. Co(dmpe)<sub>2</sub>H is more hydritic than Rh(dmpe)<sub>2</sub>H, using their ground states which are both singlets. The order of hydricity of ketone hydrides is: PhCHO CF<sub>3</sub>- > F<sub>3</sub>C-p-PhCHOPh-p-CF<sub>3</sub> > PhCHOPh- > H<sub>2</sub>N-p-PhCHOPh. The reaction energies and transition energy barriers show an excellent correlation, which matches a plot of experimental plot of turnover frequency for the transfer of hydride from a transition metal hydride to a ketone and the hydricity of the ketone. Overall, the more exothermic the reaction is, the lower the activation energy barrier consistent with the Hammond's postulate. The experimental data comes from Pacific Northwest National Laboratory (PNNL). This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, Catalysis Program on a subcontract from Pacific Northwest National Laboratory.

## **P1-45 : Bridging the experiment-calculation divide for solvation with open-source high-throughput explicit solvation software and machine learning**

Eugen Hruska  
Emory University

Solvents are essential in chemistry, yet higher-accuracy explicit solvation simulations are inhibited by the complex multi-step setup. This complexity prevents a rapid prediction of solution-phase molecular properties at the explicit solvation level and inhibits a better understanding of solvation. To fill the gap of software that supports both rapid, and accurate quantum chemistry (QC) calculations at explicit solvation level, we developed AutoSolvate, an open-source high-throughput toolkit for arbitrary solutes and solvents. AutoSolvate allows automated set up of explicitly solvated systems, equilibration, ensemble sampling with QM/MM, and extraction of microsolvated clusters. The equilibration protocol was adapted to enable high-throughput simulation of QM/MM without breaking any bonds. A prerequisite for accurate explicit solvation is the presence of equilibrated solvent shells. The minimum distance distribution function improved for non-spherical systems the validation of multiple solvent shells. Another prerequisite of accurate explicit solvation is the convergence of the simulation result with respect to the explicit solvent shell size. With AutoSolvate we reached faster convergence by including implicit solvent beyond the explicit solvent shell.

A demonstration of AutoSolvate's capabilities is the redox potential calculation of more than a hundred systems for a diverse experimental dataset (ROP313). The simulated explicit solvent redox potentials demonstrate significant systematic charge-dependent errors for the commonly used solvation setups. The successful mitigation of the systematic errors with a machine learning correction indicates further opportunity for QC calculation improvements. These results indicate that wider use of explicit solvation level simulations will lead to a better understanding of solvation.

## **P1-46 : Molecular Dynamics simulations of the intermediate states of BamA folding an outer membrane protein**

Katie Kuo  
Georgia Institute of Technology

BamA, the core component of the  $\beta$ -barrel assembly machinery (BAM) complex, is an integral outer membrane protein (OMP) in Gram-negative bacteria that catalyzes the folding and insertion of OMPs. A key feature of BamA relevant to its function is a lateral gate between its first and last  $\beta$ -strands. Opening of this lateral gate is one of the first steps in the asymmetric-hybrid-barrel model of BamA function. In this study, multiple hybrid-barrel folding intermediates of BamA and a substrate OMP, EspP, were constructed and simulated to better understand the model's physical consequences. The hybrid-barrel intermediates consisted of the BamA  $\beta$ -barrel and its POTRA5 domain and either one, two, three, four, five, or six  $\beta$ -hairpins of EspP. The simulation results support an asymmetric-hybrid-barrel

model in which the BamA N-terminal  $\beta$ -strand forms stronger interactions with the substrate OMP than the C-terminal  $\beta$ -strand. A consistent "B"-shaped conformation of the final folding intermediate was observed, and the shape of the substrate  $\beta$ -barrel within the hybrid matched the shape of the fully folded substrate. Upon further investigation, inward-facing glycines were found at sharp bends within the hybrid and fully folded  $\beta$ -barrels. Together, the data suggest an influence of sequence on shape of the substrate barrel throughout the OMP folding process and of the fully folded OMP.

### **P1-47 : Implementation of the Projective Quantum Eigensolver on a Quantum Computer**

Jonathon Misiewicz  
Emory University

The projective quantum eigensolver (PQE) is an iterative hybrid quantum-classical algorithm inspired by the "gold standard" coupled cluster method of classical computing. This presents the first hardware implementation of PQE on noisy intermediate-scale quantum devices and best practices for its use. We are able to compute an accurate and swiftly converging dissociation curve for  $\text{H}_2$  in the STO-6G basis set using qubit tapering techniques, both for the ground and first excited states. We also study the Transverse Field Ising Model. For this system, we recommend two approaches. With limited computational resources, a judicious choice of qubit encoding allows highly accurate results to be obtained without CNOT gates. But a formally exact circuit gives superior results when combined with advanced error mitigation techniques.

### **P1-48 : A scalable, service-oriented quantum-classical software stack for chemistry research and discovery**

Daniel Claudino  
Oak Ridge National Laboratory

The efforts in turning quantum computing into a routine component of scientific inquiry span a large set of disciplines. Despite recent strides in the development of quantum programming and assembly languages, the software driving most of the quantum push is still very much classical. In this context, we present XACC, a backend-agnostic quantum-classical software, and the many ways in which it can provide the quantum chemistry community with software tools for applications and development. In this presentation, we highlight several aspects that make XACC stand out in the quantum software space: 1) it is written in modern C++, enabling effective resource control; 2) it is modular by design, relying on a vast set of interfaces, which in turn allows easy extensibility via plugin implementation in a service-oriented fashion; 3) it is backend-agnostic, meaning it can target numerical simulators in personal laptops and HPC clusters, and actual quantum

computers requiring modification of just a single line of code; 4) Python users can greatly benefit from the extensive set of Python bindings; 5) end-users have ready and low-barrier access to many of the algorithms of quantum chemistry relevance; 6) entirely open-source. All these considerations are illustrated by detailing pertinent state-of-the-art algorithms and presenting some of the currently implemented plugins for quantum chemistry packages such as Psi4 and PySCF, all the while demonstrating how quantum chemists can take advantage of and contribute to XACC with their own plugins.

### **P1-49 : $\sigma$ -Donation and $\pi$ -Backdonation Effects in Dative Bonds**

Brett Smith

University of Tennessee Knoxville

The nature of donor–acceptor interactions is important for the understanding of dative bonding and can provide vital insights into many chemical processes. Here, we have performed a computational study to elucidate substantial differences between different types of dative interactions. For this purpose, a data set of 20 molecular complexes stabilized by dative bonds was developed (DAT20). [1] A benchmark study that considers many popular density functionals with respect to accurate quantum chemical interaction energies and geometries revealed two different trends between the complexes of DAT20. This behavior was further explored by means of frontier molecular orbitals, extended-transition-state natural orbitals for chemical valence (ETS-NOCV), and natural energy decomposition analysis (NEDA). These methods revealed the extent of the forward and backdonation between the donor and acceptor molecules and how they influence the total interaction energies and molecular geometries. This methodology has since been extended to analyzing the nature of the donor-acceptor interactions between carbene ligands and transition metals. [2]

[1] Smith, B. A.; Vogiatzis, K. D.  $\sigma$ -Donation and  $\pi$ -Backdonation Effects in Dative Bonds of Main-Group Elements. *Journal of Physical Chemistry A*, 2021, 125, 7956–7966.

[2] Liu, S.; Smith, B. A.; Kirkland, J. K.; Vogiatzis, K. D.; Girolami, G. S. Nature of the Short Rh-Li Contact between Lithium and the Rhodium  $\omega$ -Alkenyl Complex [Rh(CH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub>]-. *Inorganic Chemistry*, 2021, 60, 8790–8801.

### **P1-50 : Theoretical computation of X-ray absorption spectroscopy with multi-reference driven similarity renormalization group theory**

Meng Huang

Emory University

The development of high-resolution, time-resolved X-ray spectroscopy has raised the demand for new electronic structure theories for computing core-excited states. In this

study, we extended our multireference driven similarity renormalization (MR-DSRG) method to the core-excited states by combining it with a generalized-active-space self-consistent-field (GASSCF) treatment which accounts for static correlation. We have applied three different levels of MR-DSRG treatments, including perturbative theories (DSRG-MRPT2/3) and iterative theory [MR-LDSRG(2)]. These methods are benchmarked on the C, N, and O K-edge transitions of more than 40 molecules in the gas phase. The GASSCF-MR-DSRG theories show good agreement with the experimental X-ray absorption spectroscopy in both transition energy and intensities. A comparison of the computed vibrational structure for five diatomic molecules with experimental results shows that our method can accurately predict the potential energy curve of core-excited states even far from the equilibrium geometry. Dynamical correlation corrections beyond the second-order level in perturbation theory improve the accuracy of core-excited states, especially in the bond-dissociation region.

## **P1-51 : A Computational Analysis of the Isomerization of Differentially Substituted Phenylimide Rotors**

Cathryn P. Murphy

University of South Carolina, Columbia

Analyses of transition state energies for phenylimide rotor systems illuminate non-covalent interactions which are significant in lowering barriers to rotation. This investigation aimed to provide a complementary analysis of experimental data which have focused on these stabilizing forces, measuring relative reductions in transition state energies far exceeding the thermodynamic strength of the hydrogen bond. The differential capability of ortho-substituent atoms to act as  $\pi^*$  acceptors in the formation of  $n \rightarrow \pi^*$  interactions has been suggested as a potential mechanism of transition state stabilization, but is still disputed compared with the relative significance alternatively of electrostatic interactions. This investigation focused on phenylimide systems computationally, using DFT with dispersion corrections to identify transition state structures of when substituted with functional groups at ortho- and meta- positions relative to imide nitrogen. Hirshfeld partial charges on test substituent groups and imide oxygen atoms in the transition state compared with relaxed structures suggest the presence of electrostatic interactions in the planar configuration of the system which stabilize isomerization by as much as  $\sim 18$  kcal for systems substituted with less electrostatic central atoms for all initial VSEPR configurations but in particular when permitting central atoms to assume geometric positions relative to C=O within the adjacent imide functional group. Differences in trends relating Hirshfeld partial charge and rotational energy barriers between six-membered and five-membered imide ring systems suggest the role of system rigidity in defining transition state geometry for participation in stabilizing through-space interactions.

## **P1-52 : The unusual electronic structures of polynuclear mixed-valence copper compounds containing pyridylamide-based ligands**

Gerard Rowe

University of South Carolina Aiken

Based on a simple pyridyl amide-based ligand system, a wide variety of polynuclear copper compounds can be formed with a variety of oxidation states. In particular, a trapped-valence  $\text{Cu(I)}_2\text{Cu(II)}_3$  cluster that exhibits both strong exchange coupling and spin-frustration can be understood through BS-DFT calculations. In addition, an unusual, mixed-valence  $\text{Cu(I)}_2\text{Cu(II)}_2$  compound adopts an unbridged square arrangement of copper atoms. The electronic structure of this compound highlights an interesting disagreement between the solutions obtained through broken-symmetry DFT and CASSCF, despite predicting comparable singlet-triplet gaps.

## **P1-53 : Implementation of SAPT(DFT) and using hybrid xc kernels for dispersion terms**

Yi Xie

Georgia Institute of Technology

Symmetry Adapted Perturbation Theory (SAPT) has been known as one of the most effective and rigorous theoretical methods in understanding intermolecular forces in chemical systems physically, for the clear physical meaning of its results and high accuracy. Density fitting (DF) approximation has been intensely utilized in the Psi4 package to speedup various calculations, and this work focuses on implementing and testing density-fitted density functional theory (DFT) based SAPT, a variant of SAPT using DFT description of monomers. In our code, the dispersion energy with a hybrid xc-kernel was implemented, and the results of dispersion and other terms were compared to the CCSD(T) benchmark for S66 data set. The timing data of the algorithm was also analyzed, and we concluded that the  $O(N^5)$  scaling is not crucial for smaller systems.

## **Poster Session 2 (Friday, May 20<sup>th</sup>)**

### **P2-1 : Microhydration of Hexachlorophosphate Anion: Structures, Energetics, and Vibrational Frequencies from DFT and ab Initio Computations**

Anna Robertson  
University of Mississippi

The microhydration of the hexafluorophosphate anion has been the focus of many previous experimental and computational studies, due to its use in room temperature ionic liquids. This preliminary study examines the analogous hexachlorophosphate anion and its interactions with one to two water molecules ( $\text{PCl}_6^- (\text{H}_2\text{O})_n$ ,  $n = 1-2$ ), identifying the structural and energetic differences in the microhydration of  $\text{PCl}_6^-$  versus  $\text{PF}_6^-$ . A systematic investigation of the possible orientations of one to two water molecules around  $\text{PCl}_6^-$  was done. Full geometry optimizations were performed using the B3LYP density functional and the ab initio method of MP2 in conjunction with a correlation consistent triple- basis set augmented with diffuse functions on all non-hydrogen atoms (cc-pVTZ for H and aug-cc-pVTZ for P, Cl, and O; denoted as haTZ). Equivalent CCSD(T)/haTZ computations are ongoing. Harmonic vibrational frequencies were also computed for all stationary points using the same methods and basis set. Results will be presented that highlight some distinct structural and energetic differences between the small hydrates of  $\text{PCl}_6^-$  and of  $\text{PF}_6^-$ .

### **P2-2 : Recent Developments and Applications of RT-TDDFT in the MLWF Gauge**

John Bost  
UNC-CH

Real-time, time-dependent density functional theory (RT-TDDFT) has attracted much attention in recent years as a computationally attractive first-principles approach to study a variety of excited state phenomena ranging from optical excitation to electronic stopping in condensed phase systems. Formulating RT-TDDFT in spatially-localized maximally localized Wannier functions (MLWFs) gauge opens up many opportunities in both method development and applications. We employ the MLWF gauge formalism to topics of accelerating hybrid XC functionals, modeling topological pump, and to plasmon dynamics at heterojunction interface, etc.

## P2-3 : Improving the Efficiency of Real-Time Coupled-Cluster Methods

Zhe Wang  
Virginia Tech

Coupled-cluster (CC) theory is one of the most accurate methods for approximating solutions to the electronic Schrödinger equation, though its high-degree polynomial scaling with system size prevents its routine application to large molecules and clusters. Real-time coupled-cluster (RT-CC), among the most advanced time-dependent formalisms for spectroscopic properties and electron dynamics, not only suffers the same computational expense as time-independent CC theory, but is also challenging because of additional demands associated with long propagation times. Inspired by the development of efficient models in machine learning and pioneer applications of graphical processing units (GPUs) to the field of quantum chemistry, this presentation will discuss our recent progress in the implementation of real-time CC (RT-CC) algorithm involving the investigation of precision arithmetics, GPU acceleration, the choice of numerical integrators and etc.

## P2-4 : The Concordant Mode Approach for Computing Harmonic Vibrational Frequencies

Mitchell Lahm  
University of Georgia

The Concordant Mode Approach (CMA) is a method for computing harmonic vibrational frequencies using lower level of theory normal modes as a basis for higher level of theory force constant computation. CMA0 approximates harmonic frequencies at a high level of theory using lower level of theory normal modes to compute the diagonal force constants at a higher level, utilizing stationary points for each Hessian computed. Utilizing CCSD(T)/cc-pVDZ and B3LYP/6-31g(2df,p) starting Hessians for CMA0 on 116 molecules of the G2 test set yields a root mean squared deviation (RMSD) of harmonic frequencies from CCSD(T)/cc-pVTZ of  $0.48 \pm 0.47 \text{ cm}^{-1}$  and  $0.77 \pm 0.76 \text{ cm}^{-1}$ , respectively. CMA exhibits an inherent coordinate dependence.

## P2-5 : ADAPT-VQE is insensitive to rough parameter landscapes and barren plateaus

Harper Grimsley  
Virginia Tech

Variational quantum eigensolvers (VQEs) represent a powerful class of hybrid quantum-classical algorithms for computing molecular energies. Various numerical issues exist for these methods, however, including barren plateaus and large numbers of local minima. In

this work, we consider Adaptive, Problem-Tailored (ADAPT)-VQE ansätze, and examine how they are impacted by these local minima. We find that while ADAPT-VQE does not remove local minima, the gradient-informed, one-operator-at-a-time circuit construction seems to accomplish two things: First, it provides an initialization strategy that is dramatically better than random initialization, and which is applicable in situations where chemical intuition cannot help with initialization, i.e., when Hartree-Fock is a poor approximation to the ground state. Second, even if an ADAPT-VQE iteration converges to a local trap at one step, it can still "burrow" toward the exact solution by adding more operators, which preferentially deepens the occupied trap. This same mechanism helps highlight a surprising feature of ADAPT-VQE: It should not suffer optimization problems due to "barren plateaus". Even if barren plateaus appear in the parameter landscape, our analysis and simulations reveal that ADAPT-VQE avoids such regions by design.

## **P2-6 : Investigation of Competing Halogen and Hydrogen Bonding Motifs in Simple Mixed Dimers of HCN and HX (X = F, Cl, Br, I)**

Morgan Perkins  
University of Mississippi

Small molecular systems, such as the HCN/HX series (where X = F, Cl, Br, I), are particularly amenable to high-resolution, gas-phase experimental study and high-accuracy computational analysis, which can provide insight into the interplay of theory and experiment. For the X = F dimer, two different configurations have been identified both experimentally and computationally: a linear structure where HF is the hydrogen bond (HB) donor and a higher-energy, non-linear (bent) structure where HCN donates the HB. In order to compare the well-studied fluorine complex with the remaining halide dimers, we performed full geometry optimizations and harmonic vibrational frequency computations on the HCN/HX dimers and their associated monomers using CCSD(T) with a series of correlation consistent basis sets augmented with diffuse functions on all atoms except hydrogen, i.e. cc-pVYZ for H; aug-cc-pVYZ for C, N, F, Cl, and Br; and aug-cc-pVYZ-PP for I (which includes a relativistic pseudopotential used for the 28 core electrons of all I atoms), where Y = T, Q, and 5. We identified linear and bent hydrogen bonded minima for X = Cl, Br, and I, analogous to those identified for HCN/HF. In addition, a linear, halogen bonded minimum was identified for X = Cl, Br, and I. Geometric properties and energetics are compared across the series. The hydrogen and halogen bonded local minima for the Cl, Br, and I dimers are energetically competitive with each dimer's respective global minimum. Additionally, harmonic vibrational frequency shifts provide potential guides for differentiating between the different minima in experiment.

## **P2-7 : A high-level theoretical study of ethynyl radical hydrogen abstractions**

Laura Olive  
University of Georgia

The ethynyl radical, C<sub>2</sub>H, is one of the most abundant polyatomic radicals in the interstellar medium and plays an important role in fuel-rich hydrocarbon combustion processes. Hydrogen-atom abstraction is among the most prevalent reactions for the ethynyl radical and is often the main reaction pathway. In this study, the C<sub>2</sub>H + HX → C<sub>2</sub>H<sub>2</sub> + X, where HX = H<sub>2</sub>CO, HNCO, HOCN, HONO, and CH<sub>3</sub>OH, reactions have been investigated at a rigorously high level of theory at CCSD(T)-F12a/cc-pVTZ-F12. These molecules were chosen because they can be found in either interstellar or combustion environments. Various additive energy corrections have been included to converge the relative enthalpies of the stationary points to subchemical accuracy ( $0.5 \leq \text{kcal mol}^{-1}$ ). Accurate kinetics were acquired over a wide range of temperatures (20 - 5000 K), which may be useful for future studies of these reactions.

## **P2-8 : Simplified LR-TDDFT/ZORA approach for generating spin-orbit couplings for x-ray absorption spectra**

Sarah Pak  
University of Memphis

Transition metals represent a space of continual interest due to their complex electronic structure and the diverse range of possible ligands and oxidation states. Studies of transition metal complexes often rely on X-ray spectroscopies (usually at the L or M edges) and computational methods to explain spectral features and help design new experiments. Most computational approaches either account for relativistic effects at the scalar level, by omitting spin-orbit coupling terms, or completely neglect them sacrificing accuracy in favor of a lower computational cost. On the other hand, explicit ab-initio treatments of spin-orbit couplings are costly and labor intensive, restricting their applications to smaller atomic systems. In the present work, we propose a simplified approach based on linear-response time-dependent density functional theory (LR-TDDFT) and the relativistic two-component zeroth-order regular approximation (ZORA) to generate spin-orbit couplings of closed-shell molecular systems. The proposed approach was validated by computing the L-edge absorption spectra of several first and second row transition metal complexes. The method reproduces experimental data with satisfactory accuracy at a fraction of the cost of exact two-component or fully relativistic methods.

## **P2-9 : QM-cluster modeling of bioremediation and bioconversion studies of lignin with cytochrome P450 Enzyme GcoA.**

Tejaskumar Suhagia  
University of Memphis

Biological funneling of aromatic compounds produced from lignin is a viable method for monetizing its catalytic depolymerization products. For crucial reactions, such as O-demethylation, effective enzymes will be required in industrial procedures for aromatic bioconversion. We built QM-cluster models of cytochrome P450 Enzyme GcoA in complex with various catecholates using the Residue Interaction Network-based Residue Selector (RINRUS) software package. Our previous study has used an X-ray crystal structure with guaiacol and found good agreement with experiment. Rather than starting with the X-ray crystal structure, we employed production-level trajectories from 1.0 - 1.2  $\mu$ s MD simulations. From the selected MD frame, the aromatic O-demethylation capacity of cytochrome P450 enzyme GcoA was computed using Density functional theory (DFT). Hydrogen atom transfer kinetics and thermodynamics were determined for guaiacol and six additional substrates (3-methoxycatechol, anisole, guaethol, 2-methylanisole, vanillin, and syringol). A structure-activity relationship (SAR) using atomic level models was formulated between estimated activation free energies and catalytic constants (kcat) of all seven substrates, which will aid in fine-tuning the cytochrome P450's promiscuity and hence its lignin-processing capabilities.

## **P2-10 : Modulating spin-state transition temperatures with an optical cavity**

Colin Campbell  
Florida State University

We are using quantum electrodynamical density functional theory (QEDFT) to predict transition temperatures of FeII spin-crossover (SCO) complexes that are coupled to an optical cavity at varying electron-photon coupling strengths. In general, transition temperatures are found to decrease with increasing coupling strength. We also attempt to develop a simple protocol whereby changes to transition temperatures can be estimated from quantities obtained from cavity-free DFT calculations (specifically, the dipole self-energy, DSE). Unfortunately, this protocol consistently overestimates the changes induced by the cavity, highlighting the importance of relaxation effects captured by the full QEDFT simulations.

## **P2-11 : Computational Studies of Photocatalytic Transformations of Alkenes and Arenes**

Sharath Chandra Mallojjala  
SUNY Binghamton

Photocatalytic functionalization of arenes and alkenes have garnered significant interest of late as greener alternatives to traditional transition metal catalysis. Despite the rapid progress in this area, there is a significant dearth in our understanding of these reactions and the effects of the photocatalysts used. Herein, we report our investigations into amination of alkenes and arenes using density functional theory and Marcus theory to provide a general mechanistic platform for understanding the effects of photocatalysts in these transformations. These computational results were benchmarked against experimental kinetic isotope effects to further validate our mechanistic models.

## **P2-12 : Focal Point Analysis of the Low Temperature Combustion of Dimethylether**

Alexander G. Heide  
University of Georgia

In order to provide a chemically accurate surface, we have applied focal point analysis (FPA) to the decomposition of the adduct of dimethylether radical + O<sub>2</sub>. The ideal procedure for focal point analysis, and other high accuracy composite methods would utilize quadruple-zeta or, at least, triple-zeta quality basis sets for the optimization of all stationary points at the CCSD(T) level of theory; however, this becomes intractable for moderately sized molecules (>6 heavy atoms). Therefore, we test a modification to the standard FPA approach for combustion processes: utilizing a composite gradient method to achieve CCSD(T)/cc-pVQZ quality geometries at significantly reduced cost compared to the CCSD(T)/cc-pVTZ level of theory. For the surface, the CCSDT(Q)/CBS energy is targeted through basis set extrapolations up to CCSD(T)/cc-pV5Z and correlation treatment up through CCSDT(Q)/cc-pVDZ. Exact two-component scalar-relativistic, diagonal Born-Oppenheimer, frozen-core, and zero-point vibrational energy corrections are also applied.

## **P2-13 : Importance of Favorable Non-Covalent Contacts in the Stereoselective Synthesis of Tetrasubstituted Chromanone**

Laura Andreola  
University of Georgia

Automated transition state (TS) structure computations for a recently reported Pd-catalysed conjugated addition of arylboronic acids to 2-substituted chromones (Chem Sci, 2020, 11, 4602) reveal unexpected conformations of the key stereodifferentiating benzyl group on the

pyridine-dihydroisoquinoline (PyDHIQ) ligand. Detailed analysis shows that stereoselectivity is determined primarily by favorable non-covalent contacts between this benzyl group and the substrates, combined with torsional strain in the primary TS structure leading to the minor stereoisomer. This finding should inform further use and analysis of PyDHIQ and related ligands in other stereoselective transformations.

## **P2-14 : Multiscale modeling of ethylene oxidation on silver catalysts: Reaction pathway and selectivity analysis**

Siyuan Wu  
Auburn University

Ethylene oxide (EO) is one of the largest-scale products of the chemical industry and the global demand of EO market kept increasing in the past years. Accounting for the magnitude of production along with the potential decrease of reactant waste and slowing of catalyst deactivation, the improvement of selectivity within the ethylene epoxidation process is predicted to result in a tremendous economic upturn. In this project, we focused on the surface catalytic mechanism of ethylene oxidation to study the internal causes affecting the EO selectivity.<sup>1</sup> A combined multi-reaction network of ethylene oxidation process was built to deliver a self-consistent and detailed study of all possible elementary steps for partial and complete oxidation of ethylene. The details of the combustion processes in ethylene oxidation were also studied. Energetic changes of related species and pathways were calculated with plane-wave Density Functional Theory (DFT). Key surface species of both mechanisms were identified to suggest the factors for the observed productivity and selectivity of target products. The results are consistent with previous experimental and theoretical literatures which did not employ DFT and provide a great number of details on selectivity trends in ethylene oxidation network. Lastly, our study demonstrates how fundamental theoretical investigations and multi-scale modeling techniques are impacting the advancement of rational catalyst design and microkinetic modeling techniques in the light hydrocarbon processing industry.

1. Wu, S.; Tatarchuk, B. J.; Adamczyk, A. J., Ethylene oxidation on unpromoted silver catalysts: Reaction pathway and selectivity analysis using DFT calculations. *Surface Science* 2021, 708, 121834.

## **P2-15 : Reaction kinetics insights for hydrogen shift in silicon nitride nanomaterials using a supervised machine learning approach**

Yeseul Choi  
Auburn University

Interest and demand for more powerful and efficient silicon-based semiconducting materials continuously increase. Among various semiconducting materials, silicon nitride is popularly used as insulating, masking, and passivating materials due to its wide band-gap in the microelectronics industry. To produce silicon-based nanoparticles, there have been various methods such as pyrolysis, chemical vapor deposition, atomic layer deposition and sputtering. Despite pyrolysis being a basal protocol to synthesize silicon-alloyed nanoparticles and understand the synthetic mechanism, the fundamental understanding of the hydrogenated silicon nitride synthesis process is still unclear. To better understand the synthetic reaction mechanisms, more detailed knowledge of the kinetics of the elementary reaction classes is still needed. As one of the primal reaction classes, we investigated 52 hydrogen shift reactions for silicon nitrides. H shift reaction in silicon nitride was classified into three different types, and detailed reaction pathways of acyclic and cyclic monofunctional silicon nitrides were studied. We calculated the rate coefficients for 52 hydrogen shift reactions for silicon nitrides containing up to 6 atoms of silicon and nitrogen using the density functional theory and statistical thermodynamics. And Arrhenius parameters and general models suitable for each type were derived through regression analysis. The generalized models were validated using k-fold cross-validation and bootstrapping regression methods.

## **P2-16 : The Effects of Strong Correlation and Symmetry in the ADAPT Variational Quantum Eigensolver**

Luke Bertels  
Virginia Tech

Variational quantum eigensolvers (VQEs) are a class of hybrid classical-quantum computing methods which prepare and measure a parameterized state on quantum hardware and optimize the wavefunction parameters on classical hardware. While many VQEs begin with a predetermined wavefunction ansatz, ADAPT-VQE builds a problem-tailored ansatz starting from a reference state and adaptively adds operators to the ansatz from a pool of operators as chosen by the system. This flexibility to choose shorter circuits is preferable in the current noisy intermediate-scale quantum regime of quantum computing for simulating molecular systems. Because quantum simulation of molecular systems is expected to provide the strongest advantage over classical computing methods for systems exhibiting strong electron correlation, it is critical that the performance of VQEs be assessed for strongly correlated systems. As a proxy for strong correlation in chemical systems, we investigate the performance of the ADAPT-VQE on the "fermionized" anisotropic Heisenberg model, where the anisotropy parameter allows for control over the level of

correlation in the system. Additionally we analyze the role that different orbital mappings of the fermionic Hamiltonian and choices of reference state play on the compactness and performance of ADAPT-VQE. Increasing the strength of correlation in the system is seen to deepen the circuits required for ADAPT-VQE to converge, while the consistency between the symmetries of the Hamiltonian and both the operator pool and reference state leads to significantly shorter circuits than their symmetry-broken counterparts.

### **P2-17 : Investigation of an isolated nitrogen-vacancy center in diamond using projection-based embedding with periodic boundary conditions.**

Robert Smith  
Virginia Tech

Color center defects have a variety of potential applications, such as quantum sensing and qubit platforms. The most extensively studied example of the known color center defects is an anionic nitrogen-vacancy (NV<sup>-</sup>) in bulk diamond. However, modeling deep, isolated, charged defects in a bulk material remains a challenge. Typically, there is a choice between using an electron correlation capturing method in a finite cluster model or using a supercell with periodic boundary conditions that generally require the more favorably scaling density functional theory. This work explores the use of projection-based embedding with periodic boundary conditions to model NV<sup>-</sup> in bulk diamond within our recently developed partitioning approach. Formal background and proof of principle calculations will be discussed

### **P2-18 : Quantifying protein degradation: Theoretical insights on the mechanisms of non-enzymatic peptide hydrolysis**

Katherine Lawson  
Auburn University

Theoretical studies on amide hydrolysis are of interest due to their impact on the drug discovery and drug delivery sector of the biopharmaceutical industry. Therapeutic proteins account for a significant portion of the biopharmaceutical industry, while biopolymers are an attractive drug delivery system due to their ability to degrade within the body after delivering the desired therapeutic.[1,2] For degradation reactions in which therapeutic proteins and biopolymers may degrade through multiple different mechanisms, each mechanism must be analyzed to observe shared trends between reaction pathways. Additionally, due to the influence of electrostatic interactions upon reaction favorability, the interactions between the biopolymer and its solvated environment must also be quantified to obtain a more robust understanding of the modeled system. For this purpose, we conducted a computational study of a small subset of dipeptides to predict the thermodynamic properties of mechanisms of non-enzymatic amide hydrolysis to generate a

self-consistent database of thermochemical and kinetic values over a range of solvent dielectrics using Density Functional Theory (DFT). Additionally, we were able to generate a statistically significant linear correlation to predict the activation energy of the rate-determining step of the stepwise mechanism as a function of the solvent dielectric, and match our findings against qualitative and quantitative experimental trends.

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## **P2-19 : Core-Valence Separated Equation-of-Motion Coupled-Cluster for K and L edge calculations**

Brandon Cooper  
Florida State University

Equation-of-motion coupled-cluster(EOM-CC) calculations can provide an accurate description of excited states of molecular systems. These calculations carry a large cost however, particularly when one is interested in the high energy states associated with core-level process such as those involved in X-ray absorption spectroscopy. This work considers the utility of the core valence separation (CVS) approximation wherein excitations are only considered if they involve at least one core orbital. This approximation greatly reduces the cost of calculating core-level features such as K and L-edges.

## **P2-20 : The Atmospheric Importance of Methylamine Additions to Criegee Intermediates**

Henry Mull  
University of Georgia

Criegee intermediates are important targets for study in atmospheric chemistry because of their capacity to oxidize airborne species. Among these species, ammonia has received critical attention for its presence in polluted agricultural or industrial areas and its role in forming particulate matter and condensation nuclei. Although methylamine has been given less attention than ammonia, both theoretical and experimental studies have demonstrated that the additional methyl substitution on the ammonia derivatives increases the rate constants for some systems. This suggests that the methylamine addition to Criegee

intermediates could be more significant to atmospheric processes. In this work, geometries are optimized at the DF-CCSD(T)/ANO1 level for the methylamine addition reactions to the simplest Criegee intermediate and the anti- and syn-methylated Criegee intermediates. Energies for each stationary point were computed at the CCSD(T)/CBS level with corrections from the CCSDT(Q) method. Rate constants are obtained for each reaction using canonical transition state theory. Although methylamine addition proved to be a more favorable reaction relative to ammonia addition, the significantly lower concentration of atmospheric methylamine limits the prevalence of these reactions, even in the most optimal conditions. It is unlikely that the methylamine addition to Criegee intermediates will contribute significantly to the consumption of Criegee intermediates in the atmosphere.

## P2-21 : Genetic Algorithms for Inorganic Oxides

Michael Valencia

University of Mississippi

Quartic force fields (QFFs) are a simple and elegant method for computing the internuclear potential term in the Watson Hamiltonian. This method is known to give agreement with experimental results between 1 and 5 wavenumbers for fundamental modes. This procedure follows the basic steps of calculating displacement energies, deriving the force constants (changes in energy with respect to displacement) using finite differences, and finally calculating the molecular vibrational frequencies by leveraging vibrational second-order perturbation theory (VPT2).

The new program developed by the author reverses the final conversion from force constants to molecular vibrational frequencies.

This process is non-trivial, since hundreds of variables are condensed to far fewer vibrational frequencies. A genetic algorithm (GA) is capable of performing this task.

A genetic algorithm is a metaheuristic modeled after the principles of evolution proposed by Charles Darwin. In effect, organisms have a given fitness in the environment, i.e., the problem space, and compete to pass on their "genes". In this project, an organism's fitness was an optimization solution for the minimum difference between the wanted vibrational frequencies and the organism's vibrational frequencies. Thus, the most fit organisms pass on their genes and influence the next generation. Eventually, this population will trend towards the minimum on the problem surface, thereby yielding the force constants of interest. To date, this program has successfully calculated the force constants for water in less than 24 hours

## **P2-22 : Automated Generation and Theoretical Dye Prediction Website for Dye Sensitized Solar Cells**

Austin Wallace  
University of Mississippi

A database containing theoretical predictions for thousands of dyes for dye-sensitized solar cells (DSCs) is now accessible through an interactive website. DSCs use organic sensitizers to absorb light, making them a cheaper and environmentally less toxic option than current silicon-based solar cells. The sensitizing dyes can be tuned to absorb the sunlight's photons, enabling dyes to be stacked within a DSC to improve the entire DSC's efficiency. With many cost limitations to experimentally construct a database of dyes, the usage of time-dependent density functional theory (TD-DFT) can provide vertical transition energy predictions proactively to investigate dyes before investing in their synthesis. Additionally, through using a triple donor method with an electron acceptor, backbone, and donor piece to generate structures, theoretical work has generated a dye database of over 2600 structures with more structures being added regularly. Each structure is optimized with B3LYP/6-311G(d,p) before calculating electronically excited states with CAM-B3LYP/6-311G(d,p), BHandHLYP/6-311G(d,p) and PBE0/6-311G(d,p). A least squares fitting of CAM-B3LYP and PBE0 excitation energies with 72 experimental values provides an improved excitation energy prediction with a mean absolute error of 0.13 eV. The resulting data is readily accessible through a website to enable easy inspection of theoretical dyes for favorable photophysical properties, such as HOMO, LUMO, and  $\lambda_{\text{max}}$  energy predictions. Furthermore, the website provides a data analysis tool for calculating  $\lambda_{\text{onset}}$  values for both absorption and emission spectra. Ultimately, this computational approach combined with a website interface will expedite the search for dyes and will also provide guidance for future synthetic targets.

## **P2-23 : Confirmation of Gaseous Methanediol from State-of-the-Art Theoretical Rovibrational Characterization**

Noah Garrett  
University of Mississippi

State-of-the-art QFFs are used in order to generate a theoretical spectra to validate the successful synthesis of gas phase methanediol, which was recently reported for the first time. The F12-TZ-cCR and F12-DZ-cCR QFF approaches, which are based on explicitly correlated CCSD(T)-F12 energies, are used while accounting for core correlation and scalar relativistic effects. Using spectroscopic parameters from the C2 isomer of methanediol, a spectrum is generated which matches several key features of the previously reported experimental spectrum. The band origin of this feature differs by less than 3 wavenumbers from experiment. Additionally, it is found that the average difference between F12-TZ-cCR and

F12-DZ-cCR is only 4 wavenumbers for vibrational frequencies and 25 MHz for rotational constants.

## **P2-24 : Overcoming Artificial Multipoles in Intramolecular Symmetry-Adapted Perturbation Theory**

Du Luu

Department of Chemistry and Biochemistry, Auburn University

Symmetry-adapted perturbation theory (SAPT) is a well-developed methodology to describe and analyze non-covalent interactions between molecules. For analogous weak interactions within a molecule, the first versions of intramolecular SAPT (ISAPT) lead to valuable insights into the relative contributions of interaction energies. ISAPT aims to decompose the interaction of two nonbonded molecular fragments A and B covalently connected by a linker C. While some fragmentation patterns lead to meaningful ISAPT energy contributions, in other cases, unphysical results are observed, for example, repulsive electrostatic energies between hydrogen-bonded fragments. The reasons for this unphysical behavior relate to the treatment of interfragment link bond orbitals. In the original ISAPT formulation, link bond electrons with the balancing nuclear charges are assigned to the linker C. Unfortunately, this leads to artificial dipole moments at the interfragment boundaries, as the link A and B atoms are missing electrons on one of their hybrid orbitals. To tackle this problem, we propose a reassignment of the ISAPT link electrons so that each fragment, A/B or C, accounts for one electron from the link hybrid orbital. When this hybrid is constructed in the space of intrinsic atomic orbitals, the magnitude of spurious dipole moments is significantly reduced, leading to reasonable and basis-set stable values for all ISAPT corrections and all fragmentation patterns. We illustrate the performance of the new ISAPT variant on various systems exhibiting nonbonded intramolecular interactions, including pentanediols, linear and branched alkanes, and closed and open conformations of halogen- $\pi$  bonded systems that were proposed as molecular balances.

## **P2-25 : Theoretical Rovibronic Characterization of H<sub>2</sub>O<sup>+</sup> and H<sub>2</sub>CO<sup>+</sup> Using Electronically Excited State Quartic Force Fields**

Megan Davis

University of Mississippi

Recently proposed (T)+EOM/CcCR quartic force fields (QFFs) are used to calculate theoretical rovibrational properties of low-lying electronically excited states of water cation (H<sub>2</sub>O<sup>+</sup>) and formaldehyde cation (H<sub>2</sub>CO<sup>+</sup>), important species in understanding comet chemistry. The (T)+EOM approach approximates the potential surface of the target state as a combination of CCSD(T) ground state energies

and EOM-CCSD excitation energies, extrapolated to the complete basis set limit with additional corrections for core correlation and scalar relativistic effects. The resulting vibrational frequencies, rotational constants and other spectroscopic data of interest are benchmarked against QFFs performed at the EOM-CC3/avtz level as well as to available experimental data. Preliminary data shows a mean absolute difference of 20.2 wavenumbers between (T)+EOM/CcCR and EOM-CC3 for the B2 state of H<sub>2</sub>O<sup>+</sup>.

## **P2-26 : Energetics of Criegee Intermediates and the Possible Limitations of CCSDT(Q)**

James Begley  
University of Georgia

Criegee intermediates, formed from the ozonolysis of alkenes, are thought to have a role in atmospheric chemistry, from forming acid rain to impacting the oxidizing capacity of the troposphere. Although numerous studies have been conducted since their discovery, the synthesis of these species in the laboratory has ushered in a new wave of studies on these species, both theoretically and experimentally. In many of these theoretical studies, high-order corrections for correlation energy are included to account for the mid multi-reference character found in these systems. Many of these studies include a focus on kinetics, therefore calculated energies must be accurate (<1 kcal/mol in error). However, it has been previously suggested that CCSDT(Q), typically used to assess the correlation energy convergence, gives a poor description of Criegee intermediates. In this study, we compute the enthalpy of formation for a small set of Criegee intermediates, including higher order corrections for correlation energy up to CCSDTQ(P). Employing focal point analysis, the magnitude of different contributions to the energetics of these systems are compared. We hope that this data serves as a definitive reference for energy computations for these challenging molecules.

## **P2-27 : F12-TZ-cCR: A Methodology for Faster and Still Highly-Accurate Quartic Force Fields**

Alexandria Watrous  
University of Mississippi

The F12-TZ-cCR quartic force field (QFF) methodology, defined here as CCSD(T)-F12b/cc-pCVTZ-F12 with further corrections for relativity, is introduced as a cheaper and even more accurate alternative to more costly composite QFF methods like those containing complete basis set extrapolations within canonical coupled cluster theory. F12-TZ-cCR QFFs produce B and C principal rotational constants within 7.5 MHz of gas-phase experimental values for tetra-atomic and larger molecules, offering near spectroscopic accuracy in these constants

for the first time. Further, F12-TZ-cCR offers an order of magnitude decrease in the computational cost of highly-accurate QFF methodologies accompanying this increase in accuracy. An additional order of magnitude in cost reduction is achieved in the F12-DZ-cCR method, while also matching the accuracy of the traditional composite method's B and C constants. Finally, F12-DZ and F12-TZ are benchmarked on the same test set, revealing that both methods can provide anharmonic vibrational frequencies that are comparable in accuracy to all three of the more expensive methodologies, although their rotational constants lag behind. Hence, the present work demonstrates that highly-accurate theoretical rovibrational spectral data can be obtained for a fraction of the cost of conventional QFF methodologies, extending the applicability of QFFs to larger molecules.

### **P2-28 : Group 15 and 16 nitrene-like pnictinidenes**

Erica Mitchell

Center for Computational Quantum Chemistry

Pnictinidenes are an increasingly relevant species in main group chemistry and generally exhibit proclivity for the triplet electronic ground state. However, the elusive singlet electronic states are often desired for chemical applications. We predict the singlet-triplet energy differences of simple group 15 and 16 substituted pnictinidenes (Pn-R; Pn = P, As, Sb, or Bi) with highly reliable focal-point analyses targeting the CCSDTQ/CBS level of theory. The only cases we predict to have favorable singlet states are P-PH<sub>2</sub> and P-NH<sub>2</sub>. Trends observed in the singlet-triplet energy differences are discussed in light of the geometric predictions to elucidate some of the important electronic structure features. This work provides a rigorous benchmark for the singlet-triplet energy differences of fundamental Pn-R moieties and provides a firm foundation for the continued study of heavier pnictinidenes.

### **P2-29 : Automated Generation and Theoretical Predictions for Potential Near-Infrared (NIR) Dye Sensitized Solar Cells: Theoretical Dye Properties**

Taylor Santaloci

University of Mississippi

Dye-sensitized solar cells (DSCs) are simple to synthesize, low in cost, and tunable for usage. This makes them exciting candidates to replace silicon solar cells, which are difficult to manufacture and problematic to deploy. Additionally, they are susceptible to damage in extreme environments. Differently, DSCs are flexible and easily repaired making them ideal candidates for various applications. Current DSC technologies could be improved by varying the structure of the organic dye molecule in order to provide longer wavelength absorption in organic molecules. The triple donor method is one of the most common synthesis

strategies for DSC construction. This method involves the combination of an electron donor, backbone, and electron acceptor to create the dye. Computational chemistry has the capability to automate this process by combining the three structures virtually and to provide the optical properties for the resulting dyes. The present work has analyzed over 2000 potential dyes in such a process. The theoretical dyes undergo B3LYP/6-311G(d,p) geometry optimizations, and the absorption properties are computed with CAM-B3LYP/6-311G(d,p), BHandHLYP/6-311G(d,p) and PBE0/6-311G(d,p). In every instance, CAM-B3LYP excitation energies are higher in energy than the benchmark, and PBE0 is higher. The combination of TD-DFT methods and a least squares fit (LSF) model are combined to produce a predicted value. Moreover, this computational methodology opens the door for faster utilization in novel applications such as human spaceflight and planetary colonization.

## **P2-30 : Formation of Monosubstituted Cyclopropenylidenes in the Interstellar Medium**

Athena Flint

University of Mississippi

The formation mechanisms for three monosubstituted cyclopropenylidene molecules currently undetected in the interstellar medium are reported, representing new candidates for spectroscopic detection. The recent detection of ethynyl cyclopropenylidene in the ISM has prompted new investigations into the chemistry of the ubiquitous cyclopropenylidene molecule. High-accuracy CCSD(T)-F12b/cc-pVTZ-F12 calculations are used to optimize structures and generate harmonic frequencies for minima along each pathway, and ground- and excited-state potential energy scans are used to connect structures along the pathway. Molecular orbital analyses illuminate the differing abilities of different radical species to successfully bind to cyclopropenylidene under low-energy conditions. The cyano radical is found to bind to cyclopropenylidene in a similar manner to the ethynyl radical. Interestingly, the hydroxy and fluoro radicals can more easily bind to the carbene site than can the cyano or ethynyl radicals, and open up a new route for product formation. The attempted functionalization by twelve new radical species results in the stratification of cyclopropenylidene substitution into two categories - functionalization with an electronegative, sterically small group that will participate in aromatic electron donation, or functionalization with radicals containing triple bonds that force electron delocalization throughout the substituent. These results steer astrochemistry towards some of the more likely chemical reactions occurring with other gas-phase aromatic species that litter the ISM.

## **P2-31 : Spectral Signatures of Hydrogen Thioperoxide (HOSH) and Hydrogen Persulfide (HSSH): Possible Molecular Sulfur Sinks in the Dense ISM**

Charles Palmer  
University of Mississippi

Molecular sulfur in the dense interstellar medium (ISM) still eludes astronomical observation; but, somewhere there exists a molecular sulfur sink in the dense ISM where it may be hiding. Recent discovery of hydrogen peroxide (HOOH), and its suggested formation pathway, may provide a starting point for this investigation in the form of two sulfur-bearing analogs of HOOH: hydrogen thioperoxide (HOSH) and hydrogen persulfide (HSSH). The present theoretical study couples the accuracy in the anharmonic fundamental vibrational frequencies from explicitly correlated coupled cluster theory with the accurate rotational constants generated by canonical high-level coupled cluster theory to produce rovibrational spectra for use in the potential astronomical observation of HOSH and HSSH. The  $\nu_6$  mode for HSSH at  $886.1\text{ cm}^{-1}$  is within  $0.2\text{ cm}^{-1}$  of gas phase experiment, and the  $B_0$  rotational constant for HSSH of  $6979.5\text{ MHz}$  is within  $9.0\text{ MHz}$  of the experimental benchmarks implying that the current methodology is accurate and reliable. The most intense vibrational transition for each molecule are the torsions, with HOSH having the more intense transition of  $117\text{ km/mol}$  compared to HSSH's intensity of  $23\text{ km/mol}$ . Further more HOSH has a larger net dipole moment of  $1.60\text{ D}$  compared to HSSH's  $1.15\text{ D}$ . While HOSH may be the more likely candidate of the two for possible astronomical observation via vibrational spectroscopy due to the notable difference in their intensities, both HSSH and HOSH have large enough net dipole moments for detectability by rotational spectroscopy to discover a possible molecular sulfur sink in the dense ISM.

## **P2-32 : Accurate Three-body Noncovalent Interactions: the Insights from Energy Decomposition**

Sharon Ochieng  
Auburn University

Noncovalent interactions exhibit a wide range of binding characteristics governing the complex structure, energetics, and material self-assembly; as such, accurate models are required to predict these interactions. While there exist ample datasets of accurate interaction energies for bimolecular two-body complexes, the benchmark data for nonadditive three-body interactions are quite scarce. In this work, we present a benchmark dataset of noncovalent interaction energies for a diverse selection of 10 heteromolecular trimers in 20 structures. The new 3BHET dataset presents complexes that model different interactions ranging from  $\pi$ - $\pi$ , anion- $\pi$ , cation- $\pi$ , and various motifs of hydrogen and halogen bonding and their combinations within each trimer. A detailed symmetry-adapted

perturbation theory (SAPT)-based energy decomposition analysis shows that, at the two-body level, 3BHET spans the electrostatic and dispersion-dominated regions of the ternary diagram. Among the nonadditive three-body contributions, the induction energy plays a particularly important role.

### **P2-33 : Nitrate Reduction by a Surface-Conjugated Electrocatalyst: A Computational Determination of the Active Catalyst and an Observed Intermediate**

Harrison Worster

North Carolina State University

An experimentally synthesized iron-based graphite conjugated electrocatalyst (GCC-FeDIM) for use in nitrate reduction to ammonia has been characterized and studied. This catalyst, which is synthesized in a flexible two-step process, has been shown to favorably reduce aqueous nitrate into ammonia. This process is highly beneficial in water treatment for removing the harmful nitrate ion from the water, which in high quantity cause dead zones which have harmful effects on human and aquatic life. This catalyst, which has been shown to be favorable to reduce both nitrate and nitrite, exhibits one electron reduction at -0.22 V vs SCE, as well as a pH dependence when in the presence of the substrate. Additionally, EXAFS results indicate the presence of an unknown intermediate with a shorter Fe-N bond length at 1.65 Å. The aim of this computational study was to determine the pathway to formation of the active catalyst prior to the nitrate reduction process, as well as the identity of the unknown intermediate. The proposed catalyst is an Fe(II)DIM(Cl)(NO<sub>3</sub>) catalyst, which goes through a proton-coupled electron transfer (PCET) reduction at -0.17 eV VS SCE at pH 6, which is in good agreement with experimental potential. The observed intermediate has been determined to be an [Fe(II)DIM(NO)]<sup>3+</sup> complex, with a calculated Fe-N bond length of 1.61 Å, in good agreement with the observed 1.65 Å.

### **P2-34 : One- and Two-Particle-Mediated RET Between a Pair of Chiral Molecules**

Akbar Salam

Wake Forest University

Mediation of resonance energy transfer (RET) between a pair of chiral molecules by one or two passive electric dipole polarizable bridging particles is studied using quantum electrodynamics (QED) theory [1,2]. In this framework, energy is conveyed via the propagation of a single virtual photon between any two coupled centres [3,4]. Isotropic Fermi golden rule transition rates are calculated for direct and relayed transfer of excitation, and both routes are found to be discriminatory, depending on the handedness of the donor and acceptor species [5-7]. Indirect transfer is a maximum when the three or four bodies lie on a straight line. Interestingly, a multi-level model of the mediator is necessary

for bridge-assisted RET to occur. Valuable insight is acquired of energy transfer taking place between optically active systems in a dielectric environment.

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## **P2-35 : Rovibrational Quartic Force Fields of Magnesium Tricarbide - Multireference Character Thwarts a Full Analysis of All Isomers**

Donatus Atsu Agbaglo  
University of Memphis

Magnesium tricarbide isomers are studied herein with coupled cluster theory and multireference configuration interaction to support their possible detection in astrochemical environments such as the circumstellar envelope surrounding the star IRC +10216 or in terrestrial laboratories. Magnesium-bearing species may abound in the interstellar medium (ISM), but only eight (MgNC, MgCN, HMgNC, MgC<sub>2</sub>H, MgC<sub>3</sub>N, MgC<sub>4</sub>H, MgC<sub>5</sub>N, and MgC<sub>6</sub>H) have been directly identified thus far. Of several possible isomers for the related MgC<sub>3</sub> system, the most stable are the nearly degenerate diamond singlet/triplet states. Overall, this work offers quantum chemical insight of rovibrational spectroscopic data for MgC<sub>3</sub> using a quartic force field (QFF) based on CCSD(T) and CCSD(T)-F12 levels of theory at the complete basis set (CBS) limit. Additional corrections with small basis set CCSDT(Q) and scalar relativistic effects are also included in the analysis. Salient multireference character is found in the singlet diamond electronic state, which makes a definitive assignment of the ground state challenging. Nevertheless, coupled cluster-based composite energies and multireference configuration interaction both predict that the 1A<sub>1</sub> diamond isomer is 1.6 - 2.2 kcal/mol lower in energy than the 3A<sub>1</sub> diamond isomer. Furthermore, highly accurate binding energies of various isomers MgC<sub>3</sub> are provided for comparison to photo-detachment experiments. Dipole moments along with harmonic infrared intensities will guide efforts for terrestrial synthesis and spectroscopic characterization.

## P2-36 : Electronic Structure and Absorption Properties of Fe(II) Isocyanide Complexes

Eyram Asempa  
North Carolina State University

One of the challenges for the development of new sustainable solar energy conversion devices is the replacement of chromophores based on the precious and rare transition metals, such as ruthenium, by earth-abundant and cheap alternatives. Iron(II) polypyridines have received a lot of attention as potential chromophores due to the abundance, low-cost and rich coordination chemistry of iron. However, their usefulness is limited by the decay of the initially-excited, photoactive metal-to-ligand charge transfer (MLCT) states into the photo-inactive, low-lying metal-centered (MC) states via intersystem crossing. One way to address this problem is to destabilize the energies of the MC states by utilizing stronger field ligands. In this work, we employ density functional theory (DFT) and time-dependent DFT to study the effects of alkyl, aryl, and  $\pi$ -conjugated aryl isocyanide ligands on the frontier molecular orbitals, spin-state energetics and absorption properties of  $[\text{Fe}(\text{bpy})(\text{CNR})_4]^{2+}$  complexes, where bpy is 2,2'-bipyridine and CNR represents a monodentate isocyanide ligand (R = alkyl, aryl). Our results show that the energetic ordering of metal-centered electronic states of these complexes mirrors that of the Ru(II) polypyridines:  $1A < 3MC < 5MC$ . Isocyanide ligands destabilize not only the MC states, but also the MLCT states, thus blue-shifting the MLCT absorption bands. However, extending the  $\pi$ -conjugation of the bpy ligand improves the absorption properties of Fe(II) complexes, stabilizing the energies of the MLCT states.

## P2-37 : The intermediate state EOM-CC approach for doubly excited dark states

Moneesha Ravi  
University of Florida

EOM-CCSD is a well-established method for obtaining excited states dominated by single excitations such as open-shell singlets. But excited states with significant double excitation contribution are not adequately treated by EOM-CCSD. Such states often required EOM-CCSDT and sometimes even EOM-CCSDTQ to be treated right. These methods are computationally demanding methods that scale as  $n^8$  and  $n^{10}$ , respectively. Here we propose the intermediate state approach to obtain doubly excited states using EOM-CCSD, which scales as  $n^6$ . Traditionally, EOM-CC is performed on a closed shell reference state for it has a well-described single-reference coupled-cluster (SRCC) wavefunction. This poster discusses our attempt on performing EOM-CCSD on a low spin open-shell reference state and its benefits. Considering spin contamination of such states with SRCC, various tools to obtain a better MS=0 triplet state and open-shell singlet single reference CC wavefunction will be discussed. The accuracy of this approach is demonstrated with various examples.

## **P2-38 : EFP meets ANI: Modeling macroscopic systems with neural network potentials**

Shahed Haghiri  
Purdue

ANI is a neural network potential (NNP) that has been developed to circumvent the expensive computational scaling of quantum mechanical (QM) calculations and has proven itself to be as accurate as CCSD(T) methods with only a fraction of the cost. The one downside of ANI is that the network is not trained to describe long range interactions and as such is not reliable for most biological and materials systems. The Effective Fragment Potential (EFP) is a QM-based method for modeling non-covalent interactions. EFP decomposes the non-covalent interaction energy into electrostatic, polarization, dispersion, exchange-repulsion, and charge transfer terms by using perturbative expansions. Herein we attempt to incorporate EFP-derived information into ANI with the goal to produce a more general NNP capable of modeling extended molecular systems. To achieve that, EFP electrostatic potentials are used as additional input parameters for ANI. The combined network is re-trained on a set of molecular clusters. The developed computer codes will contribute to open-source LibEFP and TorchANI software libraries.

## **P2-39 : Simulating Exciton Dynamics in Large Photosynthetic Aggregates**

Leonel Varvelo  
Southern Methodist University

A longstanding challenge in simulating excitation energy transfer in molecular materials has been to efficiently scale to larger systems while not compromising accuracy. Perturbative methods can scale to large molecular aggregates, but fail in systems where the electronic coupling is comparable to the system-bath coupling. On the other hand, exact methods become computationally intractable beyond a few pigments due to catastrophic scaling with system size. Recently, we have introduced adaptive Hierarchy of Pure States (adHOPS) formalism which provides an exact framework for the time evolution of an open quantum system while achieving size-invariant scaling for large molecular aggregates. Using light harvesting 2 (LH2) complexes of purple bacteria as a model system, we build different sized aggregates which are used to study how the adHOPS basis set size scales. For large aggregates we investigate how to efficiently simulate coarse-grained observables and use them to measure quantities such as the rate of transport.

## **P2-40 : A Perturbation Theory Approach for the Diagonalization of “Strongly Correlated” Matrices**

Zachary Windom  
University of Florida

Since the advent of modern quantum chemistry, the diagonalization of extremely large matrices has been inextricably linked to solving the Schrodinger equation. Due to scaling issues, several iterative techniques have been proposed to target the lowest or highest roots of a matrix via the variational principle. In this regard, the Davidson diagonalization strategy has found ubiquitous use across many quantum chemistry software packages as - for the vast majority of standard chemistry problems - it exhibits attractive convergence properties assuming a reasonable starting guess vector and a diagonally-dominant matrix. However, in situations where either of these conditions are not met, the convergence of the Davidson technique can be poor.

In this work, we introduce a novel approach for the diagonalization of non-diagonally dominant matrices based on Brillouin-Wigner Perturbation Theory (BW-PT). This technique is characterized by redefining the zeroth order Hamiltonian after low order iteration. It is shown that the power in this approach originates from the inherent flexibility associated with the BW-PT resolvent operator, which can be optimized according to the structure of the matrix being studied. These broad conclusions are based on a benchmark of a non-diagonally dominant Hermitian matrix; notably, the water dimer Configuration Interaction Singles (CIS) built from a Natural Localized Molecular Orbital (NLMO) reference. By comparing against standard single-vector Davidson, we show this approach to be a competitive technique suitable for any matrix describing physical processes with strong couplings across matrix elements.

## **P2-41 : Energetics and Kinetics of Various Cyano Radical Hydrogen Abstractions**

Alexandra Burke  
University of Georgia

The cyano radical (CN) is an abundant, open-shell molecule found in a variety of environments, including the interstellar medium and combustion processes. In these environments, it often reacts with small, closed-shell molecules via hydrogen abstraction. Both carbon and nitrogen are reactive sites, however the carbon is more reactive with reaction barrier heights generally between 2 – 13 kcal mol<sup>-1</sup> lower than those of the nitrogen. The CN + HX → HCN/HNC + X, where X = H, CH<sub>3</sub>, NH<sub>2</sub>, OH, C<sub>2</sub>H, Cl, Br, F, CN, PH<sub>2</sub>, SH, HCO, NCO, CH<sub>3</sub>O, CH<sub>2</sub>OH, reactions have been studied at a high-level of theory, including CCSD(T)-F12. Diagonal Born-Oppenheimer and relativistic effects were also determined and contribute to the reaction enthalpies. Additionally, accurate kinetics were

obtained at a wide range of temperatures (20 – 5000K) which are in excellent agreement with existing experimentally determined rate constants.

**P2-42 : “Rotational constants and the effect of step size on quartic force field calculations for astrochemically relevant, cyclic, aluminum-containing compounds”**

Olivia Harwick

The University of Mississippi

Aluminum, oxygen, and nitrogen form strong bonds to one another. However, these motifs are rare in the interstellar medium (ISM), but no chemical rationale accounts for this. The cyclic HAlO<sub>2</sub> and HNOAlH are quintessential examples and isoelectronic with each other. Anharmonic QFF frequencies are calculated at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory for HNOAlH and at the CCSD(T)-F12b/cc-pVTZ-F12 and CcCR levels of theory for HAlO<sub>2</sub>. Structural effects are evaluated at select geometric parameters and anharmonic vibrational frequencies of HAlO<sub>2</sub> with the experimental and computational results from prior literature for cyclic AlO<sub>2</sub>. The mid-to-far-IR region is the most promising for possible, future detections of HAlO<sub>2</sub>, considering the vibrational frequencies are less than 1100cm<sup>-1</sup>, with the exception of the Al-H stretch. Further, HAlO<sub>2</sub> and HNOAlH have dipole moments of ~5D and ~4D, respectively, indicating possible, high microwave activity and therefore probable radio observation.

**P2-43 : Challenges for variational reduced-density-matrix theory: Total angular momentum constraints**

Run Li

Florida State University

The variational two-electron reduced density matrix (v2RDM) method is generalized for the description of total angular momentum (J) and projection of total angular momentum (MJ) states in atomic systems described by non-relativistic Hamiltonians, and it is shown that the approach exhibits serious deficiencies. Under ensemble N-representability constraints, v2RDM theory fails to retain the appropriate degeneracies among various J states for fixed spin (S) and orbital angular momentum (L), and, for fixed L, S, and J, the manifold of MJ states are not necessarily degenerate. Moreover, a substantial energy error is observed for a system for which the two-electron reduced density matrix is exactly ensemble N-representable; in this case, the error stems from violations in pure-state N-representability conditions. Unfortunately, such violations do not appear to be good indicators of the reliability of energies from v2RDM theory in general. Several states are identified for which energy errors are near zero and yet pure-state conditions are clearly violated.

## **P2-44 : Fermi.jl: A Quantum Chemistry Framework in Julia**

Gustavo Aroeira

Center for Computational Quantum Chemistry

Approximating molecular wave functions involves heavy numerical effort; therefore, codes for such tasks are written completely or partially in efficient languages such as C, C++, and Fortran. While these tools are dominant throughout quantum chemistry packages, the efficient development of new methods is often hindered by the complexity associated with code development. In order to ameliorate this scenario, some software packages take a dual approach where a simpler, higher-level language, such as Python, substitutes the traditional ones wherever performance is not critical. Julia is a novel, dynamically typed, programming language that aims to solve this two-language problem. It gained attention because of its modern and intuitive design, while still being highly optimized to compete with “low-level” languages. Recently, some chemistry-related projects have emerged exploring the capabilities of Julia. Herein, we introduce the quantum chemistry package Fermi.jl, which contains the first implementations of post-Hartree-Fock methods written in Julia. Its design makes use of many Julia core features, including multiple dispatch, metaprogramming, and interactive usage. Fermi.jl is a modular package, where new methods and implementations can be easily added to the existing code. Furthermore, it is designed to maximize code reusability by relying on general functions with specialized methods for particular cases. The feasibility of the project is explored through evaluating the performance of popular *ab initio* methods. It is our hope that this project motivates the usage of Julia within the community and brings new contributions into Fermi.jl.

## **P2-45 : Modeling photodissociation and cis-trans isomerization in azomethane with surface-hopping on reduced-dimensional potential energy surfaces**

Hyuk-Yong Kwon

North Carolina State University

Light-driven molecular switches are a large class of molecules that undergo isomerization between two or more metastable states in response to an electronic excitation. Azomethane, which undergoes trans-cis isomerization upon excitation with visible light, is one of the smallest representatives of this class and thus represents an ideal model system to test the development of new methods capable of modeling excited-state dynamics. Here we describe a new approach to studies of light-induced dynamics that relies on the construction of reduced-dimensional potential energy surfaces (rr-PESs) with mixed-basis sparse interpolation for ground and excited states of the molecule of interest. A surface-hopping algorithm capable of propagating dynamics on the rr-PESs was also implemented. The results of our simulations are in a general agreement with the previous computational and experimental studies of this system, suggesting a dissociation upon the photoexcitation

and internal conversion via the cleavage of the C-N bonds in 85% cases, and an even distribution of cis-trans isomers in the remaining compounds.

### **P2-46 : Tuning the catalytic activity if the synthetic enzyme KE15 with DNA**

Yi Zheng  
Virginia Tech

Comparing to natural enzymes, synthetic enzymes can be stable under non-physiological reaction conditions and broaden the range of reaction that could be catalyzed. With this ability to overcome the limitations of natural enzymes, synthetic enzymes therefore provide a promising route to develop catalysts for industrial purposes. However, in most cases the protein scaffold of synthetic enzymes is not optimized and does not contribute to the catalytic performance. In this talk, I will present a novel approach to tune the activity of synthetic enzymes, which relies on regulating electrostatic interactions in the enzyme active site. More specifically, I will show how DNA, a highly polar molecule, can be utilized as an environmental factor to induce electrostatic effects in the active site. I will present molecular dynamics simulations of the Kemp Eliminase KE15, performed with the AMOEBA polarizable force field. This method allows the computation of intrinsic electric fields in the active site, which probe and quantify the enzymatic activity. With this approach, I will show how a DNA fragment placed around the enzyme can stabilize the transition state, lowering the activation energy of the reaction. This demonstration of principle is a fundamental milestone in the development of DNA origamis as structural and functional scaffolds for enzymatic regulation.

Y. Zheng and V. Vaissier Welborn, J. Phys. Chem. B, 2022, DOI: 10.1021/acs.jpcc.2c00765

### **P2-47 : Accelerating Real-Time Coupled Cluster Methods: Local Correlation and Amplitude Dynamics**

Benjamin Peyton  
Virginia Tech

Dynamic properties computed using frequency-domain response theory suffer from three main drawbacks: the perturbing field cannot be altered or shaped, perturbing fields must be weak compared to the intramolecular forces present in the system, and only a finite number of frequencies are targeted. Time-domain or real-time approaches do not suffer from these drawbacks; however, explicit propagation of the wave function in time is exceedingly expensive. Time-domain coupled cluster in particular requires repeated evaluation of the computationally demanding amplitude residual expressions. Methods for reducing the cost of this propagation

are discussed, including local correlation and frozen amplitude schemes, motivated by investigations of the perturbed amplitude dynamics.

## **P2-48 : Predicting the Mechanism and Products of CO<sub>2</sub> Capture by Amines in the Presence of H<sub>2</sub>O**

Zachary Lee  
Morehead State University

Currently, there are two approaches being considered for the removal of acid gas pollutants: (1) sequester these gases from the atmosphere or (2) remove these gases directly upon combustion (post-combustion). Aqueous and solid-state amines have shown excellent promise for post-combustion removal of CO<sub>2</sub>, yet the overall mechanisms for these processes as well as the thermodynamics of specific products formation remains elusive. Reaction coordinates for a series of CO<sub>2</sub> capture reactions by various alkylamines and H<sub>2</sub>O were calculated at the CCSD(T)/CBS-benchmarked G3(MP2) level in the gas phase with aqueous solution calculations performed by applying an additional self-consistent reaction field approach at the MP2 level for the treatment of solution. In the gas phase, alkylamines are found to reduce the energy barrier more than catalytic waters for both carbamic acid and carbonic acid formation. In aqueous solution, the barriers to form both carbamate and bicarbonate are further reduced, with bicarbonate formation occurring if only one amine is present and carbamate formation possible only if multiple amines are accessible. The barriers for proton transfer in each reaction correlate nicely with amine basicity for alkylammonium carbamate and alkylammonium bicarbonate formation pathways. These results have implications for CO<sub>2</sub> capture by amines in both the gas phase and aqueous solution as well as in the solid state, if enough water is present. This work was supported by UNCAGE-ME, an Energy Frontier Research Center led by the Georgia Institute of Technology funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

## **P2-49 : On the reproducibility of density functional approximations**

Susi Lehtola  
Molecular Sciences Software Institute

Density functional theory is the workhorse of modern-day chemistry and materials science, and several novel density functional approximations (DFAs) are published every year. In order for the novel DFAs to become available for users of various program packages, they need to be implemented in the used programs. However, a constant problem with re-implementing literature DFAs is the lack of reliable or sufficiently accurate reference data. The lack of a common standard to test new implementations against has led to some non-equivalent implementations of commonly-used functionals such as BP86, PBE, as well as B3LYP across various program packages, as we demonstrate in this work. Our

reimplementations of recently published functionals have also revealed several problems, which were only made visible through careful benchmarks.

In order to prevent such subtle incompatibilities from arising again in the future, our main goal is to draw attention to common problems associated with the verification of novel DFAs. It is imperative to establish a common framework for the verification and testing of density functional approximations. In this work, we suggest several ways in which sufficiently accurate reference energies can be produced with freely available open source software, either with non-self-consistent calculations with tabulated atomic densities or via self-consistent calculations with a number of program packages. However, as we illustrate in this work, the numerical parameters—especially the used quadrature grid—needs to be tightly controlled to guarantee the  $\leq 0.1$  uEh level of precision required for reference energies to allow identification of equivalent implementations of DFAs.

## **P2-50 : Development of Novel 2-D and 3-D Catalytic Materials: Metal-Ammonia Complexes from Gas-Phase to Condensed States**

Benjamin Jackson  
Auburn University

Electrides are solids that contain trapped electrons in their cavities or pores. The early work of Dye and co-workers disclosed the existence of these materials by synthesizing Cs<sup>+</sup> crown ether complexes surrounded by “free” electrons. Solvated electron precursors (SEPs) are a similar class of materials but with higher tunability and applicability. They are metal-ligand complexes consisting of a metal  $Mn+(L)_x$  core surrounded by  $n$  solvated metal electrons which were displaced to the periphery of the complex. The diffuse nature of the SEP solvated electrons suggests a highly reactive reduction catalysts which are tunable through ligand functionalization, while SEPs linked through bridging ligands offer tuning for reagent molecular size. Here, high-level quantum chemical calculations are utilized to elucidate the structure and properties of diamine and alkane linked SEP dimers and the first detailed study of a SEP catalytic cycle is presented using the functionalization of CO<sub>2</sub>. An overview of SEP structure and these results demonstrate how gas-phase calculations may inform avenues for the development of novel 2-D and 3-D condensed phase catalysts.

## **P2-51 : SEQCROW: A ChimeraX Bundle to Facilitate Quantum Chemical Applications to Complex Molecular Systems**

Anthony Schaefer  
University of Georgia

SEQCROW is a bundle for UCSF ChimeraX that provides structure editing capabilities and quantum chemistry utilities designed for organic and organometallic compounds.

SEQCROW has tools for building organic molecules, generating coordination complexes, swapping ligands on organometallic complexes, and adding or modifying substituents. Computations can be prepared and run using Gaussian, ORCA, or Psi4. Computational results could be processed to produce a simulated conformer-averaged vibrational or excited state spectrum. SEQCROW is also capable of calculating percent buried volume, steric maps, cone angles, and Sterimol parameters.

## **P2-52 : Comparisons of QM-Cluster Modeling Case Studies: Catechol-O-Methyltransferase and Glycine-N-Methyltransferase**

Qianyi Cheng  
University of Memphis

Computational enzyme modeling has proven successful in revealing atomic level details of enzyme systems. Our lab has been developing the Residue Interaction Network Residue Selector (RINRUS) toolkit to algorithmically construct reproducible QM-cluster models which contain the crucial aspects of local active site chemistry. QM-cluster models were sequentially built for three catechol substrates catechol, 4-methyl catechol, and the inhibitor 3,5-dinitrocatechol in complex with catechol-O-methyltransferase (COMT) and the substrate glycine in complex with glycine-N-methyltransferase (GNMT). Different from our previous case study of the catechol-O-methyltransferase, in which 550 QM-cluster models were built based on a known X-ray crystal structure, in this study, the COMT models were built on structures obtained from molecular dynamics (MD) of the three catechol substrates. The GNMT models were built on the X-ray crystal structure. Differences between QM-cluster models generated from the X-ray crystal structure versus MD structures, and COMT versus GNMT are compared. The computed values of free energy of activation and reaction converge to an effectively asymptotic limit with respect to increasing model size and qualitatively agree with experimental kinetics. Instead of building QM-cluster models in a non-rigorous fashion, RINRUS-based QM-cluster models lead to accelerated thermodynamic and kinetic convergence, indicating a better way to construct the “right QM-cluster model” for “the right reason”.

## **P2-53 : Electronic structure of the dicationic first-row transition metal oxides**

Emily Claveau  
Auburn University

Multi-reference calculations were performed in conjunction with large basis sets to investigate the electronic structure of the ground and low lying electronic excited states of  $MO_2^+$  species, where  $M = Ti-Cu$ . Transition metal dicationic systems have been shown to be highly efficient in the activation of C-H bonds in saturated hydrocarbons. Additionally, in biological systems, transition metal dications such as the  $FeO_2^+$  oxo unit is widely studied due to its presence in intermediate forms of enzymes. This is the first systematic

investigation on these systems and provides deep insight into the reactivity and stability of the  $MO_2^+$  units. The first-row transition metal dications can be grouped into three groups: early, middle, and late transition metals. Early transition metals (Ti, V, Cr) are characterized by having stable and well separated oxo ( $M4+O_2^-$ ) ground states, middle transition metals (Mn, Fe) have oxyl ( $M3+O\bullet^-$ ) ground states with the presence of low-lying oxo excited states, and late transition metals (Co, Ni, Cu) with well separated oxyl states, lacking oxo states. Using multireference configuration interaction (MRCI) and the Davidson correction, along with coupled-cluster singles, doubles, and perturbative triple excitations (CCSD(T)), for single reference systems, periodic trends for bond lengths are reported, along with energetics, and wavefunction composition, as well as accurate spectroscopic constants. Periodic trends found from the initial, middle, and late transition metals are of paramount importance in catalysis, i.e, new insight into dissociation channels and identification of different stable minima in the potential energy surface, which is crucial for experimentalists in future catalysis investigations.

## **P2-54 : Tuning the catalytic activity of the synthetic enzyme KE15 with DNA**

Yi Zheng  
Virginia Tech

Comparing to natural enzymes, synthetic enzymes can be stable under non-physiological reaction conditions and broaden the range of reaction that could be catalyzed. With this ability to overcome the limitations of natural enzymes, synthetic enzymes therefore provide a promising route to develop catalysts for industrial purposes. However, in most cases the protein scaffold of synthetic enzymes is not optimized and does not contribute to the catalytic performance. In this talk, I will present a novel approach to tune the activity of synthetic enzymes, which relies on regulating electrostatic interactions in the enzyme active site. More specifically, I will show how DNA, a highly polar molecule, can be utilized as an environmental factor to induce electrostatic effects in the active site. I will present molecular dynamics simulations of the Kemp Eliminase KE15, performed with the AMOEBA polarizable force field. This method allows the computation of intrinsic electric fields in the active site, which probe and quantify the enzymatic activity. With this approach, I will show how a DNA fragment placed around the enzyme can stabilize the transition state, lowering the activation energy of the reaction. This demonstration of principle is a fundamental milestone in the development of DNA origamis as structural and functional scaffolds for enzymatic regulation.

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## **P2-55 : Chiral discrimination in the propylene oxide dimer and glycidol dimer case studies**

Reza Hemmati  
Auburn University

Symmetry-Adapted Perturbation Theory (SAPT) and its Functional-group SAPT (F-SAPT) variant are applied to two chiral molecules in order to elucidate chiral self-recognition for propylene oxide dimer and glycidol dimer cases. To reveal the origin of the chiral discrimination, a quantity called chirodiastaltic (chiral discrimination) energy, the energetic difference between homochiral and heterochiral diastereomers of a complex was computed. In addition, the effect of chiral interactions on the vibrational frequencies of the aforementioned molecular complexes is investigated. Two separate frequency shifts were recognized with respect to an isolated propylene oxide monomer and glycidol monomer. The results showed that the largest frequency shifts are correlated to the effect of hydrogen bonding on the O-H stretching mode, the strength of the epoxy ring involving both hydrogen bonds and the crossing between non-equivalent minima of isolated molecules.

## **P2-56 : Ab initio cavity quantum electrodynamics with equation-of-motion coupled-cluster theory**

Marcus Liebenthal  
Florida State University

Quantum electrodynamics coupled-cluster (QED-CC) theory is an ab initio many-body approach to modeling the electronic structure of a molecule strongly coupled to an optical cavity. The dipole moments of the molecule and resonant photons in the cavity couple to form a polariton, a hybrid light-matter state. For the discovery of novel chemistry using polaritons, a robust theoretical framework is necessary to understand the mechanisms behind reactions within a cavity. We present a scalable C++ implementation of QED-CC, realized with the tensor framework TiledArray, that can generate one- and two-particle reduced density matrices and utilize equation-of-motion QED-CC (EOM-QED-CC) to predict excited state properties of hybrid light-matter states.

## **P2-57 : The Molecular Building Blocks of Planets and Other Star Stuff**

Ryan Fortenberry  
University of Mississippi

The elemental abundances of rocky bodies are vastly different from the Universe at large. Our Earth is a rocky planet largely composed of oxygen followed by notable amounts of silicon, magnesium, iron, and some aluminum. However, before these atoms can form rocks which form planets, they likely must first form small molecules which can form

nanocrystals and then rocks. Our CCSD(T)-F12b/cc-pVTZ-F12 work is showing that reactions leading to such objects are both highly thermodynamically and likely kinetically favorable. Additionally, this class of small, inorganic molecules has largely been unexplored in the spectroscopic literature. High-level quantum chemical quartic force field analyses are showing that these molecules often have large dipole moments and notable infrared intensities. The anharmonic vibrational frequencies of these molecules often fall beyond 9 microns and may help to explain portions of unattributed IR spectra as well as provide evidence for the early stages of nanocrystal formation in protoplanetary disks leading to planet formation. Conversely, the presence of these molecules in planetary nebulae, supernova remnants, or other stellar corpses may indicate the previous existence of rocky planets in such former planetary systems. Additionally, our work is also showing that the formation of such molecules may give clues as to the primordial environment from which they formed.

## **P2-58 : Computational assessment of the catalytic potential of anionic transition metals centers in methane to methanol conversion**

safaa sader  
Auburn University

Although neutral and positively charged transition metals (TMs) catalysts are widely used to achieve partial oxidation of methane to methanol, selectivity remains a high-stake challenge due to the tendency of both to produce hydrogenated side products besides methanol. Anionic TMs catalysts on the other hand have been proven to be stable, efficient, and selective in achieving methanol production. To understand the catalytic potential of anionic TMs, catalytic conversion of methane to methanol (MTM) facilitated by Pt<sup>-</sup>, Pd<sup>-</sup>, Ni<sup>-</sup> and Fe<sup>-</sup> is studied computationally using DFT and explicit electron correlation methods. A moderate or high-energy barrier for the M<sup>-</sup> + CH<sub>4</sub> → HMCH<sub>3</sub><sup>-</sup> reaction step is observed compared to its cationic and neutral analogs. This protects the metal center from deactivation and improves selectivity towards methanol production over byproducts. Our DFT calculations and energetic span model-based TOFs indicated bare Pd<sup>-</sup> has the best performance among the studied metals. More importantly, calculations indicated the coordination of four methyl groups around the metal center significantly decreases the energy barriers for all Studied TMs and slightly promotes the radical pathway (via oxyl type M=O) over the [2+2] mechanism (via oxo type M=O). These results imply future research should focus on developing advanced ligand structures that can stabilize the negative charge on metal centers to achieve optimal selectivity and efficiency in MTM.

## **P2-59 : Atomistic Modeling of Voltage-Gated Sodium Ion Channel**

Taoyi Chen  
Virginia Tech

NaV channels play an important role in the human body, including heartbeat, muscle contraction, brain activity, etc. The mutations and dysfunctions of NaV channels are related to various severe diseases. This makes NaV channels appealing targets for therapeutic drugs. However, the lack of molecular level insights into the allosteric effects of voltage-gated ion channels has become an obstacle for the design of efficient and target-specific drugs. Here we present a novel computational strategy, based on electric field calculations, to identify and quantify the local molecular mechanisms that regulate ion channel function. Here, we will present conformational ensemble and MD simulations on high resolution structure of NaV channels, which capture the time and length scales corresponding to selective ion permeation. Electric field calculations can then help to rationalize the molecular origin of the driving force of ion diffusion and channel reorganization. We'll use the isolated Nav 1.7 ion channel in water and membrane-embedded Nav 1.7 to demonstrate how electric fields can be used as probes to study local effects on ion permeation, a milestone in the development of a molecular level understanding of selective permeation and allosteric effect.

## **P2-60 : Application of a Direct-Minimization SCF Solver to Proteins in Vacuum to Explore the Origin of the Near-Zero Gap Predicted by Local and Semi-Local DFAs**

Samuel Slattery  
Virginia Tech

Local and semi-local density functional approximations (DFAs) are known to underestimate the gap in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in Kohn-Sham (KS) density functional theory (DFT). This error has been especially pronounced in large systems of biological importance when calculated in vacuo, where certain DFAs have predicted that even small polypeptides have a nearly-zero HOMO-LUMO gap. When the shrinking of the gap is severe convergence of the KS equations becomes difficult or even impossible with traditional diagonalization-based solvers. Using a direct-minimization SCF solver we investigated the origin of the unphysical gaps in such systems. The solver avoids diagonalization of the KS Fock matrix entirely using quasi-Newton steps throughout and employing a limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) approximation for the Hessian built from an approximate diagonal Hessian combined with a trust-radius step restriction leveraging the low-rank structure of the L-BFGS Hessian. We demonstrate that the unphysical gaps in such systems are due to the misalignment of frontier energy levels in physically separated regions of the molecule, especially those near isolated negative charges. In all cases considered herein the physically-reasonable solution in such systems is stable but has non-Aufbau character. Our

findings question the ability of modern DFAs to describe the electronic structure of vacuum-exposed interfaces in a qualitatively correct manner.

## **P2-61 : Bond Dissociation Energies of Carbene-Carbene and Carbene-Main Group Adducts**

Kyle Edwards

The University of Alabama

A range of carbene structures and their dimers with one another and adducts with a selection of small molecule electrophiles, nucleophiles, and alkali metals were examined at the composite correlated molecular orbital theory G3MP2 level to explore ground state “carbenic” structures, their stabilities, and reactivities. Single point coupled cluster CCSD(T) theory calculations were performed on select transition, alkali, and alkaline earth metal containing structures. Differences between the general classification of carbenes as a singlet electrophilic carbene or singlet nucleophilic carbene and their given reactivity are discussed. A key quantity is the carbon-carbon bond dissociation energy for carbene dimers or the carbene-adduct dissociation energy for other species. The carbene dimer bond dissociation energies span a wide range from 10 to 170 kcal/mol. The hydrogenation energies and singlet-triplet splitting were found to correlate best with the carbene’s self-dimerization energy where other descriptors do not. The proton and fluoride affinities of the carbenes alone prove inadequate for classifying reactivity amongst classes of carbenes. The self-dimerization bond dissociation energy, hydrogenation energy, and singlet-triplet splitting of various carbenes, despite sometimes large difference in proton affinity and other indicators of reactivity, provide useable metrics to correlate substantial amounts of thermodynamic and kinetic (reactivity) information regarding these structures. This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, Catalysis Program on a subcontract from Pacific Northwest National Laboratory.

## **P2-62 : The Suppression of Critical Opalescence in a Binary Liquid Mixture**

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The critical opalescence, which is a light scattering phenomenon that only occurs in the critical region of pure fluid and liquid mixtures, is a result of the fluctuations in the concentrations of the chemical components making up the material. By applying the phase rule and isomorphism principal analysis, we predict that the critical opalescence can be suppressed upon the addition of a small amount of solute into the binary mixture. The prediction is confirmed by the turbidity measurement for four mixtures: isobutyric acid + water, 2,6-lutidine + water, nitrobenzene + dodecane, and methanol + hexane. We find that the divergence of turbidity disappears upon the addition of a completely soluble solute into

those binary mixtures. The result can also be used to explain the strong light scattering observed in the ternary mixture of 3-methylpyridine + water + NaBr where it has been postulated that the mixture supports a micro-heterogeneous phase.

## **P2-63 : Optimal tuning of range-separated hybrid functionals improving accuracy of excited state redox potentials**

Ariel Gale  
Emory University

The excited state redox potential is the fundamental electrochemical property needed for the design and discovery of photoredox catalysts. The calculation of ground state redox potentials is straightforward, but including the fluorescence energy introduces new sources of error. I used optimal tuning of range-separated hybrid functionals (OT-RHS) to improve excited state redox potential calculations in implicit solvent, exploring 3 tuning schemes and sources of error.

## **P2-64 : Atomistic Simulations on Mechanical Properties of Lignin**

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University of South Carolina

Mechanical properties of lignin, an aromatic heteropolymer constituting 20%-30% of plant biomass, are important to the fabrication and processing of lignin-based sustainable polymeric materials. Atomistic simulations are performed to provide microscopic insight into the mechanics of lignin. Representative samples of miscanthus, spruce, and birch lignin are studied. At temperature below the glass transition temperature, the stress-strain curve for lignin under uniaxial compression exhibits initial elastic response, yielding, and post-yield plastic response with increasing strain. The decomposition of the overall stress shows that the energetic component contributes to the elastic response and yielding, but remains low in the post-yield plastic regime until strain hardening sets in. The dissipative component dominates the post-yield regime before strain hardening. In addition to the three real lignin samples, minimalist model systems of monodisperse linear polymers consisting of only guaiacyl units and  $\beta$ -O-4 linkages are simulated. While the elastic response, yielding, and the plastic flow under compression do not depend on the molecular weight of the model lignin, the strain hardening under compression is enhanced as lignin molecular weight increases.

## P2-65 : Statics of Ring Di-block Copolymers: A Molecular Dynamic study

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The self-assembly of di-block copolymers yields ordered nanostructures in a wide range of morphologies, including lamellae, double gyroids, cylinders, and spheres, and thus benefits applications in various fields such as lithography, water filtration, and solar cells. Recent advances in ring-closure chemistries and purification techniques have enabled the synthesis of ring di-block copolymers. Compared with the conventional linear di-block copolymers, the more compact conformations and entanglement-free dynamics of ring di-block copolymers are anticipated to alter both the statics and dynamics of the self-assembled nanostructures and therefore provide a novel topology-based pathway to manipulate the self-assembly process. Using molecular dynamics simulations, we study the statics of symmetric ring di-block copolymer melts in the ordered lamellar phase. A ring di-block copolymer is generated with two linear blocks of antagonistic A and B monomers covalently bonding their ends to each other. An isothermal-isobaric simulation of the melt is performed to obtain the equilibrated lamellar structure. We systematically examine the lamellar spacing, the width of the interface between A and B lamellae, and the radius of gyration of the di-block rings as functions of the A-B interaction strength and the block length. We develop a scaling theory that successfully describes the observed statical properties of the di-block rings in the lamellar phase.