#### Quasi-degenerate Perturbation Theory for Singlet Fission Bi-exciton States

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Abstract: Singlet fission has been getting a lot of attention recently due to its potential to improve the efficiency of solar cells. One of the key steps in the process is the disentangling of the spin coupled triplet states. This process depends on the bi-exciton binding energies and the extent of delocalization of the bi-exciton spectrum. Most of the models used to study the bi-exciton states are based on dimer models due to the cost of computation. Mapping the singlet fission chromophore to a two site spin lattice allows us to study larger systems like tetracene crystals which are inaccesible using an ab initio method. We use a quasi-degenerate perturbation theory approach on the Heisenberg Hamiltonian to study the bi-exciton spectrum. We derive parameters for exciton hopping  $t_{ab}$  and effective exchange interaction  $K_{ab}$  from the spin Hamiltonian. We also demonstrate the effect of these parameters on the bi-exciton spectrum.

### The Performance of Explicitly Correlated Methods for the Computation of Anharmonic Vibrational Frequencies

#### <u>Donatus Agbaglo</u> & Ryan C. Fortenberry Georgia Southern University

Anharmonic vibrational frequencies for closed-shell molecules computed with CCSD(T)-F12b at the triple zeta level differ from significantly more costly composite energy methods by a mean absolute error (MAE) of 7.5 cm-1 per fundamental frequency. Comparison to a few available gas phase experimental modes, however, actually lowers the MAE to 6.0 cm-1. Open-shell molecules have an MAE of nearly a factor of six greater. Hence, open-shell molecular anharmonic frequencies cannot be as well-described with only explicitly correlated coupled cluster theory as their closed-shell brethren. As a result, the use of quartic force fields and vibrational perturbation theory can be opened to molecules with six or more atoms whereas previously such computations were limited to molecules of five or fewer atoms. This will certainly assist in studies of more chemically interesting species, especially for atmospheric and interstellar infrared spectroscopic characterization.

## The proto-Nucleic Acid Builder (pNAB): A Software Tool for Constructing Nucleic Acid Analogs

#### <u>Asem Alenaizan</u>, Joshua Barnett, Nicholas V. Hud, C. David Sherrill, Anton S. Petrov Georgia Institute of Technology

Nucleic acid analogs (XNAs) are compounds that are structurally similar to DNA and RNA that can be constructed by altering the nucleobase, (deoxy)ribose sugar, and/or the phosphate group. Besides their medical applications, XNAs are used in the study of synthetic biology and the origin of life. Determining plausible three-dimensional (3D) structures of XNAs is essential in exploring their properties. The proto-Nucleic Acid Builder (pNAB) is a C++/Python software program backed by Open Babel and with a Jupyter notebook interface that constructs physically reasonable 3D structures of XNAs given the chemical structures of the backbone and the nucleobases. Using general force fields, weighted Monte Carlo conformational search is performed to explore the backbone configurations of the nucleic acid strands with varying helical parameters, and plausible structures are generated. We demonstrate the utility of this program in the prediction of the structures of reported XNA systems and the design of new analogs.

#### Probing the O-H and C-H activation for the neutral and charged species of ruthenium mono-oxide species. Ground and excited states calculations

<u>Nuno M.S. Almeida</u>, Isuru R. Ariyarathna and Evangelos Miliordos Auburn University We investigated the ground and excited states of the neutral and charged species of ruthenium mono-oxides using state-of-the-art quantum chemical methodologies. A detailed electronic structure analysis revealed the bonding properties of the bare metal oxides ground, and excited states. Potential energy curves for the different complexes were calculated using a multi-reference approach (MRCI). We subsequently probed the O-H and C-H bond activation strength for water and methane using the bare metal mono-oxides as model systems. We also considered different ligands and examined how they could affect the bond activation step. The energetics of this reaction-step were analyzed and discussed using high-level multireference approaches.

## Extending the Aufbau principle of solvated electron precursors to the second solvation shell: The case of M(NH3)4@12NH3 (M=Li, Be+, B2+)

#### <u>Isuru R. Ariyarathna</u>, Filip Pawłowski, Joseph Vincent Ortiz and Evangelos Miliordos Auburn University

The M(NH3)4 (M=Li, Be+, B2+) systems consist of one electron in a quasi-spherical molecular orbital in their ground state. Excited states are produced by promoting this outer electron to pseudo-p, d, f shaped orbitals. The previously introduced Aufbau principle for Be(NH3)4+ and Li(NH3)4 has an 1s, 1p, 1d, 2s, 1f, 2p, 2d order. In the current work we have studied the excited states of M(NH3)4@12NH3 (M=Li, Be+, B2+) systems using high-level ab initio calculations, where twelve NH3 molecules bind to the inner M(NH3)4 via H-bonding. We have optimized each of these structures under the CAM-B3LYP level of theory and calculated vertical excitation energies. Similar to the M(NH3)4, the M(NH3)4@12NH3 clusters host an electron in a quasi-s type (1s) orbital (ground state) or to bigger 1p, 1d, 1f, 2s, 2p shaped orbitals (excited states). Here we report optimal geometries, CASSCF and P3+ vertical excitation energies, and ionization energies of the M(NH3)4@12NH3 clusters.

#### Electronic and charge-transport properties of donor-acceptor cocrystals

#### <u>Ajith Ashokan</u>, Caitlin Hanson, Jean-Luc Bredas, and Veaceslav Coropceanu Georgia Institute of Technology

Donor-acceptor (D-A) co-crystals are currently of great interest due to their potential use in electronic devices. Here, we have investigated a series of D-A mixed-stack co-crystals, with alternating D and A molecules (-D-A-D-A-). The co-crystals are based on tetracyano-quinodimethane (TCNQ), FmTCNQ (fluorinated derivatives of TCNQ), hexafluorotetracyanonaphthoquinodimethane (F6TCNNQ), or pyromelliticdianhydride (PMDA) as acceptor molecules and benzothienobenzothiophene (BTBT), Cn-BTBT (BTBT with different lengths of alkyl side-chains), anthracene, benzo-di-thiophene, pyrene, carbazole, triphenylene, phenanthrene, perylene, or stilbene as donor molecules. We employed density functional theory calculations based on B3LYP/ 6-31G (d, p) level of theory to elucidate the electronic, vibrational, and charge-transport properties of these systems. In the case of Cn-BTBT-FmTCNQ co-crystals, we also investigated the impact of the extent of fluorine substitution and of the length of the alkyl chain. We find that fluorine substitution to the acceptor backbone (TCNQ) leads to a significant increase in the conduction bandwidth of the co-crystal. Several co-crystals are also

shown to display ambipolar charge-transport properties. Overall, the results of our calculations compare well with available experimental data.

#### Application of the Gibbs Phase Rule and Critical Point Universality to Predict Critical Effects in Solid-Liquid Phase Equilibria

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The opposite sides of the liquid-liquid coexistence curve in the phase diagram of a mixture of two partially miscible liquids converges at a point termed the critical point of solution. Such binary mixtures can be used as solvents for chemical reactions involving heterogeneous equilibria. The intensive thermodynamic variables describing chemical equilibrium in the system can be divided into two classes called "fields" and "densities". A field variable, such as temperature or pressure, has a value which is uniform across coexisting phases. By contrast, a density variable, such as mole fraction or molar volume, has a unique value in each coexisting phase. The Gibbs phase rule can be used to calculate the number of variables, F, that must be fixed in order to describe the position of chemical equilibrium. Under ordinary laboratory conditions, the temperature and pressure are always fixed. Any other fixed variable is then necessarily a density variable. The principle of critical point universality, which is thought to govern all critical phenomena, predicts that when F = 3, the derivative of any density variable with respect to any field variable will diverge toward infinity as the critical point is approached.<sup>1</sup> The sign of the divergence correlates with the enthalpy of reaction as predicted by the Gibbs-Helmholtz equation.<sup>1</sup> By contrast, if  $F \ge 4$ , no critical effect is predicted.<sup>1</sup> In careful experiments involving adsorption,<sup>2</sup> ion exchange,<sup>3</sup> and solid solubility,<sup>1,4-6</sup> we have shown that under conditions of fixed temperature and pressure, the derivative of the extent of reaction with respect to temperature diverges in the critical region, when F = 3. There are no known exceptions to this rule.

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### Conformational Energetics of Urea and Thiourea Near the CCSD(T) Complete Basis Set Limit

#### <u>Kayleigh R. Barlow</u> and Gregory S. Tschumper The University of Mississippi

This study provides the first relative conformational energies near the CCSD(T) complete basis set limit for the low-lying stationary points of urea and thiourea. Full geometry optimizations were performed on ten conformations and eight conformations of thiourea using the MP2 method and a series of Dunning's correlation consistent basis sets (cc-pVXZ for X = D, T, Q, and 5; denoted XZ). Harmonic vibrational frequencies were computed to characterize each stationary point as a minimum (ni = 0), transition state (ni = 1) or higher order saddle point (ni  $\ge$  2) on each potential energy surface. Additional computations were performed with an extra set of tight "d" functions placed on sulfur (using cc-pV(T+d)Z for S and cc-pVTZ for C, H, and O) which were found to have no impact on the relative energies. Five urea conformations and four thiourea conformations with relative energies lower than 10 kcal mol-1 were then optimized at the CCSD(T)/TZ level of theory. Single-point energy computations were then performed upon the CCSD(T)/TZ optimized geometries at the CCSD(T)/XZ level of theory, where X = D, T, Q, 5, and 6.

#### CrystaLattE: Automated Calculation of Lattice Energies of Organic Crystals

#### <u>Carlos H. Borca</u>, Brandon W. Bakr, Lori A. Burns, and C. David Sherrill Georgia Institute of Technology

Crystal Structure Prediction (CSP) comprehends two challenging tasks: efficient structure sampling, to obtain possible polymorphs of a crystal; and accurate lattice energy determination, to enable distinction between polymorphs. The latter remains the main challenge of successful CSP. Herein, we introduce CrystaLattE: a software tool that automates dual-level parallel computation of lattice energies of molecular crystals. Our code is designed with the aim of computing lattice energies accurately enough to discriminate between low energy polymorphs of organic crystals. CrystaLattE uses the many-body expansion approach and exploits the long-range three-dimensional periodic order of crystals to automatically compute lattice energies within chemical accuracy. Our software is designed to be connected to the Quantum Chemistry Common Driver and Databases (QCDB) and it leverages some of its unique features. CrystaLattE is also interfaced with the computational chemistry package PSI4, which is employed to execute the energy computations. The algorithm is written in Python 3 and it is distributed as free, open-source software. We also present a new benchmark database of crystal lattice energies calculated with CrystaLattE. This database displays a hierarchical, multiscale scheme, featured in our code, that employs the CCSD(T)/CBS method for the most relevant interactions and MP2/aug-cc-pVDZ for more distant interactions. Based on the data from this set, we discuss the predominance of the two-body interactions contribution in contrast with that of higher-order terms in the many-body expansion. We also analyze how higher-order terms may become more important depending on the nature of the interaction in crystal lattices. Our results greatly impact the field of CSP, by providing an automated method to compute highly-accurate energies that can complement an efficient structure sampling code.

### Characterizing Magnesium Acetylide and its Cation in Silico for Spectroscopic Detection

#### <u>Joseph E. Burns</u>, Qianyi Cheng, Ryan C. Fortenberry, Nathan J. Deyonker The University of Memphis

Although magnesium-bearing compounds in the condensed phase are found abundantly in the Interstellar Medium (ISM), only five known gas phase species have been confirmed using spectroscopic methods. Magnesium acetylide and its cation are theorized to exist in the ISM and have recently been synthesized in a lab. As a complement to experimental work we have computed rovibrational spectral data for the two molecules using coupled cluster theory. This work improves upon previous literature by including further corrections beyond CCSD(T) and employing quartic force fields (QFF) in the interest of calculating higher-order spectroscopic properties. QFF methods using conventional cluster versus explicitly correlated coupled cluster gives comparable fundamental vibrational frequencies; better agreement exists with the cation. Our quantum chemical approach proves to be effective for the study of inorganic molecules in the ISM. These methods can be used to assist the detection of possible astrochemicals.

### Noncovalent Interactions in Networks of Trimethylamine N-oxide, Guanidinium Cation, and Water

#### <u>Mary Hannah Byrd</u><sup>1</sup>, Genevieve Halingten-Verville<sup>2</sup>, Nathan I. Hammer<sup>2</sup>, Shelley A. Smith<sup>1</sup>, and David H. Magers<sup>1</sup> <sup>1</sup>Mississippi College <sup>2</sup>University of Mississippi

Guanidinium chloride, trimethylamine N-oxide (TMAO), and urea all belong to a small class of organic compounds called osmolytes, which have been studied extensively because they play an important role in biological functionality. Urea and quanidinium chloride are known to denature proteins while TMAO promotes their folding. All of these systems contain many sites for hydrogen bonding, and interactions with water are certainly important to their biological functionality and their abilities to influence protein stability. In previous work, we have studied networks of TMAO, urea, and water to begin to understand how TMAO can promote folded protein stability and also counteract the denaturing effect of urea. In the current study, we have replaced urea with guanidinium cation to see if the interactions are similar or different. Optimum geometries and the corresponding vibrational frequencies of networks of TMAO, guanidinium cation, and water have been computed using density functional theory. The DFT functionals employed are the M06-2X high nonlocality hybrid functional from Thular and Zhao, and the ωB97XD functional from Head-Gordan and coworkers which includes empirical dispersion. The basis sets employed are two of Dunning and coworkersâ€<sup>™</sup> correlation consistent basis sets with diffuse functions: aug-cc-pVDZ and aug-cc-pVTZ. In addition, implicit solvation effects have been examined using the polarizable continuum model for solvation with water as the solvent on many of the optimized networks identified. We gratefully acknowledge support from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

#### Unraveling the Mechanism of Polyethylene Microstructure Modulation using a Redox-Active Ni-based Olefin Polymerization Catalyst

## <u>Robert C. Chapleski, Jr.<sup>1</sup></u>, Jesse L. Kern<sup>2</sup>, W. Curtis Anderson, Jr.<sup>1</sup>, Brian K. Long<sup>1</sup>, Sharani Roy<sup>1</sup>

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Redox-switchable catalysis is of great interest in the field of polymer chemistry for its potential to produce tunable structures of functionalized synthetic polymers. Recently, a Ni-based Brookhart-type catalyst has shown a change in the degree of alkyl branching in polyethylene products following reduction of the catalyst.[1][2] Though such a tunable capability has been shown, neither the mechanism that leads to switchable branch formation nor the structures of the reduced catalyst and resulting active species are completely understood. Here, results of dispersion-corrected TPSSh/cc-PVTZ calculations allow us to not only examine catalyst structure but also to elucidate the nature of this catalytic mechanism to atomistic detail. We find a difference in branching ratios stems from a balance in steric and electronic effects, mainly at the reagent-ethylene addition steps, which is expressed not only in addition-product energies but also in the deviation from square planarity around the Ni center. The changing interplay between steric and electronic factors also affects the selectivity of reagent binding to the catalyst. With larger reagents such as hexene, an additional steric interaction involving the alkyl tail of the reagent, which is imposed by square planarity moreso in the reduced system, leads to a difference in alkene-binding ratios when the catalyst is co-dosed with ethylene and these larger reagents. Finally, we extend our findings to suggest electronic modifications to the catalyst which in concert with redox switchability can enhance the branching-ratio tunability of the catalyst. We hope that these results provide insight into the development of a nextgeneration redox-switchable catalysts capable of producing a desired ratio of product functionalization.

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#### Acylation and Deacylation Mechanism and Kinetics of Penicillin G Reaction with Streptomyces R61 DD-peptidase

<u>Qianyi Cheng</u>, Nathan J. DeYonker University of Memphis

D-alanyl-D-alanine transpeptidases (DD-peptidases) are bacterial enzymes involved in the crosslinking of peptidoglycan to form the cell wall, necessary for bacterial survival. The cross-linking can be inhibited by antibiotic beta-lactam derivatives, such as penicillin G, through acylation, wherein they strongly bind to DD-peptidase and inactivate the enzyme. DD-peptidases are also known as penicillin-binding proteins (PBP). The acyl-enzyme complex of DD-peptidase may undergo further deacylation. However, when the enzyme is covalently bound to antibiotics the deacylation step is predicted to be severely rate-limiting, leading to competitive inhibition with the peptidoglycan. To understand the acylation and deacylation reaction mechanisms and kinetics of a PBP reaction with penicillin G in atomic-level detail, a residue interaction network based on the X-ray crystal structure of Streptomyces R61 DD-peptidase with the penicilloyl acyl-enzyme complex was constructed to build two quantum mechanical (QM) cluster models of the enzyme active site. The QM models were used to compute transition state and intermediate structures and evaluate thermodynamic and kinetic properties of the proposed mechanism. By means of density functional theory, acylation and deacylation pathways were identified. The acyl-enzyme complex lies in a deep thermodynamic sink, and deacylation was found to be the rate-limiting step. The usage of QM cluster models is a promising technique to understand, improve, and design antibiotics to disrupt function of the Streptomyces R61 DD-peptidase.

#### In situ Low-temperature Pair Distribution Function (PDF) Analysis and Molecular Dynamics Simulations of CH<sub>4</sub> and CO<sub>2</sub> Hydrates

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Natural gas hydrates (NGH) occur in ocean floor and sub-surface permafrost deposits and are stable at moderate to high pressures and low temperatures. They are a clathrate structure composed of hydrogen bonded water cages that accommodate a wide variety of guest molecules. CO<sub>2</sub> and CH<sub>4</sub> hydrates both crystallize as the cubic sI clathrate and form a complete solid solution. NGH are concurrently a promising methane source and body for CO<sub>2</sub> sequestration. Low temperature neutron total scattering data were collected at the Spallation Neutron Source (SNS) Nano Ordered MAterials Diffractometer (NOMAD) beamline on gas hydrates synthesized with D<sub>2</sub>O. Guest molecule motion within cages and interactions between gases and cages are investigated through the hydrate stability and decomposition regions. Data were collected from 2-80 K at 55 mbar and from 80-270 K at 25 bar on CO<sub>2</sub>, CH<sub>4</sub>, and (CH<sub>4</sub>)<sub>0.5</sub>-(CO<sub>2</sub>)<sub>0.5</sub> hydrates. Pair distribution function (PDF) analysis of total scattering experiments, combined with classical molecular dynamics (MD) simulations, are used to understand how intermolecular interactions between the guest molecules and water lattice impact the atomic structure and thermodynamic stability of gas hydrates. MD simulations of large (~26,000) atom hydrate systems provide atomic configurations to fit neutron PDF data using Reverse Monte Carlo (RMC) analysis, characterizing the effects of CO<sub>2</sub> and CH<sub>4</sub> as guest molecules on the disordered crystal structure and decomposition of gas hydrates. The MD simulations provide PDFs broken down into partial pairs, nuclear density distributions, and an analysis of the total energy into guest-guest, guest-host and host-host contributions. Structure and thermodynamic studies will provide a more comprehensive understanding of CO<sub>2</sub>-CH<sub>4</sub> solid solutions, exchange kinetics, and implications on hydrate structure, as well as predictions of how NGH deposits will respond to changing environmental conditions.

### The Quest for a Local Representation of Virtual Spaces for Embedded Wave Functions

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Embedding approaches that enable wave function-in-density functional theory (WF-in-DFT) have evolved into a very successful avenue to obtaining the typical accuracy of the former, with roughly the same computational cost as the latter. Recent theoretical advances based on projective enforcement of orthogonality among occupied orbital subspaces, namely, projection-based[1] and Huzinaga, [2, 3] provide an exact, straightforward, and chemically intuitive framework for tackling extended systems wherein the chemistry/physics is fairly local. However, the validity of these strategies is largely dependent on mapping the atomic assignment in terms of distinct subsystems onto appropriate orbital subspaces, which was successfully addressed in our recent paper.[4] Despite all this progress, one difficulty still remains. These embedding schemes only concern with the occupied space, meaning that the embedded orbitals are correlated with the entire unpartitioned virtual orbital space, which can be insurmountably large for high-level wave functions. Here we present our recent efforts to efficiently truncate the virtual space such that the selected virtuals are those which best correlate with the embedded subsystem, providing a systematic route to a compact and more local representation of the virtual space within the scope of embedding theories. By projection of the virtual space onto a minimal basis, we define a simple path toward an iterative reconstruction of the embedded virtual space whereby a small subset of active virtuals are included at each time and in decreasing order of correlation energy recovery. We have found that this approach displays remarkable convergence toward the untruncated energies once the minimal basis is extended with a few higher angular momentum functions. Such a performance is further improved in the computation of relative energies, showing striking reduction of the active virtual space, which can be as small as 10%of its original dimension, while staying within chemical accuracy.

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## Ab initio investigation of ground states of NbO0

<u>Emily Claveau</u> and Evangelos Miliordos Auburn University

Neutral Niobium monoxide, NbO0, was studied using both multi-reference configuration interaction and couple cluster calculations, in conjunction with large basis sets. Full potential energy curves were constructed and bonding patterns were proposed for several low-lying electronic states of this species. Numerical results obtained from these calculations include accurate equilibrium bond lengths, harmonic vibrational frequencies, anharmonicities, excitation energies and bonding energies.

#### Lanczos integrators for time-dependent coupled-cluster theory

#### <u>Brandon C. Cooper</u> and A. Eugene DePrince III Florida State University

This work studies the short iterative Lanczos (SIL) and asymmetric short iterative Lanczos (ASIL) methods as numerical integrators within time-dependent (TD) equation of motion (EOM) coupledcluster (CC) theory. The integrators performance is assessed by comparing linear absorption spectra computed at the second order approximate coupled cluster (CC2) level of theory, against spectra obtained through fourth order Runge-Kutta (RK4) integration. The Lanczos methods provide a significant improvement over RK4 for TD-EOM-CC simulations; the computational cost of converging a spectrum is reduced by roughly a factor of 4 for the ASIL method and 10 for the SIL method. We also show that the spectra for the Lanczos methods are of the same quality though the computational cost of the SIL method is half the ASIL method.

#### Rovibrational Characterization of [AI,O,C,N] Isomers Using Quartic Force Fields

#### <u>Megan C. Davis</u>, Tarek Trabelsi, Joseph S. Francisco and Ryan C. Fortenberry University of Mississippi

Aluminum oxycyano compounds may be present in the interstellar medium. The theoretical rovibrational spectra of several low-energy isomers of the [Al,O,C,N] potential surface have been determined using ab initio quartic force field techniques. The geometries were optimized at the CCSD(T) level using the aug-cc-pV5Z basis set with an additive core-correlation correction using the Martin Taylor basis set. The quartic force field was then constructed at the CCSD(T) level using a complete basis set extrapolation, with additive corrections for core correlation and relativistic effects creating the CCCR QFF. Each of the isomers was determined to have an intense vibrational mode.

#### Can Density-Functional Theory Simulate Complex Solvent Effects? A Study of Chiral Imprinting Using Molecular Dynamics and Quantum Chemistry

#### <u>Ruhee Dcunha</u>, T. Daniel Crawford Virginia Tech

The challenge of assigning the absolute stereochemical configuration to a chiral compound can be overcome via accurate ab initio predictions of optical rotation, a sensitive molecular property that is further complicated by solvent effects. The solvent's "chiral imprint" – the transfer of the chirality from the solute to the surrounding achiral solvent – is explored here using conformational averaging and time-dependent density-functional theory (TD-DFT). These complex solvent effects are taken into account via simple averaging over a molecular dynamics trajectory together with the explicit quantum mechanical consideration of the solvent molecules within the solute's cybotactic region. We consider several axes along which the system's optical rotation varies, including the sampling of the dynamical trajectory, the quality of the one-electron basis set, and the use of continuum solvent models to account for bulk effects.

#### Rotational and Vibrational Fingerprints of the Oxywater Cation, a Possible Precursor to Abiotic O2

#### <u>Weston Del Rio</u> and Ryan C. Fortenberry University of Mississippi

Coupled cluster quartic force fields are used to determine the vibrational frequencies of the oxywater cation (H2OO+), an interesting molecule which could potentially serve as an intermediate for the production of molecular oxygen without an organic agent. 665 displacements of the atoms (according to the molecule's internal symmetry coordinates) produce the potential energy surfaces/quartic force fields (QFFs) of its doublet and quartet states. These QFFs enlist CCSD(T) with the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets, which were extrapolated to the complete basis set, and are then corrected for core electron correlation as well as for relativity. The rotational and vibrational spectra obtained can then be used to determine the presence of this molecule on comets, protoplanets, and other interstellar media, potentially serving as a progenitor of abiotic molecular oxygen.

### Reproducible, Rational, and Rigorous QM-cluster Enzyme Models

#### <u>Nathan J. DeYonker</u>, Qianyi Cheng, Thomas J. Summers University of Memphis

Research using various types of multiscale enzyme simulations has inarguably provided answers to "grand challenge" questions in chemistry and biochemistry, especially using QM/MM, ONIOM, or QM-only cluster models. Despite decades of calibration studies and comparisons of QM and QM/MM results, a dearth of published, algorithmic guidelines or online tutorials exists. The quantitative

relationships between composition or size of the active site/QM region and computational accuracy are still poorly understood. Calibration studies of enzyme thermodynamics/kinetics usually employ only 2-15 different enzyme models, and like published applications of QM-cluster models, they frequently lack reproducible structural data. Development of a software toolkit called RINRUS (Residue Interaction Network ResidUe Selector) has allowed calibration of QM-cluster models on an unprecedented, fine-grained scale. By generating hundreds of unique QM-cluster models from 120 – 530 atoms in size, the convergence of thermodynamic and kinetic properties of the Catechol-O-methyl transferase (COMT) enzyme is analyzed. Our data will be incorporated into a reproducible and systematic rules-based approach for designing QM and QM/MM mechanistic studies of enzymes.

#### Using Dyson orbitals and vertical electron binding energies to predict superacidity in protonated carboranes

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Abstract: Superacidic protonated carboranes have conjugate bases with large vertical electron detachment energies (VEDEs), nodal structures in Dyson orbitals and shallow electrostatic potentials. Closo  $CHB_{11}X_{11}^-$  (X = H, F, and Cl) VEDEs and Dyson orbitals were obtained with the non-diagonal, renormalized, second order (NR2) and renormalized partial third order (P3+) for the final states,  ${}^{2}E_{2} < {}^{2}E_{1}$ . The anionic base's second VEDE correlates with superacidity of the protonated carborane and the predicted electron affinities of the doublet radicals exceed the threshold for a superhalogen (3.6 eV).[1]



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# Basin hopping approach to global exploration of self-consistent field solution space

#### <u>Xinju Dong</u> University of Louisville

Recent research has suggested that the multiple solutions to the self-consistent field (SCF) equations may have utility in the description of excited state processes. Algorithms that can explore and characterize SCF solution space are required to develop subsequent methods that can utilize multiple SCF solutions. Our recent work developed a procedure to linearize SCF space through a Lie algebraic approach. Easier implementation of search algorithms can be achieved in the linear vector space associated with the Lie algebra and then mapped to the SCF solution space. This presentation details our implementation of the basin hopping algorithm. Basin hopping is a stochastic approach to locate the global minimum of a function. In this case, we borrow the idea and apply it to searches of SCF solution space, with steps determined by a Metropolis-Hastings algorithm. In addition, the different interesting solutions that are found will be detailed.

## **Investigation Into Transition Metal Photocatalytic Materials**

<u>Clint Evrard</u> University of Louisville

Single-site transition metal oxide photocatalysis has been suggested as a potential route for the development of new materials with enhanced catalytic performance. The partial oxidation of methane is an example of an industrially important reaction where application of single-site photocatalysis could yield an improved and economically feasible process. Experimentally, selective partial oxidation of methane was observed in the presence of vanadium oxide clusters dispersed on a mesoporous silica scaffold (MCM-41). However, there are several open mechanistic questions regarding the nature of the photoactive species and of the reaction intermediates. In this presentation I show our work examining the electronic structure of excited states in the vertical excitation region of VO4/MCM-41 in order to i) determine the length scale of electronic structure changes upon photoexcitation, ii) examine the electronic structure of excited states responsible for the observed photoactivity, and iii) compare theory with experiment to determine if our computational model is suitable for further investigation into the reaction photocycle.

### Computational Studies of the Interaction between Human Topoisomerase IIα and α-(N)-Heterocyclic Thiosemicarbazones with Molecular Dynamic Simulations

*<u>Florence Fabunmi</u>, Tao Yu* Tennessee Technological University

A series of complexes made by  $\alpha$ -(N)-heterocyclic thiosemicarbazones and copper (II) were studied and previous research has shown that the  $\alpha$ -(N)-heterocyclic thiosemicarbazone (TSC) metal complexes are systematically more active in the inhibition of the human topoisomerase II $\alpha$  (TopolI $\alpha$ ) than the ligands without metals. In this work, the goal is to use computational methods to investigate the interaction between the Cu(II) thiosemicarbazone (TSC) complexes and topoisomerase II $\alpha$ , and the mechanism of the inhibition by these compounds. Experimental data suggest that the Cu(II)-TSC complexes induced high levels of DNA cleavage in topoisomerase II $\alpha$  mediated plasmid cleavage assay. The Cu(II)-TSC complexes with methyl, ethyl and tert-butyl substitutions are slightly more effective than those with benzyl and phenyl groups. The  $\alpha$ -(N)-heterocyclic ring substrates of the TSCs, including benzoylpyridine, acetylpyridine, and acetylthiazole, do not exhibit a significant difference in TopolI $\alpha$ -mediated DNA cleavage. The molecular docking and molecular dynamics simulations were used to study the binding interface between the Cu(II)-TSC complexes and TopolI $\alpha$  and estimate their interaction energies.

## Astrochemistry Made Easy(er) by Quantum Chemistry

#### <u>Ryan C. Fortenberry</u> University of Mississippi

The chemistry of the Earth is tied to only a small set of conditions while most of the rest of the Universe is often grossly different from terrestrial circumstances. Consequently, astrochemical experiments can be quite difficult to perform, but quantum chemistry does not suffer the same difficulties. Here, quantum chemistry is applied to the prediction of gas-phase spectroscopy and molecular formation of various "unstable" molecular systems including proton-bound complexes (i.e. OC—H+—CO), noble gas molecules (i.e. ArCH2+, NeON+, & ArOH+), premineral molecules (i.e. Mg2O2 & MgF2), and odd bonding in chalcogen hydrides (H2S—S+). Additionally, recent work in our group has shown that newer quantum chemical theories such as explicitly correlated methods (F12b) can be utilized effectively to produce experimentally-comparable vibrational frequencies at a reduced cost, but this still only extends the sizes of the molecules to be studied potentially up to benzene. However, reparamenterized semi-empirical methods designed solely to treat hydrocarbons are showing promise in predicting the spectra of small molecules with a significant savings in time potentially allowing for anharmonic vibrational frequency computations of large polycyclic aromatic hydrocarbons and potentially even nanocrystals.

#### An Efficient Physics-based Model of Structural Features in Composite Materials by Hierarchical Decomposition of the Radial Distribution Function

<u>Valerie García-Negrón</u>, Akinola D. Oyedele, Eduardo Ponce, Orlando Rios, David P. Harper, and David J. Keffer University of Tennessee-Knoxville

X-ray and neutron scattering techniques are commonly used to study materials at various structural scales. Composite materials containing both crystalline and amorphous domains generate diffraction patterns that are often difficult to interpret. One approach is to perform atomistic simulations of a proposed structure, from which the analogous diffraction pattern can be obtained for validation. The structure can be iteratively refined until simulation and experiment agree. The practical drawback to

this approach is the significant computational resources required for the simulations. In this work, an alternative approach based on a hierarchical decomposition of the radial distribution function is used to generate a physics-based model allowing rapid interpretation of scattering data. In order to demonstrate the breadth of this approach, it is applied to a series of carbon composites. The model is compared to atomistic simulation results in order to demonstrate that the contributions of the crystalline and amorphous domains, as well as their interfaces, are correctly captured. Because the model is more efficient, additional structural refinement is performed to increase the agreement of the simulation result with the experimental data. This model provides quantitative and qualitative insight into the structure of the composite by parameterization of the crystallite size and volume fraction of crystalline and amorphous phases. We intend to include a total model for three lignin carbon processed conditions (1000 °C, 1500 °C, and 2000 °C) to introduce the structural changes in one specimen.

#### Spectroscopic Accuracy of Diatomic Molecules with Multiple Quantum Chemistry Programs

#### Zach L. Glick, Lori A. Burns, C. David Sherrill Georgia Institute of Technology

Practical quantum chemistry (QC) calculations often require features exclusive to different software. However, specifying identical systems in various programs can require expert-level knowledge of each. The Quantum Chemistry Common Driver and Databases (QCDB) provides a simple Python interface to multiple QC programs. In this work, a set of small diatomic molecules (BH, HF, C2) are optimized with a high-accuracy focal-point approach, incorporating corrections for both scalar relativistic effects and the Born-Oppenheimer approximation. The potential energy curve is then used to calculate spectroscopic constants for the molecules, which are shown to be in good agreement with experiment. This optimization scheme makes use of the Psi4, NWChem, GAMESS, and CFOUR programs.

## Conventional Strain Energies of Thiaphosphirane and the Thiaphosphetanes

<u>Makenzie Griffing,</u> Sarah D. Newell, Shelley A. Smith, and David H. Magers Mississippi College

The conventional strain energies for thiaphosphirane, 1,2-thiaphosphetane, and 1,3-thiaphosphetane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models to investigate the effect of third-row elements on the strain energies of three- and four-membered rings. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using self-consistent field (SCF) theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional, the M06-2X high nonlocality hybrid functional from Thular and Zhao, and the  $\omega$ B97XD functional from Head-Gordan and coworkers which includes empirical dispersion. The basis sets employed are Dunning and

coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, cc-pV(D+d)Z,

cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets are also investigated to determine the effect of the extra d function for sulfur and phosphorus on the overall results. Results are compared to the conventional strain energies of small cyclic hydrocarbons and to other heterocyclic systems. We gratefully acknowledge support from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

#### **Computational Studies on Substrate Binding Motifs in Dissimilatory Sulfite Reductase**

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Evolving for nearly 3.5 billion years, sulfite reduction is one of the earliest known types of energy metabolism [1]. Dissimilatory sulfite reductases (dSirs) are consequential to sulfur metabolism, catalyzing a six-electron reduction of sulfite to sulfide:

 $SO_3^{2^-} + 6e^- + 8H^+ \rightarrow H_2S + 3H_2O$ 

Our study aims to elucidate substrate binding and activation mechanisms in the active site of dSir. We constructed the active site model based on crystallographic, spectroscopic, mutational, and kinetic studies [2-4]. The models consist of four side-chains (Arg $\alpha$ 170, Arg $\alpha$ 98, Lys $\alpha$ 211, and Lys $\alpha$ 213), two water molecules, a heme- and siroheme-Fe<sup>2+/3+</sup> center, three different spin states for each Fe, and three substrates (HSO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, and NO<sub>2</sub><sup>-</sup>). Additionally, we investigate the role of the [4Fe-4S] metallo-cofactor by including it in our model. To study the binding and activation mechanisms, we applied DFT/B3LYP/def2-TZVP level of theory with the ORCA program [5]. Our preliminary results include relative energetics of various spin states, geometric and molecular orbital analysis, and interaction energies describing the differences in substrate-binding motifs.

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### ADAPT Ansatz VQE: Adaptive Derivative-Assembled Pseudo-Trotter Ansatz Variational Quantum Eigensolver

#### <u>Harper R. Grimsley</u>, Nicholas J. Mayhall Virginia Tech

Molecular simulation is a longstanding classical problem for which quantum algorithms seem likely to show significant quantum advantage. Prevalent among these quantum algorithms are variational quantum eigensolvers, or VQEs, which rely on parametrizing molecular wavefunctions in terms of unitary operators, evaluating these unitaries with qubits, then using that data to optimize the molecular structure. The most familiar version of this approach to chemists is a quantum implementation of unitary coupled cluster, a variational but classically intractable variant of coupled cluster where the excitation operators have their adjoints subtracted from them, making them unitary. In a traditional unitary coupled cluster calculation, there are the same number of parameters as in ordinary coupled cluster for the same level of truncation. We have developed an improved algorithm which decreases parameter count dramatically while improving accuracy, Adaptive Derivative-Assembled Pseudo-Trotter VQE, or ADAPT VQE. As its name suggests, this method selects operators from a pool based on the size of their gradients, avoiding unhelpful operators and favoring the most important ones. This framework has shown dramatic improvement over traditional unitary coupled cluster, and is promising for bringing larger systems within reach of existing quantum computers.

# Chiral discrimination by intermolecular interaction energies and vibrational spectroscopy in propylene oxide dimers

#### <u>Reza Hemmati</u>, Konrad Patkowski Auburn University

In this project, we investigate the chiral recognition of homochiral and heterochiral H-bonded propylene oxide dimers. One way for doing that is to calculate the vibrational frequencies of propylene oxide complexes which demonstrates the interaction results in largest frequency shifts, splittings, and chiral recognition effects in the lowest, torsional vibrational mode of the non-interacting monomer.

To this aim, propylene oxide (PO) dimers were optimized and 12 stable configurations found at the MP2/(aQZ,a5Z)+Delta CCSD(T)/aTZ level of theory in which six of them were homochiral and the other six heterochiral. It is also demonstrated that the H-bond stretching frequencies distinguish the strongest H-bonded complexes which lead to the dominating chiral diastereomers.

### Spin-Flip IP/EA: Handling Spin & Spatial Degeneracies With Applications to Double Exchange Systems

<u>Shannon E. Houck</u>, Nicholas J. Mayhall Virginia Tech Single-molecule magnets (SMMs) have been of recent interest due to their potential applications to data storage and quantum computing. One prerequisite for a SMM is that it have a high-spin ground state; however, it is difficult to build molecules with this property because antiferromagnetic coupling mechanisms tend to dominate. Molecules exhibiting double exchange behavior are likely candidates, but they are difficult to model using traditional single-reference approaches because they exhibit spin and spatial degeneracies. We have introduced a new n-spin-flip ionization potential/electron affinity (nSF-IP or n-SF-EA) approach that handles both spin and spatial degeneracies using non-particle-conserving and non-spin-conserving operators. We apply our method to several systems which exhibit strong correlation or double-exchange behavior and discuss the importance of adding orbital relaxations in the form of hole and particle excitations.

#### Computational Study of Dehydration and Dehydrogenation of Alcohols on Supported Oxide Catalysis Based on Cyclic (MO2)n (M=Ti, Zr and Hf, n = 2-4) Clusters

#### <u>Yiqin Hu</u>, Zongtang Fang, Monica Vasiliu, and David A. Dixon The University of Alabama

Alcohol dehydration and dehydrogenation on transition metal oxide clusters (MO2)n (M=Ti, Zr, Hf and n = 2-4) have been studied using density functional theory (DFT) with the B3LYP functional and correlated molecular orbital theory at the coupled cluster CCSD(T) level. The reaction starts with ethanol Lewis acid-base addition to a metal center followed by proton transfer from the alcohol OH to a lattice oxygen. The ethanol Lewis acid-base interaction energies are predicted to be -20 to -35 kcal/mol. The formation of the metal hydroxide/ethoxy couple is not a redox process. Chemisorption leading to formation of the metal hydroxide/ethoxy couple is -40 to -90 kcal/mol. For dehydration, formation of metal hydroxide/oxide/ethanal is endothermic. The proton on the l<sup>2</sup>-C will transfer either to the bridge oxygen -O- or the terminal oxygen -M=O of the catalyst followed by a loss of ethylene. Dihydroxides bonded to the metal will further form a water molecule. The ease of loss of the water depends on the energy barrier. For dehydrogenation, the proton connected to the α-C can transfer either to the metal that the ethanol is attached to, or to the closest bridge oxygen leading to loss of acetaldehyde. The protons on the metal and oxygen can form H2 whereas the protons attached to the two oxygens with the metal in the middle will not form H2 because the product has a higher enthalpy at 0K than the transition state. This work is supported by the U.S. DOE Office of Science, Basic Energy Sciences, Catalysis program.

### Non-Transition-Metal Catalytic System based on Al-Doped Graphene for N2 Reduction to NH3

#### Yonghui Tian, Shuangli Hu, Xiaolan Sheng, Yixiang Duan, Jacek Jakowski, Bobby G. Sumpter, <u>Jingsong Huang</u> Oak Ridge National Laboratory

The prevalent catalysts for natural and artificial N2 fixation are known to hinge up transition-metal (TM) elements. Herein we demonstrate by density functional theory (DFT) calculations that Al-doped

graphene is a potential non-TM catalyst to convert N2 to NH3 under ambient conditions in the presence of relatively mild proton/electron sources [LutH]+ and CoCp\*2. In the integrated structure of catalyst, the AI center serves as a binding and catalytic site while the graphene framework serves as an electron buffer during the successive proton/electron additions to N2 and its various downstream NxHy intermediates. The initial hydrogenation of N2 can readily take place via an internal H transfer from the graphene framework to the N2 ligand bound to the AI binding site. The presence of alkali Li+ ion as an additive can substantially facilitate the binding and activation of N2 at the initial reaction stage and the exchange of NH3 with N2 at the final stage of the proposed catalytic cycle. During the reactions, the graphene moiety shows multiple oxidation states, whereas that of AI approximately remains constant. These findings demonstrate the feasibility of utilizing AI-doped graphene as a non-TM catalyst for N2 reduction to NH3 in a manner similar to that in the homogeneous catalysis based on TM complexes operated under mild conditions. They also highlight the significance of heteroatom-assisted H transfer in the design of synthetic catalysts for N2 fixation.

#### Quantum chemistry on quantum computer: benchmark, unitarymapped imaginary time evolution

#### <u>Renke Huang</u>, Francesco A. Evangelista Emory University

Developing accurate and  $e\bar{r}f$ cient quantum-classical algorithms for solving quantum chemistry problems on the quantum computer remains challenging. The first part of this poster is a study on the correlation strength in a model four-hydrogen system, to provide a benchmark for testing quantum chemical methods on quantum computers. The main idea of this part is to interrogate how the exact energy and the correlation energy change with respect to variations of simple geometric parameters. The second part is the implementation of the unitary-mapped imaginary time evolution algorithm and the test case for computing FCI potential energy surface of the hydrogen molecule.

## A computational study of CO2 interactions with functionalized calixarene molecules

John H. Hymel, Jacob Townsend, Konstantinos D. Vogiatzis University of Tennessee

High carbon emissions have shown a strongly correlated trend with rising global temperatures as the world's climate undergoes a dramatic shift. Work to mitigate the potential damage using methods such as metal organic frameworks (MOFs), covalent organic frameworks (COFs) and polymeric membranes have proven successful in large scale approaches; however, research is still being performed to enhance the capabilities of these materials to be used in an industrial scale. One area which could lead to the improvement of these methods is the discovery of functionalized species with a greater interaction strength for CO2 which additionally selectively bind CO2 over other gas molecules. Calixarenes, named after their resemblance to a chalice, are promising candidates for use in gas separations due to their large basket shape which allows for the possibility to bind multiple CO2 molecules per site. In this study, density functional theory (DFT) calculations were performed on various functionalized calixarene molecules to explore their interactions with CO2 and determine their

viability for this type of separation. A molecular database of functionalized calixarene structures have been generated by IMolGen, an in-house software for molecular database generation. Conclusions from this study can aid in guiding synthetic efforts for materials incorporating these functionalized materials.

#### Elucidation of the Reaction Mechanism of C<sub>2</sub>+N<sub>1</sub> Aziridination from Tetracarbene Iron Catalysts

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Aziridines, the nitrogen analogue of epoxides, are of significant interest in the pharmaceutical industry due to their antibiotic and anticancer properties. Organometallic complexes have shown great promise for the stereospecific, catalytic synthesis of aziridines by combining an alkene (C<sub>2</sub>) and azide (N<sub>1</sub>). Two generations of iron-tetracarbene complexes developed by the group of David Jenkins have shown catalytic activity with organic azides, showing varying reactivity with different classes of azides.<sup>1,2</sup> The stereochemical retention of the aziridine product also differs between the two complexes with the less reactive catalyst giving better stereochemical retention. For both generations of catalyst, aziridination is found to be in competition with the formation of a metallotetrazene product, experimentally requiring excess alkene to push the reaction toward the desired direction. In the present work, we have used density functional theory (DFT) to understand the aziridination mechanism of the two generations of catalyst. Our work reveals the key difference in catalytic activity is a result of the charge on the macrocycle where one generation is charge neutral while the other is doubly cationic. Aziridination with these two generations of catalyst are thermodynamically similar; however, the charge difference leads to different kinetic barriers along the aziridination pathway. Additionally, we have found metallotetrazene formation can be prevented without the need for excess alkene when bulky azides are used. We are currently using the insight gained from this study to design enantioselective iron-tetracarbene catalysts that do not require excess alkene loading.

\*These authors contributed equally.

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#### Quantum chemistry benchmark for near time quantum computing

### Jacek Jakowski, Alex McCaskey, Zach Parks, Shirley Moore, Raphael Pooser, Travis Humble

Oak Ridge National Laboratory

We present a quantum chemistry benchmark for noisy intermediate-scale quantum computers that leverages the variational quantum eigensolver, active space reduction, a reduced unitary coupled cluster ansatz, and reduced density purification as error mitigation.[1] We demonstrate this benchmark on the 20 qubit IBM Tokyo and 16 qubit Rigetti Aspen processors via the simulation of alkali metal hydrides (NaH, KH, RbH),with accuracy of the computed ground state energy serving as the primary benchmark metric. Our results demonstrate the characteristically high noise level present in near-term superconducting hardware, but provide a relevant baseline for future improvement of the underlying hardware, and a means for comparison across near-term hardware types. We also demonstrate how to reduce the noise in post processing with specific error mitigation techniques. Particularly, the adaptation of McWeeny purification of noisy density matrices dramatically improves accuracy of quantum computations, which, along with adjustable active space, significantly extends the range of accessible molecular systems.

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#### Ab initio investigation of ground and excited electronic states of ZrO

#### <u>Benjamin Jackson</u>, Evangelos Miliordos Auburn University

Zirconium monoxide, ZrO, was studied by multi-reference configuration interaction using large basis sets in conjunction with effective core potentials. Complete potential energy curves were constructed and bonding patterns are proposed for several low-lying electronic states. Our numerical results include accurate equilibrium bond lengths, harmonic vibrational frequencies, anharmonicities, excitation energies, and binding energies for both ground and excited states.

#### Intrinsic Energetics of Proton Transfer in Concentrated Binary (HCI)m(H2O)n Clusters

<u>Sarah N. Johnson</u> and Gregory S. Tschumper University of Mississippi

(HCI)m(H2O)n clusters, where  $m \ge 2$ ,  $n \ge 1$  and  $m + n \le 6$  have been optimized using density-fitted second-order Møller-Plesset perturbation theory (DF-MP2) with a correlation consistent triple- $\zeta$  basis set augmented with diffuse functions on non-hydrogen atoms and an extra set of tight d functions for chlorine (cc-pVTZ for H, aug-cc-pVTZ for O, aug-cc-pV(T+d)Z for Cl; denoted ha(T+d)Z). Harmonic

vibrational frequencies were computed in order to confirm that 52 unique configurations were minima (i.e., ni = 0) on the DF-MP2/ha(T+d)Z potential energy surface and to obtain the zero-point vibrational energy correction as well as the room temperature Gibbs contributions. Single point energy computations were performed upon the DF-MP2/ha(T+d)Z optimized configurations with explicitly-correlated coupled-cluster theory that includes all single and double substitutions as well as a perturbative estimate of the connected triple substitutions (CCSD(T)-F12) and the analogous ha(Q+d)Z basis set. A variety of low energy configurations exhibit proton transfer (i.e., CI-/H3O+), especially in the hexamer systems. These concentrated (HCI)m(H2O)n clusters also exhibit double proton transfer (i.e., (HCI)m-2(CI-)2/(H3O+)2(H2O)n-2) minima within tetramer, pentamer and hexamer systems. Most of the characterized proton transfer configurations share a common hydrogen bonding topology. Specifically, the proton donor(s) tend to accept two hydrogen bonds, while the proton acceptor(s) tend to donate two hydrogen bonds.

#### Computational Studies of Neutral and Cationic (UO3)n Clusters: Cluster Formation and Decomposition

#### <u>Paula Kahn</u>, Monica Vasiliu, David A Dixon University of Alabama

Uranium oxides are important species in nuclear fuel processing and the environmental cleanup of nuclear waste at Department of Energy nuclear weapons production sites. Uranium oxides also play a role in commercial nuclear waste storage. Uranium oxide, mined as UO3 and processed into UO2, is used as fuel in nuclear cycles. The UO2 is exposed to oxidizing conditions at various steps leading to the formation of additional uranium oxides. UO2 from spent fuel is not oxidized back into UO3, but rather oxidized into U3O8. The uranyl dication, UO2 2+ has been the subject of numerous studies due to the stability of the +VI oxidation state. We are studying neutral, dication and monocation small (UO3)n clusters for n = 1 to 6. Electronic structure calculations are at the density functional level of theory (DFT), with hybrid B3LYP exchange-correlation functional and aug-cc-pVnZ(O)/cc-pVnZ-PP(U) basis sets, as well as at the correlated molecular orbital theory CCSD(T) level, the latter for benchmarking. Clustering energies, relative energies, total dissociation energies, and ionization potentials are predicted for neutrals and ions. The Natural Population Analysis results based on the Natural Bond Orbitals (NBOs) provide insights into the role of unpaired 5f electrons as well as the role of valence 6d electrons. The role of the uranyl moiety and the uranium formal oxidation state in controlling the structures will be described. This work is supported U.S. Department of Energy, Office of Science, Basic Energy Sciences, Heavy Element and Separation Chemistry Program.

## Oriented Electric Fields Selectively Control the Multistate Reaction Pathways in Azobenzene

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Oriented external electric fields (OEEFs) have potential to control and catalyze chemical reactions through stabilization of charge separation. In fact, OEEFs are hypothesized to play an important role in enzymatic reaction rate enhancement.<sup>a</sup> Recent experimental developments have corroborated theoretical results to demonstrate that OEEFs can be applied to yield substantially different reaction yields and outcomes.<sup>b</sup> However, the vast majority of studies into the mechanistic effects of OEEFs have either been limited to the ground state or the vertical excitation region. In this work we examine the application of OEEFs to the control of excited state (ES) reaction pathways.

ES reaction pathways typically involve a number of different electronic diabats that differ significantly in their electronic structure and so can potentially be finely controlled through OEEFs. In addition, the permanent electric dipole often displays significant variation in both magnitude and direction over the course of ES reaction path, providing a further opportunity for control of potential energy surface (PES) modification through OEEFs. Through multiconfigurational *ab initio* calculations, the effect of OEEFs on the  $S_0$ ,  $S_1$ ,  $S_2$  and  $S_3$  PESs of azobenzene were examined in attempt to understand the OEEFs arrangements that can be used for the control of the photoisomerization process. Controlling *cis-trans* isomerzation in azobenzene is of interest for the development of energy storage devices.<sup>c</sup> We demonstrate how the use of OEEFs, aligned with the azobenzene photoexcitation induced dipole, affects the position of the conical intersection on the PES and can modify the quantum yield of isomerization. Using orthogonally aligned electric fields, we demonstrate independent control of the ground state process that determines the rate of backisomerization from *cis* to *trans*, control of which determines *cis* lifetime as well as a potential route for *cis* to *trans* energy discharge.

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# Comparison of full-DFT and semiempirical tight-binding methods in modeling the branching pathway of a Ni-diimine polyethylene catalyst

#### Jeffrey A. Laub and <u>Jesse L. Kern</u> Randolph College

Homogeneous olefin polymerization catalysts are capable of producing a range of polymer microstructure depending on the reactor conditions, identity of the metal center at the active site, and the electronic properties of the supporting ligands. Of particular interest, recent findings in the area of redox-switchable polymerization catalysis have motivated the use of electronic-structure calculations for finding the electronic and thermodynamic causes of the differentiated polymer microstructure. In this study, we compare two methods for the determination of the energetics of the branching pathway in Ni-diimine polyethylene catalysts: an expensive all-electron DFT method (TPSSh/cc-pVTZ) and a lower-cost semiempirical method (GFN-xTB). Both methods are in qualitative agreement with each other and with the experimentally observed polyethylene branch content. We conclude that the faster GFN-xTB method is accurate enough to be used as a screening and design tool for next-generation catalysts.

# Theoretical study of a complete catalytic cycle for methane to methanol transformation facilitated by metal methoxides

#### <u>Shahriar N Khan</u>, Evangelos Miliordos Auburn University

In this study, we have developed a complete catalytic cycle for Methane to Methanol (MTM) transformation by using quantum mechanical tools. Our proposed catalytic cycle comprises of three stages, namely C-H bond activation, oxidation and isomerization. Metal methoxide cation (CH3OFe+) has been used as a catalyst to activate C-H bond transforming methane to methanol. Then an oxidant (N2O) has been used to oxidize the metal to form metal oxide followed by an isomerization reaction that reproduces CH3OFe+ to complete the catalytic cycle. Moreover, this catalytic pathway suppresses other side reactions. We have employed Multi Reference Configuration Interaction, Coupled Cluster and Density Functional Theorem calculations to construct the energy landscape. It has been found that multi-reference calculations are necessary to capture the complicated nature of the system. And in the future, this research will be expanded further by studying the effect of different ligands in this system.

### Electronic Structure of Diatomic 3d-Transition Metal Oxides and the Effects of Ligand Field Introduction

Justin Kyle Kirkland and Konstantinos D. Vogiatzis University of Tennessee, Knoxville

Diatomic metal oxides play an important role in spectroscopy, catalysis and materials design. In terms of catalytic activity, metal-oxide active sites are prominent species in the activation of C-H bonds and

oxygen atom transfer (OAT) mechanisms. The catalytic activity of these species can vary drastically from metal to metal due to differing electronic structures. For instance, iron(IV)-oxo model complexes have received a lot of attention due to their presence in nature and high catalytic activity. However, manganese(IV)-oxos, while catalytically active, provide much less kinetic improvement over its iron analogue. Herein, we have performed an in-depth study of the electronic structure for all the 3d-transition metal-oxide species. Firstly, the bare, diatomic metal-oxide species has been studied using high-level multireference methods (CASSCF/CASPT2) to elucidate the nature of the speciesâ€<sup>™</sup> chemical bond. Next, weak and strong ligand fields were introduced to determine the effect of the field on the reactivity. Our conclusions will allow for a thorough understanding of the effect the electronic structure of the metals has on the activity of the active site as well as provide heuristics which can guide the synthesis of novel M3d-O species.

Title: Modeling of Structural Features in Lignin Based Composite Materials by Hierarchical Decomposition of the Radial Distribution Function

Authors: Dayton G. Kizzire, Valerie García-Negrón, David P. Harper, David J. Keffer

#### Abstract:

X-ray and neutron scattering experiments can characterize the local atomic environment via a radial distribution function. However, for complex composite materials, the interpretation of the RDF remains a substantial challenge. The difficulty grows when at least one phase is amorphous. The correlation of the RDF to a set of material descriptors, such as crystalline domain size, crystalline volume fraction, total density, is an iterative, computational process. Large scale classical molecular dynamics (MD) simulations can be used to generate a guess of the structure and the corresponding RDF, which can be compared directly to experiment, but each iteration is costly. A significantly more efficient approach for the interpretation of RDFs of complex materials is the Hierarchical Decomposition of the RDF (HDRDF), in which the total RDF is decomposed into components, some of which are modeled with static atomic structures and others of which are modeled as continuous mesoscale objects. The HDRDF approach has been shown to use roughly one million times less computational resources compared to MD simulation. We report progress on the development of a second generation of the HDRDF software, which extends the capability to arbitrary domain geometries. We apply the technique to the interpretation of neutron and x-ray scattering of lignin-based nanostructured carbon composites, which have application as high-performance lithium ion battery anodes.

## Explicitly correlated dispersion and exchange dispersion energies in symmetry-adapted perturbation theory

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In SAPT (Symmetry-Adapted Perturbation Theory), second-order dispersion  $E_{disp}^{(20)}$  and exchange dispersion  $E_{exch-disp}^{(20)}$ energies describe inter-molecular correlation effects, constituting a reliable tool in examination of the nature of interaction energies<sup>1</sup>. Importantly, dispersion energy using the SAPT approach provides the possibility of studying these contributions independently from others and can be added on top of any energy decomposition methods. However,  $E_{disp}^{(20)}$  and  $E_{exch-disp}^{(20)}$ suffer from a serious problem, namely they are notably slowly convergent with respect to the basis set size. It has been shown that the explicitly correlated F12 methods greatly speed up the convergence of electron correlation energy. Therefore, they were adapted for dispersion energy resulting with  $E_{disp}^{(20)}$ -F12 and  $E_{exch-disp}^{(20)}$ -F12. The performance of our methods was examined on the A24 Database<sup>2</sup>, comparing results to benchmarks calculated with aug-cc-pV6Z + hydrogenic midbond functions. The investigation of fixed, fixed diagonal as well as fully optimized Ansätze leads to the deduction of the most accurate and the most computationally efficient approach. We also present the comparison of  $E_{disp}^{(20)}$ -F12 and  $E_{exch-disp}^{(20)}$ -F12 with the SAPT-F12(MP2) method<sup>3</sup>.

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## Modeling the Formation of Atmospheric S-Based Brønsted Acid Gases and Their Degradation Effects on MOF-2 Nanoclusters

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The sequestering and conversion of Lewis acid gases produced during combustion is important for reducing pollution. Metal organic frameworks (MOFs) are of significant interest for their roles as catalysts or sorbents for acid gas sequestration; however, MOFs are expensive to synthesize and can chemically degrade in acid gas environments. Lewis acid gases produced from the combustion of fossil fuels can react with H<sub>2</sub>O to form Brønsted acid gases capable of readily degrading MOFs. Potential energy surfaces (PESs) were calculated for the formation of Brønsted acid gases from the addition reactions of H<sub>2</sub>O and H<sub>2</sub>S to SO<sub>x</sub>. Adsorption of these SO<sub>x</sub> based Brønsted acids to Co, Cu and Zn MOF-2 was modeled by binding the acid to one of the metal centers of the cluster through one of the oxygens in the acid ligand. The subsequent degradation of these clusters was modeled by deprotonating the acid ligand and protonating the BDC or formate linker of the MOF cluster. The displacement of BDC linkers by the conjugate base of these Brønsted acids was also modeled to include the possibility of degradation by SO<sub>x</sub> based Brønsted acid gas conjugates. These results provide insights into how to reduce MOF degradation and to improve acid gas conversion by MOFs. 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.

### Mechanisms of Mobile Ion Hopping in Polymerized Ionic liquids

#### <u>Xubo Luo</u>, Hongjun Liu, and Stephen J. Paddison The University of Tennessee

Polymerized ionic liquids (polyILs) present a subclass of solid polymer electrolytes, where the free ions are mobile while the counter ions are grafted to the polymer chains [1]. As a result of their unique chemical and physical properties, polyILs are a new class of materials with potential applications as the electrolytes for battery and fuel cells [2]. It is believed that ionic conductivity is dependent on the chemical structures of both the polymer and counter ions [3], which enables us to tune the properties of polyILs.

To systematically study the effects of chemical structure and the choice of ions, molecular dynamics (MD) simulations where undertaken to provide atomic-level information of the ion hopping mechanisms. Four types of hopping were identified as: (1) intrachain; (2) interchain; (3) non-associating free ions; and (4) rattling. To find out the effects of different cationic groups and the length of alkyl tails, simulations were performed for poly(n-alkyl VIm) and poly(n-alkyl VATMA), with the counter ion of TFSI<sup>-</sup>. Structural properties were analyzed from the results. The numbers of associating cations and chains to the anions were calculated, and the changing in the anion hopping types were found for the systems mentioned above. This quantitative analysis should guide the design of polyILs for electrochemical applications in the future.

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### Open-Source Numerical Tensor Algebra Library for Heterogeneous Computing in Quantum Many-Body Theory

#### <u>Dmitry I. Lyakh</u> Oak Ridge National Laboratory

Numerical tensor algebra is the computational cornerstone of quantum many-body theory. With the raise of GPU computing, it becomes important for scientific codes to have easy access to an efficient GPU-enabled implementation of basic tensor algebra primitives in the form of a standalone software library. The TAL-SH library provides such an implementation of basic tensor algebra operations, most importantly the tensor contraction operation, for multicore CPU and NVIDIA GPU. The library exposes convenient math-like user interface for C, C++, and Fortran programmers, thus enabling integration with any quantum chemistry application written in any of these popular HPC programming languages. Although TAL-SH allows the user to specify the execution device for each tensor operation explicitly, it fully automates the underlying data management, transfer and synchronization between different devices present on a heterogeneous computing node, thus letting the user to fully focus on high-level algorithm expression instead of low-level details. TAL-SH provides both synchronous and asynchronous semantics for tensor operation API, where the completion of each tensor operation can

either be enforced eagerly or deferred for a later query (NVIDIA GPU only). Additionally, TAL-SH is capable of efficiently utilizing multiple NVIDIA GPU for multiple tensor contractions running concurrently on each GPU as well as for a single large tensor contraction when it does not fit into GPU memory.

GITHUB: https://github.com/DmitryLyakh/TAL\_SH

This research used resources of the Oak Ridge Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC05-00OR22725.

#### A variational approach for the calculation of excited states

#### <u>Andrew Mahler</u>, Lee M. Thompson University of Louisville

Understanding excited-state processes is of importance in a number of biological, chemical and physical applications, including photosynthesis, photovoltaics and photocatalysis. Response-based approaches, such as time-dependent density functional theory and equation-of-motion coupled cluster, can give accurate prediction of electronic structure around the Franck-Condon region, providing that the type of excitation is amenable to the method of calculation. However, simulation of excited state reaction paths involves possible electronic degeneracies and nonadiabatic effects that require a multireference description. Although accurate, multireference approaches are frequently too expensive or technically challenging to be applied to realistic systems. In this presentation, I demonstrate our developments for the application of symmetry-broken self-consistent field solutions. The results of the excited-state resonating Hartree-Fock approach are examined, demonstrating the utility of the method for the calculation of excited state properties.

### A dynamical correlation model for variational two-electron reduced density matrix driven complete active space self-consistent field methods.

#### <u>Elvis Maradzike,</u> A. E. DePrince, III Florida State University

We present a dynamical electron correlation model for the variational two-electron reduced density matrix (v2RDM-) driven complete active space self-consistent field (CASSCF) method, a polynomially scaling implementation of CASSCF that is capable of treating much larger active spaces than is possible with configuration interaction driven CASSCF. The model is based on Pernal's adiabatic connection (AC) between two Hamiltonians: one corresponding to a many-electron system described at the CASSCF level of theory and another corresponding to the same many-electron system described at a level of theory in which electrons are fully interacting. We implement this type of correction for the dynamical correlation energy within the context of v2RDM-CASSCF, using approximate transition density matrices obtained from applying the extended random phase

approximation (ERPA). We compute potential energy curves along the dissociation coordinates for a set of small molecules. We find, using full valence active spaces, that ground state energies computed at the corrected v2RDM-CASSCF level of theory show smaller errors at all geometries, relative to full CI, when compared with those from n-electron second order perturbation theory (NEVPT2). We subsequently compute reaction energies at the AC-v2RDM-CASSCF level of theory.

## Computational studies of alkanol reaction pathways on a SrTiO<sub>3</sub> perovskite surface

<u>K. Reid Mason</u>, Robert C. Chapleski Jr., and Sharani Roy The University of Tennessee, Knoxville

In an effort to understand the role of charge transfer and electron donation from an alkyl group on reaction pathway selectivity, Density Functional Theory (DFT) calculations were used to explore proton transfer and selectivity of subsequent competing dehydration and dehydrogenation pathways for various alkanols adsorbed on  $SrTiO_3(001)$ .

Geometry optimization calculations are used to determine adsorption energies on the  $SrTiO_3(001)$  surface for each alkanol prior to and following the initial transfer of the hydroxyl proton to the surface. The energies of these states can then be compared to evaluate the roles of adsorbate structure and size of the electron-donating alkyl group on protonation upon adsorption, and thus on subsequent dehydrogenation/dehydration steps.

Following optimization, vibrational frequency calculations verify that each optimized alkanol structure on the surface indeed corresponds a to minimum value on the potential energy surface. These theoretical spectra, as well as rate and equilibrium constants resulting from adsorption energies, and molecular geometries of adsorbed species, are then compared to vibrational sum-frequency generation spectroscopy results for experimental systems as performed by our collaborator, Dr. Benjamin Doughty at ORNL.

Not only do our results highlight the role of electron donation by the alkyl group on reaction pathway selectivity but they also are a part of a larger effort to elucidate the role of a pre-reaction geometry on conversion selectivity of alkanols on catalytic perovskite surfaces.

#### Uncovering f-Block Element Separations Pathways Through Computational Methods

<u>Marcos Mason</u>, Caris Smith, Monica Vasiliu, David A. Dixon University of Alabama

Closure of the nuclear fuel cycle is contingent, in part, on the development of effective separations processes for the selective removal of desired radionuclides from used nuclear fuel allowing for further transmutation. Liquid-liquid separation techniques involving multidentate, soft Lewis basic donors have demonstrated significant promise in recent decades. Due to the inherent hazards of radioactivity, cost, and transient nature of many of the f-block elements, experimental studies are difficult and expensive. Density functional theory was used to predict the ability of different ligands based on bis-1,2,3-triazolylpyridines to separate the Gd/Cm pair and the Am/Eu pair in the +3 oxidation state in water and butanol. Different charge states of the ligand were also studied. The

nitrogen in the chelating group has diminished basicity due to its participation in the ligand's delocalized π-system. The basicity of the groups have been predicted to develop correlations with the separations. This work is supported by the U.S. DOE Office of Science, Basic Energy Sciences, Separations program.

### Selecting Basis Sets, Density Functionals, and Relativistic Corrections for Computations of Lanthanide-Containing Molecules

<u>Gavin A. McCarver</u>, Robert J. Hinde, Konstantinos D. Vogiatzis University of Tennessee, Knoxville

The urgency for more efficient separation processes for lanthanides in solution necessitates a better understanding of the electronic structure of lanthanide containing molecules. Prior to performing these calculations, however, we must first determine which level of theory is required to predict the properties of these molecules accurately. Previous studies have sought to determine which theoretical method best models the electronic structure of lanthanide containing molecules but, as of yet, no such study has examined a diverse enough ensemble of methods to definitively determine a method that provides accurate results across a broad range of molecules. Here, we investigate an ensemble of density-functional-based electronic structure methods that includes fifteen functionals. seven basis sets, and three relativistic corrections. The methods in this ensemble have been tested to gauge their accuracy with respect to both the thermodynamic properties of lanthanide diatomics and the geometric properties of larger molecular complexes; these tests have generated a database of several thousand individual electronic structure calculations. From this database, it has been shown that the TPSSh/Sapporo/DKH method combination leads to the lowest mean absolute deviation with respect to both properties studied. In addition, preliminary work has shown that this method is able to accurately capture the trends observed in lanthanide separation using the Bis(2-ethylhexyl) phosphate ligand.

#### Approaches for Machine Learning of Ab Initio Intermolecular Properties

#### <u>Derek P. Metcalf</u>, Daniel Nasciemento, Alexios Koutsoukas, Steven Spronk, Daniel Cheney, C. David Sherrill Georgia Institute of Technology

Accurate estimation of non-covalent interaction (NCI) strength is a fundamental challenge in many fields including pharmacology and materials science. Ab initio quantum mechanical methods like symmetry adapted perturbation theory (SAPT) provide accurate and physically meaningful interaction energy information, but are intractable to compute for large systems like those in drug binding. In this work, we adapt existing tools in machine learning and chemistry to train accurate and transferrable models for prediction of intermolecular properties. We introduce and remedy some idiosyncrasies of the intermolecular problem and propose some best practices in these tasks, including specialized intermolecular descriptors, data curation, and choice of machine learning model.

## **TDDFT Modeling of TiO2 Using Bulk-Mimicking Finite Clusters**

#### <u>Alexander Matthew Meyer</u>, Pragathi Darapaneni, James Dorman and Kenneth Lopata Louisiana State University

We have completed a computational study using TDDFT of an anatase TiO2 crystal as well as a TiO2 crystal under different electric fields. Using an embedded cluster model we have performed real-time time-dependent density functional theory (RT-TDDFT) calculations on rutile and anatase TiO2 clusters to replicate X-ray absorption near edge structure XANES spectrum. The crystals can then be used to model their responses when exposed to different electric fields to analyze any trends in the XANES spectrum. These are then used for verification against previous results from literature and experiment.

#### Describing Atomic Oxygen Interactions with Ag(110) Using a Site-Specific Adsorption Model

#### <u>Carson Mize</u>, Sara Isbill, and Sharani Roy University of Tennessee, Knoxville

Industrially, transition metals are commonly used as catalysts for the functionalization of hydrocarbons. One such example is the epoxidation of ethylene, which uses a silver surface as the catalyst. Ethylene oxide can be further oxidized to form ethylene glycol, an important industrial feedstock used in the production of antifreeze. Despite the extensive amount of research that has been done on this system, the catalytic mechanism is not well understood, specifically how atomic oxygen interacts with various facets of the silver surface. Previous work from both our group and the literature, have shown oxygen atoms adsorbing not only to the surface but also penetrating beneath the surface to the subsurface of Ag(111). However, fewer studies investigate the interaction of atomic oxygen with other low Miller-index surfaces of silver, like Ag(110). In this work, we have used density functional theory (DFT) to study the adsorption of atomic oxygen on the surface and in the subsurface of Ag(110) at various oxygen coverages. In contrast to the behavior found on Ag(111), our work finds surface adsorption to always be energetically favored over adsorption in the subsurface. Additionally, we have used these results to develop an adsorption model that describes the adsorption of atomic oxygen as a sum of pairwise interactions. When compared with our calculated DFT values, it is found that the model qualitatively describes the interaction of atomic oxygen with Ag(110) as a function of coverage. While adsorption in the second subsurface region, the subsurface between the second and third layers of our six-layer computational supercell, is described well by our model, adsorption on the surface and in the first subsurface region have different trends than those calculated with DFT. This result is encouraging due to the simplicity of our model.

#### Unique error metric and lower-bound in Kohn-Sham Density Functional Theory

Mohammad Mostafanejad and Albert Eugene DePrince III

#### Florida State University

Levyâ€<sup>™</sup>s constrained search (CS) method can be adopted to solve the inverse Kohn-Sham (KS) equations and provide a way to measure the density and the energy errors resulting from approximate exchange-correlation (XC) functionals, simultaneously. The total energy density functional is then replaced with its universal kinetic energy counterpart as the most natural metric for the density error analysis in KS density functional theory (KSDFT). We use our new metric to analyze the density-driven error in strongly correlated systems such as the bond dissociation in N 2 molecule and rank the XC functionals for atomic and molecular sets. Based on rigorous mathematical inequalities on the universal kinetic energy density functional, CS-KSDFT can also naturally provide a lower bound to the kinetic correlation energy contribution to the XC energy. This lower bound can be combined with lower bounds on the non-classical part of the Coulomb interaction contribution such as that of Lieb-Oxford to provide a global lower bound on the XC energy. The resulting numerical data for the atomic and the molecular systems conform to our lower bound for the kinetic correlation energy.

#### Conventional Strain Energies of Thiirane, Thietane, Borylthiirane, 2-Borylthietane, and 3-Borylthietane

#### <u>Summer L. Nash</u>, Mary Morgan Mohamed, Shelley A. Smith, and David H. Magers Mississippi College

A previous study in our group revealed that thiirane is less strained than cyclopropane and that thietane is less strained than cyclobutane. A different study of ours revealed that cyclopropylborane is much less strained than cyclopropane. The current study investigates if these effects might be additive. Could a boryl group on thiirane and thietane reduce their strain even more? To answer this question, the conventional strain energies for borylthiirane, 2-borylthietane, and 3-borylthietane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models and compared to the conventional strain energies of thiirane and thietane. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory (MP2), and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06-2X high nonlocality hybrid functional from Thular and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. We gratefully acknowledge support from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

### Computational analysis of lamin A structure and dynamics

#### <u>Acacia Nicholson</u>, Quentin Johnson Berry College

Hutchinson–Gilford progeria syndrome (HGPS) is a rare genetic disorder that results in rapid aging of young children. Patients with HGPS can, at best, expect to live into their late teens with the current treatment options. HGPS stems from mutations in the LMNA gene, which encodes the filament

protein lamin A. This protein is used as a scaffold structure at the nuclear membrane and has roles in maintaining the genome in the interior of the nucleus. The downstream effect of mutations that cause HGPS is the mis-splicing of LMNA mRNA, which produces progerin, a lamin A mutant that contains a deletion of 50 amino acids near the C-terminus of the protein. This severe change in the protein's primary structure prevents it from fulfilling its intended function. Although potential pathways that contribute to disease pathologies have been proposed, there is a lack of molecular understanding of why progerin is unable to complete normal lamin A functions. Here, we conduct molecular dynamics simulations of progerin and lamin A and compare the ensemble of structures to better understand how the structure and dynamics of the two proteins differ. This study will illuminate the underlying alteration in structure and dynamics in progerin which lead to negative downstream effects. This information may be used in further drug development studies to better treat HGPS.

#### Setca Abstract

#### Joseph Senan O'Brien and C. David Sherrill

#### May 2019

Calculating Coulomb and exchange integral matrices during Fock matrix construction presents a major bottleneck in Hartree-Fock and post-Hartree-Fock methods due to their  $O(n^4)$  scaling. Numerous techniques, such as density fitting and Schwartz screening, exist to mitigate this problem. Formally, density fitting reduces the scaling of constructing the atomic orbital integrals associated with these calculations to  $O(n^3)$ ; and in practice they can be reduced to  $O(n^2)$ by Schwartz Screening. This leads to the interesting situation where, at a crossover point, conventional approaches that formally scale as  $O(n^4)$  outperform methods with  $O(n^3)$  formal scaling due to system size. These system sizes also force quantum chemical software packages to use disk storage for the necessary atomic integrals. This problem can be circumvented by simply recalculating the involved atomic orbital integrals in a direct scheme. We do not currently employ a direct scheme in our density fitted regime, so our users see the cross-over between performance of these two methods occur prematurely. We are proposing to add this capability to extend the cost-savings associated with density fitting to larger systems.

## Examining properties of Catechol-O-methyltrasnferase while systematically increasing QM-cluster model size.

#### <u>Manuel A. Palma</u>, Thomas Summers, Qianyi Cheng and Nathan. J. DeYonker University of Memphis

(COMT) Catechol-O-Methyltransferase is an enzyme that deprotonates catecholamine neurotransmitters like dopamine by transferring a methyl group from S-adenosyl methionine (SAM) to its substrate, deactivating the latter. Because of the simplicity of the reaction, this enzyme has been extensively studied using both QM-only "cluster" and QM/MM models. Convergence of structural and thermodynamics properties requires large radial distance-based models because of the oblong shape of the active site. To improve model accuracy, we have used Residue Interaction Networks (RIN) to systematically build QM-cluster models of the enzyme active site, expanding models based upon interactions rather than distance. Properties such as reaction energy, transition state free energy and structural information are computed at the B3LYP/6-31G(d') level of theory with implicit solvation and empirical dispersion corrections. Convergence of properties is evaluated against several distanceand interaction-based methods for increasing model size. The results of this work give insight into more efficient ways of constructing enzyme models.

## Gas Phase Spectra of MgF2 and MgH2 Molecules and their Dimers: A Possible Connection from Gas-Phase Molecules to Planet Formation

#### <u>C. Zach Palmer</u> and Dr. Ryan C. Fortenberry Georgia Southern University

A better-calibrated method for examining planet-forming regions, such as protoplanetary disks, could be rovibrational molecular spectroscopy observation of certain pre-mineral molecules rather than the usual but less affiliated gaseous organic compounds. Planets are created when molecule forming grains come together, but how the molecules form the grains is a topic of concern for both astrophysics and planetary science alike. Four atoms have been shown to be frequently related to planetary formation: Fe, Si, Mg, and O. Magnesium, however, has been shown to have higher relative plentitude in exoplanetary host stars. Magnesium Fluoride (MgF2), which comprises the rare mineral sellaite, and Magnesium Hydride (MgH2) were chosen for analysis as they are simple magnesium-bearing molecules. The monomer and dimer forms of (MgF2)n and (MgH2)n with n = 1-2 are analyzed using high-level quantum chemical computations known to produce accurate results. If the vibrational transitions that are predicted in this work can be observed in the aforementioned planet-forming regions, the initial period of mineral body formation can be indicated.

### Confinement Effects on Electrostatic Screening, Structure, and Dynamics of Ionic Liquids

<u>Suehyun Park</u>, Yi-Jung Tu, Jesse McDaniel Georgia Institute of Technology

lonic liquids are utilized in many electrochemical applications in which they are subject to nanoconfined environments. In confined systems, the structure and dynamic properties of ionic liquids are altered since a high portion of ions is close to the confining wall, causing significant deviations from bulk properties. Furthermore, it is known that neat ionic liquids obey fundamental electrostatic screening conditions known as Stillinger-Lovett sum rules, and but it is unclear how these screening conditions extend to and influence the properties of confined systems. To fully utilize ionic liquids in electronic devices, fundamental understanding these confinement effects is needed. We use molecular dynamics simulations to investigate the ionic liquids [BMIM+][BF4-] and [BMIM+][PF6-] in nano-confinement regimes of 2.5 to 4.5 nm. We analyze how structural properties such as number density and the charge correlation are affected by confinement lengthscale. Interestingly, we find that [BMIM+][BF4-] exhibits a non-linear dynamics in diffusion coefficient as a function of confinement length. We additionally analyze the Stillinger-Lovett(SL) sum rules describing the screening condition of electrolytes, which provides the rigorous connection between the structure and electrical properties. We computed Stillinger-Lovett (SL) sum rules to explain this nonlinearity and study the screening condition in confinement. This work contributes to understanding of the connection between sum rules and structure and dynamics of ionic liquids in confined system, resulting in better prediction of designing new electrochemical supercapacitors.

#### Performances of QTP functionals for the excited state energies

#### <u>Young Choon Park</u>, Ajith Perera, and Rodney J. Bartlett University of Florida

We have developed the density functionals based on the IP-condition [1], namely QTP (Quantum Theory Project) functionals [2-5]. For many molecules tested, the QTP functionals have shown to give excellent results for the ground and excited state energies and properties. In this presentation, we show the excitation energies based on the QTP functionals extensively. Different types of excitations, core to high-lying Rydberg excitation energies are compared with other density functionals and high-level ab initio calculations.

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#### **Conformational Analysis of Pi-Conjugated Organic Oligomers**

#### Morgan A. Perkins,\* Thomas L. Ellington, and Gregory S. Tschumper

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Successful application of organic semiconducting oligomers in electronic devices, such as light emitting diodes (LEDs) or field effect transistors (FETs), depends partly on the oligomer's rigidity to interconversion and the material's solid-state packing efficiency [1,2]. In this work, the torsional profiles of furan- and thiophene-containing oligomers are examined with and without the presence of an electron accepting unit, such as 2,1,3-benzothiadiazole (BTD). MP2 and CCSD(T) computations on the smaller oligomers are used to calibrate the conformational energetics from some popular density function theory (DFT) methods (i.e., B3LYP, M06-2X, and  $\omega$ B97XD). These less demanding DFT and MP2 procedures are employed in conjunction with a correlation consistent, triple- $\zeta$  basis set (cc-pVTZ) to more thoroughly characterize the smaller oligomers via full geometry optimizations and harmonic vibrational frequency computations. These methods are also used to carry out torsional scans of a wide range of systems in order to probe the relative energies of various *syn* and *anti* configurations ( $\tau$ (XCCY)  $\approx 0^{\circ}$  or 180°, respectively, where X,Y = O or S) along with the associated barriers to interconversion.



Oligomer structure with possible substituents R and R' (from left to right): hydrogen, thiophene, furan, and BTD

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### Basis Set Superposition Errors in the Many-Body Expansion of Molecular Properties

#### <u>Benjamin G. Peyton</u>, T. Daniel Crawford Virginia Tech

The underlying reasons for the poor convergence of the venerated many-body expansion (MBE) for higher-order response properties are investigated, with a particular focus on the impact of basis set superposition errors. Interaction energies, dipole moments, dynamic polarizabilities, and specific rotations are computed for three chiral solutes in explicit water cages of varying sizes using the MBE including corrections based on the site-site function counterpoise (or "full-cluster" basis) approach. In addition, we consider other possible causes for the observed oscillatory behavior of the MBE, including numerical precision, basis set size, choice of density functional, and snapshot geometry. Our results indicate that counterpoise corrections are necessary for damping oscillations and achieving reasonable convergence of the MBE for higher order properties. However, oscillations in the expansion cannot be completely eliminated for chiroptical properties such as specific rotations due to their inherently non-additive nature, thus limiting the efficacy of the MBE for studying solvated chiral compounds.

## Benchmark interaction energy studies on the S66 and S66x8 datasets using explicitly correlated approaches with bond functions

#### <u>Ian Pimienta</u> and Konrad Patkowski Auburn University

The effect of adding midbond functions into the conventional and explicitly correlated (F12) calculations of noncovalent interaction energies of complexes in the S66 and S66x8 databases is investigated. The addition of bond functions is shown to provide large improvements for conventional CCSD(T) and CCSD(T)-F12 variants. In general, the mean unsigned errors (MUEs) of the CCSD and triples contributions obtained from conventional and explicitly correlated approaches are smaller when bond functions are used. There is a slight degradation in MUEs for the triples part when the commonly employed MP2-F12/MP2 scaling is used in calculations with bond functions. The much milder CCSD-F12b/CCSD scaling leads to more accurate results and is the recommended choice when bond functions are included. The performance of the CCSD(Tbb)-F12b variant with the (3s3p2d2f) set of bond functions typically provides the most accurate results. Comparison of the MUEs for the different CCSD(T)-F1

2 variants employing different sets of bond functions is presented.

# Molecular modeling of methane transport in silicate frameworks.

Hadi Rahmani, Tom Pace, and Peter Kekenes-Huskey

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The conversion of abundant methane into more useful petrochemical compounds has numerous industrial applications. Silicates including zeolites have emerged as effective catalysts for methane conversion, but generally require high operating temperatures and pressures to significant product generation. However, recent developments have rendered possible methane conversion in aqueous solutions at ambient temperatures. However, much is poorly understood about the reaction/diffusion processes in such materials, such as how confinement of water, methane and other substrates in nano-scale, porous silicate materials shape methane transport and adsorption. To shed light on these factors, we have developed molecular dynamics-based simulations of methane/water transport in silicate materials that are coupled to meso-scale models of methane reaction/diffusion in bulk materials. Using this framework, we have quantified how methane thermodynamics and transport are modulated by the structure of water confined to silicate nanopores. This quantification has yielded first-principles estimates of methane diffusion that differ significantly from bulk solution. We will discuss this protocol and its findings in the context of methane conversion.

## Approximate Spin-adapted Treatment of Single Reference Coupled Cluster for Open-shell Molecules

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#### ABSTRACT

Single reference coupled cluster methods are well established that it gives the most accurate results for most non-degenerate closed-shell ground states. However, it can be inadequate when the zeroth order wavefunction is dominated by more than one slater determinant. Here, we explore the possibility to extend SR-CC theory for excited states and open shell molecular systems by fixing the appropriate amplitudes to the values determined by spin or spatial symmetry. This scheme is expected to accelerate the process of approaching the exact solution which is generally achieved by including higher cluster operators. We report the preliminary results for a set of molecules having two active electrons in two spatial orbitals.

#### How Do Amine Bridges Affect Conjugation in Monomacrocyclic Dendrimer Models?

#### <u>*R. Shelby Ruiz, Aubrey Smyly, Trent Selby, David H. Magers, and Shelley A. Smith* Mississippi College</u>

Due to previous work conducted by the Mississippi College Computational Chemistry Group, it was determined that when forming monomacrocyclic dendrimer models, flat, two-dimensional systems seem to occur more often when 2-pyridinyl groups are utilized. This project originated when the Mississippi College Organic Research Group (MC-ORG) synthesized dendrimer models that were not as flat as desired. Dendrimers need this "flat" orientation in order to retain their conjugation, and therefore, their light harvesting properties. The MC-ORG dendrimers being synthesized contain ethynyl units that are theoretically being locked in place by ether connections. The goal of this research is to determine whether reducing the hydrogen interactions in the bridge between the 2pyridinyl rings would further assist in forming flat dendrimers and retaining conjugation. To do this, amine bridges are placed between the 2-pyridinyl groups that will theoretically lock the ethynyl bridges in place and form flat dendrimers. This amine connection is studied with different carbon lengths in the bridge and in the positions both ortho and meta to the ethynyl groups. To investigate these questions, optimum structures are computed at the SCF and DFT levels of theory. The functionals employed are B3LYP, M06-2X, and  $\omega$ B97XD. The basis sets employed are Dunning and coworkers' correlation consistent basis sets, cc-pVDZ and cc-pVTZ. All calculations use correlation consistent basis sets. Finally, time-dependent DFT calculations are used to investigate the UV-Vis spectra to determine if these various amine connections will improve conjugation within the structure. In the future, NICS calculations will be conducted to determine the aromaticity, and therefore further prove if conjugation is retained. We gratefully acknowledge support from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

### The Rovibrational Characteristics of Ammonia Borane

<u>Spencer C. Rushing</u>, Ryan C. Fortenberry, and Gregory S. Tschumper University of Mississippi

The vibrational frequencies of ammonia borane have been observed experimentally, but their features are convoluted due to a high density of similar frequencies. Quantum chemistry is uniquely suited to describe these features, but Fermi resonances cloud even these attributions. This work utilizes trusted quantum chemical approaches in quartic force field descriptions of the potential for providing anharmonic vibrational frequencies. While the entire vibrational spectrum is still partly in question, this CCSD(T)-F12b/cc-pVTZ-F12 study will help to shed more light on this datively-bonded molecule.

### Electronically Excited States of Closed-Shell, Functionalized Benzene (-CN, -OH, -C2H) Anions

#### <u>Taylor Santaloci</u> and Ryan Fortenberry University of Mississippi

Electronically excited states of closed-shell anions come in singles or at most pairs and typically transpire beyond the visible spectrum into the near-infrared. This makes them tantalizing candidates for carriers of the diffuse interstellar bands (DIBs), a series of astronomically ubiquitous absorption features known for over a century. The recent detection of benzonitrile in space makes functionalized polycyclic hydrocarbons (PAHs) an interesting candidate field for exploring their application to the DIBs. Benzene is functionalized with CN, OH, and C2H in this study and optimized using B3LYP and MP2 with aug-cc-pVDZ basis set. Optimization of functionalized benzene molecules show that closed shell anions of this class have electron binding energies in the 1-2 eV range. The resulting electronically excited states also fall within this range making them interesting potential DIB carriers.

#### Geometries, Energetics and Harmonic Vibrational Frequencies of Structurally Diverse Hydrated Halide Ions by the 2-body:Many-body Method

#### <u>Thomas More Sexton</u>, Caroline Anne Rader and Gregory S. Tschumper University of Mississippi

Energetics, optimized geometries, and harmonic vibrational frequencies of water-halide clusters (H2O)n X– (where n = 2 - 4 and X = F, Cl, Br, or I) are investigated with CCSD(T), MP2, and the QM:QM 2-body:Many-body CCSD(T):MP2 method [1-3], in which all one- and two-body terms are captured at the CCSD(T) level and three-body and higher terms are captured at the MP2 level. We have recently demonstrated that CCSD(T):MP2 (and even the analogous CCSD(T):RHF scheme) provides results of CCSD(T) quality at substantially reduced cost, while MP2 struggles to reproduce CCSD(T) frequencies for both water clusters and halide-water clusters [3,4]. Here the efficiency and accuracy of the 2b:Mb method is exploited to probe a more structurally diverse set of cluster configurations and to extend this analysis to larger triple- and quadruple-zeta quality correlation consistent basis sets to obtain CCSD(T) quality benchmark values for these halide-water complexes.

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#### Direct Entropy Calculation from Molecular Dynamics Simulation

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Entropy, and the related thermodynamic properties free energy and chemical potential, are difficult to calculate from classical Molecular Dynamics (MD) simulations. Thermodynamic integration methods requiring simulations at many temperatures are cumbersome and time consuming and fluctuation based methods have been shown to lack sufficient accuracy. Here we discuss the limitations of thermodynamic integration and fluctuation methods and then explore an entropy functional method based on radial distribution functions (RDFs) and atomic correlation functions produced from MD simulations. RDFs and atomic trajectories for Body-Centered Cubic (BCC) Fe were produced from MD simulations using the Johnson potential. With these simulation results, we first demonstrate a correction of the RDF based Kirkwood functional for the entropy of liquids before revealing a correlation function method for the entropy of solids. Finally, these new results are shown to have good agreement with results from thermodynamic integration for the temperature range 10<sup>2</sup> K to 10<sup>7</sup> K for BCC Fe.

## Intramolecular Hydrogen Bonding in Epoxide, Thiirane, Aziridine and Phosphirane Containing Cyclopentanols

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#### Abstract

A recent computational analysis of the stabilizing intramolecular  $OH \cdots O$  contact in 1,2-dialkyl-2,3-epoxycyclopentanol diastereomers has been extended to thiirane, aziridine and phosphirane analogues. Density functional theory (DFT), second-order Møller-Plesset perturbation theory (MP2) and CCSD(T) coupled-cluster computations with simple methyl and ethyl substituents indicate that electronic energies of the *cis* isomers are lowered by roughly 3 to 4 kcal mol<sup>-1</sup> when the OH group of these cyclopentanol systems rotates to form an attractive intramolecular contact with the O, S, N or P atom on the adjacent carbon. The results also suggest that S and P can participate in these stabilizing intramolecular interactions as effectively as O and N in constrained molecular environments. The intramolecular  $OH \cdots O$ ,  $OH \cdots S$ ,  $OH \cdots N$  and  $OH \cdots P$  contacts also appreciably increase the covalent OH bond length and significantly decrease the OH stretching vibrational frequency in every system with shifts typically on the order of  $-41 \text{ cm}^{-1}$ .

## DAT 30: Dative Bonding Benchmark Database

#### <u>Brett Smith</u>, Konstantinos Vogiatzis The University of Tennessee Knoxville

Dative bonding (also known as coordinate covalent bonding and dipolar bonding) is a two-electron covalent bond where the bonding electrons are donated from one species. It is unique in that at the dissociation limit the bond is heterolytically cleaved, and the donor species is left with the electrons previously donated. It is disguisable from a traditional covalent bond in that significantly polar, considerably weaker and elongated bonds [1]. This is commonly seen in Lewis acid-base pairs, in this study the electron pair acceptors are borane, beryllium, aluminum halides, and chromium, tungsten and platinum coordination complexes with a wide variety of electron pair donors. Standard density functionals have limited success in these systems [2]. Preliminary results have shown that both, hybrid functionals with a large percent of Hartree-Fock exchange and range-separated functionals perform well in systems containing dative-bonds. We have developed the dative-bond database comprised of 28 molecular systems that exhibit dative bonding entitled DAT28. These 28 molecular systems are comprised of 16 small systems, and 12 larger metal containing systems. A variety of hybrid, double-hybrid, meta GGA, GGA and range-separated density functionals; B2PLYP, B3LYP, BP86, TPPSH, TPSS, M06-2X, PBE0, PBE, CAM-B3LYP, and wB97-X are being tested and evaluated based on their relative performance in comparison to a higher level of theory as a reference. For the 16 smaller systems; reference calculations are done using explicitly-correlated coupled-cluster singles doubles and perturbative triples, CCSD(F12)(T), at the complete basis set limit using a two point Helgaker's extrapolation scheme[3,4]. The goal of this study is to provide a comprehensive evaluation of various density functionals and their performance on the DAT28 benchmark, in order to evaluate density functionals and other methods with trusted reference values.

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#### Multiscale Modeling of a Functionalized Surface Catalyst for Hydrogen Peroxide Production

#### Yuriy Snyder Randolph College

We have computationally explored modifications to the anthraquinone catalyst used in hydrogen peroxide (HP) production toward the goal of decreasing activation energies and tethering the catalyst to a surface. The computational method GFN2-xTB was used to optimize anthraquinone molecules, with varying R-groups, and calculate barrier heights for the reaction incorporating these newly modified molecules. The 2-azulenyl and 6-azulenyl substituents were the most effective at lowering the barrier height for the HP production pathway. DFT calculations (B3LYP/def2-TZVP) in Psi4 were utilized to obtain electron densities throughout the modified anthraquinone molecules. Charge distributions were visualized using WebMO. The charge distributions indicated the electron donating

and withdrawing effects of each molecule. Future research directions include tethering the modified catalysts to a surface in the form of a self-assembled monolayer and performing molecular dynamics using a reactive forcefield.

#### Quantifying Protein Contact Networks through Residue-Residue Pair Interaction Energies

#### <u>Thomas J. Summers</u>, Baty Daniel, Qianyi Cheng, and Nathan J. DeYonker University of Memphis

As the fields of computational chemistry and bioinformatics continue to grow, opportunities arise to utilize bioinformatic methods to improve computational modeling. Simulations of enzymes are notoriously challenging as their large size inhibits modeling the whole enzyme with highly accurate but computationally expensive quantum mechanical (QM) methods. Instead, only the most chemically important "active site" residues/substrates/cofactors are modeled in a QM-region and the rest of the enzyme is either modeled with molecular mechanics (QM/MM) or absent (QM-only). How to determine which species are important to include in the QM-region remains ambiguous, and current practices for model construction typically suffer from human bias and reproducibility issues. We propose using protein topology to construct Residue Interaction Networks (RINs) for prediction of appropriate QM-models of enzyme active sites. Using the RIN of a bioengineered threonyl-tRNA synthetase (PDB4S03), gualitative and semi-guantitative topological properties are mapped to quantitative residue interaction energies computed using symmetry adapted perturbation theory (SAPT) at the SAPT0/jun-cc-pVDZ level of theory. Statistical multivariate analyses are used to construct models for predicting interaction energies from the topological descriptors. The results provide insight into how computationally inexpensive RINs might effectively serve as a basis for constructing protein models.

## Data-driven Acceleration of the Coupled-cluster Eigensolver

#### <u>Jacob Townsend</u> and Konstantinos Vogiatzis University of Tennessee

Solving the coupled-cluster (CC) equations is a cost-prohibitive process which exhibits poor scaling with system size. These equations are solved by determining the set of amplitudes (t) that minimize the system energy. Here, a novel approach to predict the converged coupled-cluster singles-and-doubles amplitudes, thus the wavefunction, is explored by using machine learning and electronic structure properties inherent to the MP2 calculation. Features are collected from quantum chemical data, such as orbital energies, one-electron Hamiltonian, Coulomb and exchange terms. The data-driven CCSD (DDCCSD) is not an alchemical method since the actual iterative coupled-cluster equations are solved. However accurate energetics can also be obtained by bypassing solving the CC equations entirely. Our preliminary data shows it is possible to achieve remarkable speedups in solving the CCSD equations. Further applicability and hurdles for larger-scale implementations will be discussed.

## Characterization of inner-layer capacitance from constant voltage molecular dynamics

#### <u>Yi-Jung Tu</u>, Sam Delmerico, Jesse G. McDaniel Georgia Institute of Technology

Applied voltage to an electrode can strongly influence the structure and electrochemical processes at the electrode-electrolyte interface, which are crucial to the energy storage performance of supercapacitors. We develop and implement a new constant potential molecular dynamics (MD) method that is utilized with ab initio, polarizable force fields to characterize the microscopic features at the electrode-electrolyte interface as a function of external voltage. We investigate the parallelplate capacitance of pristine graphite electrodes combined with several organic solvents as well as [BMIm+][BF4–] solutions at various concentrations. Analysis of the double layer capacitance shows that the total capacitance for bulk solvents is rationalized through the combination of the inner layer and diffusion layer contributions. On the other hand, when [BMIm+][BF4-] is present in the capacitor, the total capacitance shows contribution only from the inner layer, as counterions at this layer provide excellent charge screening for the diffusion part of the liquid. This indicates that charge accumulation in the inner layer is important for the enhancement in the double layer capacitance, and increasing the surface roughness of the electrode may help accumulate charges at the electrode surface. Surprisingly, we find that the inner layer capacitance for most of solvents and [BMIm+][BF4-] solutions are very similar, regardless of the types of organic solvents and the [BMIm+][BF4-] concentrations. This results from the hydrophobic nature of alkyl groups interacting with the hydrophobic graphene sheets, and these hydrophobic interactions are sufficiently strong to prevent the polar groups of solvent molecules and electrolyte ion from interacting with the charged surface. This finding implies that hydrophobicity of carbon electrodes is an important consideration for optimizing the inner layer capacitance.

### Spinel Nanocrystals for Insights into Planet Formation

#### <u>E. Michael Valencia</u>, Ryan C. Fortenberry University of Mississippi

Spinel (MgAl2O4) mineral structures may give insights into the evolution of protoplanetary disks and oxygen-rich stars. This MP2 and CCSD(T) study has shown that both a triple cyclic monomer and a planar hexagonal monomer with a radical oxygen provide reasonable pathways to the creation of dimer and trimer structures. Surprisingly, the trimer structure appears to be planar, but further research is necessary to determine the role that spinel may play in planetary formation. The structures, vibrational frequencies, and relative energetics are provided for more than a dozen different monomers, dimers, trimers, and tetramers in order to elucidate the possible aggregation of the constituent atoms into the possible creation of spinel nanocrystals.

### An adiabatic connection formalism for doubly-occupied configuration wavefunctions as a new approach to capture dynamical correlation in strongly correlated systems

#### <u>Nam Vu</u> Florida State University

Multireference perturbation theory is the one of most popular method to capture dynamical correlation for strongly correlated system, yet its use is limited by its high computational cost and strong dependence on the choice of active space. In this work, we would like to introduce a more "black box" method that employs adiabatic connection formalism to capture dynamical correlation from DOCI wavefunction ansatz. The advantage of this routine over traditional ones is that it is based on seniority zero wavefunctions which intrinsically describe strong correlation of chemical system. The polynomial scaling of DOCI calculation can be archived by direct variation of the one- and two- electron reduced density matrices (RDMs) that possess the same structure as those derived from the DOCI wavefunction. The realization of missing correlation energy in the AC framework subsequently requires solutions of a series of eigenproblems based upon the extended random phase approximation (ERPA), which uses knowledge of the 1- and 2-RDMs from DOCI. We show that this approach can efficiently recovers electron correlation in some classic strongly-correlated systems, provided that the seniority zero sector of the Hilbert space is sufficient to capture most of the static correlation of such system.

# Spin splittings from first-order symmetry-adapted perturbation theory without the single exchange approximation

#### <u>Jonathan Waldrop</u> and Konrad Patkowski Auburn University

Recently, the symmetry-adapted perturbation theory (SAPT) first-order exchange term was extended to low-spin complexes resulting from the interaction of high-spin open-shell monomers by way of the spin-flip electronic structure formalism [1]. This presentation describes the next step in the development of the resulting spin-flip SAPT (SF-SAPT), specifically the production of an improved expression for the first-order exchange energy that forgoes the common single exchange approximation of SAPT and replaces it with a single spin flip approximation [2]. To derive the complete exchange term, it is seen that the single spin flips can be treated as a specific subset of the double excitations needed for the calculation of the second-order exchange-dispersion term. The new expressions can be seen to go beyond the Heisenberg Hamiltonian description of the previous method. This new methodology is tested on a selection of small systems to gauge the effect of removing the single exchange approximation, then applied to the determination of the singlet-triplet splitting of several larger pancake-bonded complexes.

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### Electron correlation in chemical bonds II. LiH and LiH+

#### <u>Shehani T. Wetthasinghe</u>, Vitaly A. Rassolov University of South Carolina

Accurate and efficient description of the electron correlation energy is one of the main problems faced by the electronic structure theory. At the same time, the primary object of study by the electronic structure theory is a chemical bond. According to previous work, the electron correlation of H2 - a molecule containing only two electrons and the simplest chemical bond - has been observed to have relatively complicated behavior as a function of bond distance. Our study extends this investigation of the correlation energy to LiH and LiH+ molecules, which are 3- and 4-electron systems from the united atom limit to complete bond dissociation. We find an unusual complexity of the correlation energy dependence on the bond distance. The obtained accurate correlation energy profiles are used to study the performance of the established correlation models; in particular, density functional models are found to be reasonably accurate in the description of the LiH molecule and are deficient in LiH+.

Coordination Modes of Nitrogen to Molybdenum: An ab initio Electronic Structure Study

Maria V. White, Justin K. Kirkland, Konstantinos Vogiatzis University of Tennessee, Knoxville, Tennessee

The development of novel catalysts that can reduce N<sub>2</sub> at mild conditions is of significant interest for the chemical process of ammonia synthesis. High ammonia yields have been attained under ambient conditions utilizing complexes baring molybdenum metal centers. Examination of small clusters composed of nitrogen and molybdenum contributes to the elucidation of the electronic structure and binding motifs of larger molecular systems. *Ab initio* calculations of various molybdenum-nitrogen coordination modes in their neutral and ionic states were performed using multi-configurational (MC) wavefunction theory to examine the bonding between nitrogen and Mo centers. Complete Active Space Self-Consistent Field (CASSCF) and its extension to second-order perturbation theory (CASPT2) methods were employed. The electronic structure of the molybdenum nitrido (MoN) and the mononuclear end-on-bound species (MoN<sub>2</sub>) has been elucidated. Multiple minima were found on the potential energy surfaces of various electronic and spin states of MoN. For all states of MoN<sub>2</sub> considered, the minima lie in the dissociation limit of Mo and N<sub>2</sub>. These results will help us understand the reactivity of known catalytically active complexes and might provide insight into the development and improvement of synthetic catalyst based on the biological mechanism of nitrogen fixation.

# Nuclear wavefunction dynamics with trajectory guided fully adaptable gaussian bases

#### <u>Sachith Wickramasinge</u>, Sophya Garashchuk University of South Carolina

Recent experiments [1] illustrate the importance of nuclear quantum effects, such as tunneling, zeropoint energy and non-adiabatic transitions, on the properties of large molecular systems and materials. The conventional quantum molecular dynamic methods, however, are impractical for applications to general systems beyond a few dimensions, due to the exponential scaling of the wavefunction representation in terms of fixed bases or grids with the system size. Thus, we are developing a quantum dynamics approach which employs adaptable time-dependent Gaussian bases [2]. The Gaussians are guided by the quantum trajectories [3], which follow the evolution of the probability density in time, generating an efficient wavefunction representation in configuration space. The Gaussian bases with adaptable width, center, momentum and phase parameters, are described and their performance is examined for several model systems.

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# Versatility of the QTP family of DFT functionals: Predicting Fermi contact and extended system's band gap

#### Zachary W. Windom, Ajith Perera, Rodney Bartlett University of Florida

Due to its favorable scaling and relatively high accuracy, Kohn-Sham Density Functional Theory (DFT) has transitioned into a dominating workhorse of quantum chemistry that is routinely applied in the study of chemical structure and reactivity while encompassing a variety of fields ranging from the vapor and condensed phases, as well as the solid state. In spite of this the exchange-correlation potential of conventional DFT face significant hurdles, for example, in minimizing the self-interaction error, obtaining the qualitatively correct one particle spectrum, and rectifying the delocalization error of many electron systems. However, by reparamaterizing existing functionals to satisfy the DFT analog of Koopman's theorem, the Quantum Theory Project (QTP) line of density functionals has proven successful in mitigating these issues in addition to correctly describing a variety of phenomena ranging from vertical excitation and charge-transfer energies to reaction barrier heights. Here, we present a further examination of the capabilities of the QTP-00, QTP-01, and QTP-02 functionals in describing the band structure of (rutile) TiO2 as well as the isotropic hyperfine coupling of 13 radical molecules. Preliminary results suggest that the QTP family of functionals predict the experimental band gap while also offering competitive results for Fermi contact, as compared to various standard DFT functionals and CCSD(T) results.

#### The Shapes of the Smallest Rocks

<u>Charlie Worth</u>, Ryan C. Fortenberry University of Mississippi

Through exploration of the molecular arrangements of both enstantite and forsterite, more can be understood regarding planetary formation. These two minerals represent more than 50% of the Earth's volume, making them significant in the formation of potentially habitable planets. The data for the structures, relative energies, and vibrational frequencies for the monomers, dimers, and trimers of MgSiO3 (enstantite) and Mg2SiO4 (forsterite) are produced. MP2/6-31+G\* computations indicate that joined rings are the lowest energy bonding motif present in the enstantite systems. However, the forsterite structures are more complex. The vibrational frequencies have low anharmonicities and notable intensities. These data may help in observing protoplanetary disks or supernova remnants in order to determine the possible presence of planets.

#### Efficient Implementation of Density Functional Theory Based Symmetric Adapted Perturbation Theory

#### <u>Yi Xie</u>, Daniel G. A. Smith and C. David Sherrill 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 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. The current program in Psi4 is shown to be problematic in dispersion energies, and we have spotted the reason and have a plan to fix it. We also tested for the timings of the Psi4 DFT-SAPT program and showed that while it is efficient, it can be further optimized to reduce cost

#### **Calculation of Accurate Low Intensity Strong Field Ionization Rate**

<u>Mengqi Yang</u>, Kenneth Lopata Louisiana State University

Strong field ionization is an important part in the ultra-fast dynamic probes like high-order harmonics generation (HHG). Due to the strong interaction with the electromagnetic fields, the ionization process is out of the perturbation theory. Due to the strong interaction with the electromagnetic fields, the ionization process is out of the perturbation theory. This problem can be circumvented by incorporating a complex absorbing potential (CAP) into the studying system to remove the outgoing electron density. The resultant calculation is comparable with experiment until it enters a relatively low

laser intensity region. Because of the finite basis sets, the overlap between the occupied orbitals and the CAP causes leakage in the system, which introduces significant errors when the field intensity is relatively low. This poster will demonstrate a promising filter to leaking system, by projecting the CAP into the molecular orbital and zeroing the overlap between CAP an d occupied orbitals manually.

### Apply Machine Learning Models in Predicting Magnetic Moment of Ferrite Material

#### <u>Jiazhou Zhu</u>, Rachel Getman Clemson University

In this work, we expand methods from computationally driven design of catalysts to designing ferrite materials. Specifically, computational material involves using density functional theory (DFT) to calculate magnetic moment as they occur over a handful of ferrite material. We would like to correlate the magnetic moment of ferrite material with electronic structures, connections, compositions and other quantities of ferrite material. All the quantities are free of computational calculations and used to set up complete userdefined features sets to fully describe the ferrite material we are interested in. We apply machine-learning algorithm to build a model that correlates the magnetic moment and defined features. We run hundreds of calculations to set up a database which will be taken as the train and test sets to be able train the machine learning model to achieve higher accuracy. Also we employ features selection algorithm in our model to be able to get rid of those redundant features and develop the feature sets in able to increase the accuracy of machine learning model in a separate way. Finally, we would like develop a model free of calculation-derived descriptors will enable the screening of vast chemical

spaces with surrogate machine-learning models, which can be used to identify design rules and isolate lead molecules for further investigation.

## Proton Dissociation and Transfer in Protic Ionic Liquids (PILs)

#### Zhenghao Zhu, Xubo Luo, and Stephen J. Paddison University of Tennessee, Knoxville

Protic ionic liquids (PILs) have attracted significant attention due to their promising properties and potential use in various applications. Recent studies revealed exceptionally strong decoupling of proton conductivity from structure relaxation in a mixture of lidocaine with phosphoric acid. [1] Proton conductivity in this mixture even exceeds that of phosphoric acid at the same viscosity. Both lidocaine and phosphoric acid have proton donor and acceptor sites that facilitate the formation of a well-connected hydrogen bond network contributing to their high proton diffusivity. Thus, it is necessary to study the effects of the molecular geometry of both the acid and base, the number of the proton donating and accepting sites on the acid and base, and the solvation on the proton dissociation and transfer.

In this study, fully optimized structures of pairs and clusters of the phosphoric acids (PAs) with different bases (lidocaine, imidazole, creatinine, and trimethylammonium) were determined through ab initio electronic structure calculations at the B3LYP/6-311G\*\* level of theory in both the gas phase

and the SMD model. The molecular binding energies of PA and the base molecules were calculated from both the uncorrected and zero-point energies (ZPEs) corrected total electronic energies based on the same level of theory. Subsequently, potential energy surface (PES) scans for the transfer of a proton for pairs and clusters of the acids with various bases were performed at the same level of theory to study the effects of different bases and the number of PAs on the dissociation of PA and the proton transfer energetics. The results reveal that dissociated protons are generally more favorable in the SMD model since the continuum solvation model stabilizes the charge separation.

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