

SETCA

2009 ANNUAL MEETING OF SOUTHEASTERN THEORETICAL CHEMISTRY ASSOCIATION

SETCA 2009 Program

Friday Morning		Friday Afternoon		Saturday Morning	
8:30 am	Registration	1:40 pm	Garegin A. Papoian* The University of North Carolina at Chapel Hill	8:30 am	Edward Valeev* Virginia Tech
9:00 am	Akbar Salam* Wake Forest University	2:10 pm	Yongmei Wang University of Memphis	9:00 am	Ilya Balabin Duke University
9:30 am	Steven Wheeler University of Georgia	2:25 pm	Bin Chen* Louisiana State University	9:15 am	Daniel Kosov* University of Maryland
9:45 am	Vitaly Rassolov* University of South Carolina	2:55 pm	Yaroslava Yingling North Carolina State University	9:45 am	Gabor Czako Emory University
10:15 am	Xiangqian Hu Duke University	3:10 pm	Break	10:00 am	Break
10:30 am	Break	3:30 pm	Carlen Ben UT Knoxville	10:20 am	Stefano Curtarolo* Duke University
10:50 am	Hao Hu* Hong Kong University	3:45 pm	Michael-Rock Goldsmith US-Environmental Protection Agency	10:50 am	Wes Crill North Carolina State University
11:20 am	Kyungwha Park Virginia Tech	4:00 pm	Yi-Qin Gao* Texas A&M University	11:05 am	Melissa Pasquinelli North Carolina State University
11:35 am	Shengli Zou* University of Central Florida	4:30 pm	Ram Prasad Bora University of Miami	11:20 am	Xiongce Zhao* Oak Ridge National Laboratory
12:05 am	Erin Johnson Duke University	4:45 pm	Brian Dominy Clemson University	11:50 am	SETCA annual meeting
12:20 pm	Lunch	5:00 pm	Poster & Reception		
		7:00 pm	Dinner		

*Invited speaker

Invited Speakers:

Long-Range Intermolecular Interactions via the Method of Induced Moments

Akbar Salam, Wake Forest University

The fundamental physical theory describing the coupling of electrons and photons is quantum electrodynamics (QED). Its characteristic feature is the imposition of quantum mechanics to the electromagnetic field, as well as to the system of material particles. Numerous successful applications have followed in the areas of single- and multi-photon absorption, emission and scattering of light, and to interactions occurring between particles at long-range. The most frequently employed method of solution for such problems is diagrammatic time-dependent perturbation theory. For higher-order processes, however, the proliferation in the number of time-orderings can prohibit computation. In this talk, an alternative physical viewpoint and calculational scheme is presented within the framework of non-relativistic QED for evaluating energy shifts between interacting species, namely the induced multipole moment method. Applications include retarded dispersion forces between molecules in ground and excited states, modification of the interaction energy by external radiation, and discriminatory interactions.

Semi-classical electron correlation operator

Vitaly Rassolov, University of South Carolina

We revisit a concept of a correlation operator, introduced 10 years ago as a possible method to model electron correlation effects with single determinant wavefunctions. First, we review various original hand-waving arguments that point to a general form of such an operator. Next, we show that a semi-classical approach yields the specific form of a correlation operator. Finally, we apply it to few model system and discuss merits and challenges of using this correlation operator to study chemical problems.

Catalysis and conformational dynamics of well structured wild-type and molten globular mutant chorismate mutases

Hao Hu, University of Hong Kong

We simulated the reactions catalyzed by the well folded wild-type and the molten globular mutant chorismate mutases, focusing on the origin of the catalytic power of the molten globular enzyme and the change of enzyme conformational dynamics along the reaction processes. With the ab initio QM/MM minimum free-energy path method, we were able to determine the height of reaction barriers in good agreement with experimental measurement. The interactions between the enzyme and substrate were analyzed in detail to reveal the interactions responsible for the catalysis. Examining the conformational dynamics of the enzyme reveals the different dynamic transitions between the reactant and transition states, for the wild-type and mutant enzymes, respectively. Our results provided new insights into the important topic for the correlation between conformational dynamics and enzyme catalysis.

Raman scattering enhancement and fluorescence quenching around a metal nanoparticle

Shengli Zou, Department of Chemistry, University of Central Florida

Using electrodynamics and molecular dynamics method, we investigate the surface enhanced Raman scattering near metal nanoparticles and film surfaces. Enhanced local electric field near and far away from a film surface was investigated using the discrete dipole approximation method. The enhanced Raman scattering near a particle surface was examined with a driven force molecular dynamics method. The enhancement and quenching of the fluorescence signal of a molecule adjacent to a metal nanoparticle are explored with the coupled dipole approximation method.

Atomistic and Coarse-Grained Modeling of DNA and Chromatin

Garegin Papoian, UNC Chapel Hill

DNA undergoes very large compactification in cells of higher organisms. We are developing coarse-grained computational models that would allow simulating the way thousands of DNA base pairs and tens of thousands of protein residues interact to condense into a higher order structure, called chromatin. Towards this goal, we have recently derived a coarse grained force field for DNA, using renormalization group inspired technique, which has been rigorously validated against accurate all-atom simulations. We have also applied this approach to coarse-grain simple electrolyte solutions, which, in turn, allows us to include explicit ions in coarse-grained polyelectrolyte models. In a related study, our atomistic computer simulations of a nucleosome, the basic DNA-protein complex unit, allowed us to rationalize condensation of mobile counter ion around these biomolecules. These calculations are used in an ongoing work to coarse-grain electrostatic interactions in the nucleosomal core particle.

Towards understanding the nucleation mechanism for multi-component systems: An atomistic approach

Bin Chen, Louisiana State University

Despite decades of intense research efforts, the molecular details of atmospheric nucleation processes have been elusive and highly debated. Although laboratory experiments and field studies have provided important insights in the chemical species that are actively involved in these nucleation processes, there is very little information on the atomic-level structure of critical nuclei. The problem originates from the activated nature of these processes and the inherent difficulty in the direct probing of the critical nuclei as they are transient and their occurrence probabilities are extremely low. This presentation will focus on the recent development of the aggregation-volume-bias Monte Carlo (AVBMC) based simulation method and the application of this atomistic approach to the molecular-level characterization of various multi-component vapor-liquid nucleation processes. Topics will be selected from: (i) ternary nucleation of water, n-alkane, and alcohols; (ii) ion enhanced nucleation of water; and (iii) extension of the AVBMC technique to the crystal nucleation in super cooled clusters.

Attosecond Chemistry

Daniel Kosov, University of Maryland and Universite Libre de Bruxelles (Belgium)

In atoms and molecules electrons move, interact and exchange places on the attosecond (10^{-18} s) time scale. All standard pictures (molecular orbitals, atomic orbitals, or band structure) are valid only when electron dynamics is slow enough so that the electrons have enough time to adjust to produce a mean field. Attosecond spectroscopy has been recently used to capture experimentally multi-electron dynamics in real time providing for the first time direct time-domain insight into electron-electron correlations. In my talk I will first review recent attosecond experiments relevant to multi-electron dynamics in molecules, then I will discuss theoretical approaches to describe collective ultra-fast responses of correlated many-particle systems.

The hydrophobic and hydrogen bonding interactions in polypeptides

Yi Qin Gao, Texas A&M University

An efficient sampling method was used to calculate the free energy landscape for the folding of polypeptides and small proteins. Special attention was paid to analyze the relations between the folding rate and the hydrophobicity of the side chains and between the strength of the backbone hydrogen bonds and the hydrophobicity. It was shown that the relative hydrogen bond strength correlates well with the hydrophobicity of its local environment. Urea denaturation simulations showed that the kinetics of hydrogen bond breaking (e.g., the order by which individual hydrogen bonds are broken) also correlates with the local environment of the hydrogen bonds. Further, these denaturation studies showed that the breaking of protein hydrogen bonds is more likely initiated by the attack of the amide groups by water molecules, although the denatured structure is stabilized by hydrogen bonds with both water and urea. These results suggest that urea denatures protein through both direct and indirect effects. The physical chemistry reason behind the effects of urea and other co-solvents (denaturants and osmolytes) will also be discussed.

Recent advances in explicitly-correlated electronic structure methods

Edward Valeev, Virginia Tech

Many problems in molecular sciences (bond energetics, spectroscopy, weak interactions, etc.) require highly-accurate and systematically-improvable description of electronic structure. The traditional many-body methods, such as the celebrated coupled-cluster (CC) method, can be used to approach the exact solution, but are severely limited by the slow convergence of the error with respect to the size of the basis set. This so-called basis set problem of the many-body methods is rooted in the inappropriate form of the many-electron expansions used in the traditional methods. Here I will briefly review the history of explicitly-correlated many-body methods, which can be considered the first-principles solution to the basis set problem, and discuss the recent development of practical R12 methods pursued in several groups around the world. In particular, I will highlight our group's work in the area of perturbative R12 methods, which are especially simple without any loss of robustness. We

typically observe that an R12 method need only a modest triple-zeta basis set to match the precision of its more expensive quintuple-zeta standard counterpart. In closing I will discuss a universal R12 approach that can be used to improve any traditional and non-traditional many-body methods.

Disorder-order transitions in Fe nano-catalysts

Stefano Curtarolo, Duke University

Fe and Fe:Mo nanoclusters are becoming the standard catalysts for growing single-walled carbon nanotubes (SWCNTs) via chemical vapor decomposition (CVD). Contrary to the Gibbs-Thomson formalism, experimental results show that reducing the size of the catalyst beyond a certain limit requires increasing the (minimum) growth temperature. This apparent paradox is addressed in terms of solubility of C in Fe nanoclusters. By using first principles calculations, an innovative thermodynamic model is constructed to determine the behavior of the phases competing for stability. As a function of particle size, there are three scenarios: steady state-, limited-, or no-growth of SWCNTs, corresponding to unaffected, reduced, and zero solubility of C in the clusters. The results are extended to Fe-Mo binary catalysts. The 15+ year long-standing question about the effects of Mo concentration on the growth capability is finally answered. Research sponsored by ACS and Honda.

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Simulation study of interaction between DNA and C60

Xiongce Zhao, Oak Ridge National Laboratory

Molecular dynamics simulations are performed to study the binding of C60 or its derivatives with DNA segments in aqueous solution. Despite the hydrophobic nature of C60, our results show that fullerenes strongly bind to nucleotides and form stable C60-DNA hybrids, with binding energies five times larger than that for two fullerenes in aqueous solution. C60 binds to double-strand DNA, either at the hydrophobic ends or at the minor groove of the nucleotide. C60 binds to single-strand DNA and deforms the nucleotides significantly. When the DNA molecule is damaged, fullerenes can stably occupy the damaged site. Simulations indicate that C60 derivatives also form stable hybrids with DNA segments, with binding energies similar to those of pristine C60 and DNA. But the interaction mechanism of C60 derivatives with DNA segments strongly dependent on the type and size of the functional groups. For C60 derivatives with a short functional group, the binding is still dominated by the hydrophobic force. In contrast, C60 derivatives with a long functional group can associate with DNA by entanglement of its hydrophilic chain to the backbone of the DNA through hydrogen bonds. For C60 derivatives with two short acid groups, two different types of interaction were observed, one dominated by hydrophobic interaction and the other one dominated by hydrogen bonds.

Presented Talks

Through-Space Effects of Substituents on Non-Covalent Interactions and Molecular Electrostatic Potentials of Arenes

Steven Wheeler, UCLA and Center for Computational Quantum Chemistry, UGA

Recent progress in our understanding of substituent effects in non-covalent interactions with aromatic rings (pi-pi, CH/pi, and cation/pi interactions) will be discussed, as well as the origin of changes in electrostatic potentials (ESPs) around substituted arenes. It is often assumed that changes in ESP plots are due to local changes in the electron density. This assumption is most prevalent when ESP plots are used to rationalize trends in non-covalent interactions with arenes. In this case, it is common to equate changes in the ESP above the center of substituted benzenes, for example, with changes in the pi-electron-density. We show that changes in the aryl pi-electron density are not necessary to reproduce ESP plots of many substituted benzenes; substituent effects are mostly due to through-space effects. More complex examples of substituted arenes are taken from the fields of host-guest chemistry, crystal design, and drug design. Implications for general non-covalent interactions with aromatic rings will be addressed and the connection to previous work regarding direct through-space effects of substituents on pi-pi and cation/pi interactions discussed.

A gradient-directed Monte Carlo approach to molecular design

Xiangqian Hu, Duke University

The recently developed linear combination of atomic potentials (LCAP) approach allows continuous optimization in a discrete chemical space, and thus is useful in the design of molecules for targeted properties. To address further challenges arising from the rugged, continuous property surfaces in the LCAP approach, we developed a gradient-directed Monte Carlo (GDMC) strategy as an augmentation to the original LCAP optimization method. The GDMC method retains the power of exploring molecular space by utilizing local gradient information computed from the LCAP approach to jump between discrete molecular structures. It also allows random MC moves to overcome barriers between local optima on property surfaces. First, the combined GDMC-LCAP approach is demonstrated for optimizing nonlinear optical properties in a class of donor-acceptor substituted benzene and porphyrin frameworks at the quantum mechanical level. Second, GDMC is applied to protein sequence design and protein folding using the HP lattice model and RosettaDesign. The GDMC algorithm proves to be particularly efficient and significantly improves the sampling of the sequence and conformation spaces. In summary, the GDMC approach is general and robust for discrete global optimization problems as long as the gradients can be constructed from a continuous treatment of the discrete molecular space.

Electron transport through the single-molecule magnet Mn12

Kyungwha Park, Virginia Tech

Single-molecule nanomagnets drew great attention due to their intriguing quantum properties despite their large magnetic moments. Recently, there have

been a large amount of efforts to build and characterize monolayers of single-molecule nanomagnets and single-molecule nanomagnets bridged between electrodes. There were also theoretical efforts to study such systems based on many-body model Hamiltonians. However, there is still lack of understanding effects of local environmental factors on electron transport through single-molecule magnets. We investigate the electron transport through the single molecule magnet Mn12 using the non-equilibrium Green's function method in conjunction with density-functional theory. Considering two representative molecular geometries relative to electrodes and different interfaces/contacts, we discuss the coupling constant between the Mn12 and the electrodes and the charge distribution of conduction electrons over the Mn12, as well as current-voltage characteristics.

Implications of Delocalization Error for Thermochemistry and Bonding

Erin Johnson, Duke University

We discuss the performance of approximate density functionals for main-group thermochemistry from the perspective of the delocalization error. This error causes approximate functionals to give too low energy for delocalized electron densities, as in highly conjugated systems. Conversely, our findings imply that there is a region of highly localized electron density in bicyclic rings and sterically crowded systems that is under-stabilized by functionals with inherent delocalization error. Examination of properties of the density and its reduced gradient reveals that such localized regions are characteristic of non-covalent interactions, including steric repulsion, pi-stacking, and hydrogen-bonding.

Multiscale Modeling of DNA condensation by polycations

Yongmei Wang, University of Memphis

The condensation of DNA helices into compact bundles by multivalent cations has long been studied because of its importance to several experimental and biological processes. Recently, the prospect of condensing DNA with long polycations has been investigated for the potential use of DNA-polycation complexes in gene therapy treatments. Despite the great interest in using polycations as gene therapy vectors, currently available polycation-based gene therapy treatments are insufficient and suffer from a lack of knowledge of the basic physics that govern the formation of DNA-polycation complexes and their structures. Many aspects of DNA condensation by polycations are not well understood. We have thus performed fully atomistic simulation of DNA condensation by polyethyleimine (PEI) and poly-L-lysine (PLL). The simulation revealed a great deal of useful structural information about DNA-polycation complex formation. This talk will present our computational investigation on DNA condensation by polycations and how these computational investigation have improved the understanding of DNA condensation by polycations.

Understanding self-assembly of nucleic acids into advanced materials

Yaroslava Yingling, North Carolina State University

Nucleic Acid molecules can be engineered into novel nanostructures

using the straightforward molecular recognition properties of base pairing. However, the structures are not determined by base pairing alone and unpaired residues play a critical role in nanodesign and superassembly. Yet there is a limited understanding of the rules of formation of RNA and DNA materials. For successful design we need to understand and control the intermolecular associations, natural tendency, favorability and various physical components. We use molecular dynamics to understand the processes driving the self-assembly processes of natural and synthetic nucleic acids. We discovered that in nanoparticles and most organisms the loop-loop assembly process depends on the presence of electronegative and hydration channel. The properties of these channels and the sequence determines the stability, the hydrogen bonding interactions and the angle of the distinct kink between stems. We also show that in layer by layer assembly of nucleic acids films the length of a stem is crucial for the accumulation of the film.

X-ray absorption spectra within the core-hole approximation: An implementation in NWChem

Ben Carlen, UTK

Density functional theory is used to calculate the core excitation spectra of Ti containing catalytic building blocks. Specifically, the core-hole approximation is used. In this scenario, the excitation energies of core electrons are calculated using the approximation that the core energy level be constrained to be unoccupied throughout the relaxation process of the other orbitals. This allows a more accurate determination of the resulting x-ray spectra. The method described has been integrated into NWChem.

Prenatal Plasma Proteins, Playstation 3 and Predictive models for Public Health: a-fetoprotein Alliterated

Michael-Rock Goldsmith, US-Environmental Protection Agency

"Who has seen the abominable α -fetoprotein (AFP)?" Although perhaps one of the most studied proteins (> 10,000 citations), surprisingly very few structural studies are available for human AFP. As the primary protein constituent of plasma in early gestation (throughout post-natal year 1), we ask what makes AFP, a member of the albumin family, so unique? In this study we develop homology models of AFP based on albumin scaffolds and compare and contrast differences between both structures on equal footing. We discuss several important differences that provide AFP privileged access to a critical developmental window, organogenesis. We also discuss the structural, electrostatic, and biophysics of the modeled structure in the context of biology, and explore the implications of variations between its cousin, albumin, on a site-by-site basis: a "Trojan-horse" in a unique and complex environment. We further refine these models with libraries of ligands known to bind to AFP and develop a virtual screening tool to discern preferential binding of ligands to AFP versus albumin. We use the tool to screen a library of FDA-approved drugs, environmental chemicals, nutritional chemicals and lifestyle chemicals using an ultra-high-throughput molecular docking code optimized for the parallel GPU

architecture of modern computer gaming devices, and discuss AFP-enabled selectivity as a result of these experiments. These in silico studies provide an added incentive to invest efforts in both structural studies on AFP, and development of both structure and ligand-based approaches to compare and contrast chemical space determinants of selectivity for adult (albumin) and early life-stage (AFP) plasma binding that may assist in elucidating life-stage specific body-burden and dose-enablement.

Enzyme-substrate (A β 40 and A β 42) Interactions and the Catalytic Mechanism of Insulin Degrading Enzyme (IDE)

Ram Prasad Bora, University of Miami

Insulin degrading enzyme (IDE) is a Zn-containing metallopeptidase involved in the degradation of the monomeric forms of amyloidogenic substrates such as insulin-B chain and Alzheimer's amyloid beta peptides (A β 40 and A β 42). The up-regulating of this enzyme and designing of drug molecules that can mimic its activity represent promising therapeutic avenues for the treatment of Alzheimer's disease. We have performed molecular dynamics (MD) simulations to study the conformational occupancy and the interactions of the full-length substrates, A β 40 and A β 42, in the catalytic chamber of IDE in its active form. Our simulations showed that the substrates undergo conformational changes inside the catalytic chamber and the cleavage sites lie in the vicinity of the active site of the enzyme. We have also investigated the mechanisms for the hydrolysis of Phe-Phe, His-Gln and Lys-Gly peptide bonds of A β 40 by IDE at the B3LYP level. The computed barrier of 14.3 kcal/mol for the hydrolysis of Lys-Gly bond was found to be 4.1 and 8.0 kcal/mol lower than for Phe-Phe and His-Gln peptide bonds respectively.

Towards a biophysical characterization of enzyme evolution

Brian Dominy, Clemson University

Enzymes evolve to optimize their catalytic efficiency in the context of a biochemical reaction network in part by stabilizing the transition state of a specific reaction. However, the physical chemical basis of enzyme evolution is not very well understood and the factors responsible for the optimization of catalytic efficiency during evolution have not been well quantified. In the context of transition state theory, free energy calculations within the classical charmm potential are applied to substrate and transition state analog complexes and used to estimate the impact of mutations on the activity of the HIV protease enzyme. These purely classical calculations are statistically shown to capture this activity information through comparison with recently published experimental results. A more detailed examination of the calculated binding energies suggests ground-state destabilization as a viable physical mechanism underlying the evolutionary optimization of this enzyme. An application of the Michealis-Menten rate laws in the context of the biological environment associated with the activity of HIV protease also supports the mechanism of ground-state destabilization. This study demonstrates that large-scale applications of free energy methods applied to classical molecular models can yield results that are predictive of changes in

enzyme activity through mutation, and can also provide insight into the molecular and physical origins of enzyme evolution.

Coarse-grained modeling of signal transduction in GPCRs

Ilya Balabin, Duke University

G protein-coupled receptors (GPCRs) are seven transmembrane-helix proteins that perform highly specific ligand binding and communicate a broad variety of signals across the cell membrane. Signal transduction in GPCRs is mediated by relatively subtle structural changes that are difficult to identify in the background of thermal fluctuations. We describe a new model of allosteric communications in GPCRs that addresses the fundamental riddle of signaling: the structural origin of the receptor agonism (specific signaling response). The model successfully identified the allosteric sites and the structural changes that mediate signal transduction in two GPCRs, human beta2-adrenergic receptor and bovine rhodopsin. Implications are discussed for understanding the receptor agonism, particularly the recently observed "biased agonism" (selected activation of specific signaling pathways), and for developing rational structure-based drug design strategies.

Accurate ab initio potential energy surface, dynamics, and thermochemistry of the $F + CH_4 \rightarrow HF + CH_3$ reaction

Gabor Czako, Emory University

There have been many experimental and theoretical studies of the gas-phase reactions of a halogen atom and a hydride molecule, e.g. H_2 , H_2O , NH_3 , CH_4 and their isotopologues. Among the atom+diatom systems the $F + H_2 \rightarrow HF + H$ reaction has received a lot of attention. Since an atom+diatom system has "only" three internal degrees of freedom, the dynamics of the above-mentioned reaction have been studied by sophisticated quantum methods. In the case of an atom+polyatom reaction quasiclassical trajectory (QCT) calculations are frequently used in order to describe the nuclear dynamics. The QCT method propagates the nuclei classically while the required forces, i.e. potential gradients, are computed quantum mechanically by solving the related electronic Schrödinger equation. An accurate full-dimensional global potential energy surface (PES) for the $F + CH_4 \rightarrow HF + CH_3$ reaction has been developed based on 19,384 UCCSD(T)/aug-cc-pVTZ quality ab initio energy points obtained by an efficient composite method employing explicit UCCSD(T)/aug-cc-pVDZ and UMP2/aug-cc-pVXZ [X = D, T] computations. The PES contains a first-order saddle point, $(CH_4\cdots F)SP$, separating reactants from products, and also minima describing the van der Waals complexes, $(CH_4\cdots F)vdW$ and $(CH_3\cdots HF)vdW$, in the entrance and exit channels, respectively. The structures of these stationary points, as well as those of the reactants and products have been computed and the corresponding energies have been determined using basis set extrapolation techniques considering (a) electron correlation beyond the CCSD(T) level, (b) effects of the scalar relativity and the spin-orbit couplings, (c) diagonal Born-Oppenheimer corrections (DBOC), and (d) zero-point vibrational energies and thermal correction to the enthalpy. Variational vibrational calculations have been

carried out for (CH₃---HF)v_dW in full (12) dimensions. QCT calculations of the reaction using the new PES are reported. The computed HF vibrational and rotational distributions are in excellent agreement with experiment.

Atomistic + Continuum Multi-scale Modeling of Single Asperity Gold-Gold Contact in an RF MEMS device

Wes Crill, North Carolina State University

The gold contacts of failed RF MEMS devices often show what appear to be melted and re-solidified asperity tips. The mechanism by which this occurs is not well established, but a potential precursor for this could be the formation of nanowires between the asperity contacts. The thermal contribution of Joule heating through these asperities could have a profound impact on the size and behavior of these wires. To understand the influence of electrical potential on nanowire formation in gold-gold RF MEMS contacts, we have carried out simulations of the pull-apart of a single asperity contact using large-scale molecular dynamics simulations coupled to a continuum treatment of Joule heating and heat transfer. The initial asperity geometry, which was derived from a finite element fractal model of a contact blunted by plasticity, contained a 550 nm² asperity on a 7500 nm² substrate that is brought into contact with another flat substrate of the same size. As the contact is pulled apart, the simulations show dislocation emission in the substrate surrounding the asperity contact as well as a nanowires being drawn between the surfaces. The kinetics of wire drawing and defect formation are found to be strongly voltage dependent. When constant current is maintained, the increase in contact resistance that accompanies nanowire formation escalates the magnitude of voltage supplied, further altering defect formation behavior. The correlation between the nanowire formation, voltage conditions and plastic deformation will be discussed and compared to experimental structures observed for hot switching of gold MEMS.

Molecular simulations of carbon nanotubes wrapped with polymers

Melissa Pasquinelli, North Carolina State University

Molecular dynamics simulations were used to study the interaction between a zig-zag single-walled carbon nanotube (SWCNT) and polymer chains with varying degrees of saturation, aromaticity, and aliphaticity. The simulations indicate that polymers with both flexible and rigid backbones tend to wrap around the SWCNT, although in different conformations. Flexible backbones like nylons and polyesters wrap in a random conformation, whereas semi-rigid backbones like polyethylene terephthalate (PET) partially wrap in an S-conformation. Poly-p-phenylenevinylene (PPV) and other polymers with rigid backbones wrap in a distorted helical orientation. Polymers with bulky and aromatic side groups such as polymethylmethacrylate (PMMA) and polystyrene (PS) prefer to coil rather than wrap the SWCNT, although PS showed some pi-pi interactions with the SWCNT. Other trends and the correlation of these features to experimental measurements will be discussed.

Poster Abstracts:

1. Sequence effects on the charge transfer in DNA

Alexander Balaeff, Duke University

The effect of DNA sequence on charge transfer (CT) properties is modeled for the DNA sequences GT_nG (studied experimentally by Giese et al., 2001) and GA_nG . In singly oxidized DNA, the terminal Gs serve as a hole donor and acceptor separated by a bridge of $n=1-5$ AT base pairs. The model employs a combined quantum mechanical and molecular dynamics approach to describe CT at room temperature. Ensembles of DNA structures are obtained for each sequence by molecular dynamics and the energy and localization of the hole are calculated for each structure by a semi-empirical INDO/s method. The hole delocalization between a G and its neighboring A is found to be significant in the GA_nG sequences, resulting in the formation of GA "super-donors/super-acceptors". Consequently, the hole is less likely to be localized solely on a G or on the bridge than in the GT_nG sequences. We therefore predict that the transition between the superexchange and hopping CT regimes occurs at a longer bridge length in the GA_nG sequence than at $n=3$ measured by Giese et al. for the GT_nG sequence.

2. IR Driven Electron Tunneling in Donor-Bridge-Acceptor Systems

Horacio Carias, Duke University

We apply Floquet theory to a simple model of optically driven inelastic electron transfer in a doubly bridged donor-bridge-acceptor (DBA) system. A model system for which elastic tunneling would be symmetry forbidden is considered here. It has been previously demonstrated that inelastic tunneling allows electron transfer (ET) in this system. Further analysis in the framework of Floquet theory reveals that interaction with a photon field may increase the probability of inelastic tunneling and thus enhance the ET rate. Also, a similar system for which symmetry allowed tunneling is modulated by inelastic interactions is developed. Analogies with solid state systems are discussed and connections with experiment are explored.

3. Isotope Labeling to Determine Ligand Exchange Processes at Molecular Organo-rhodium Clusters Supported in a Zeolite and the Reaction of Lanthanides with Fluorinated Methanes

Mingyang Chen, The University of Alabama, Department of Chemistry

The technological advantages of solid catalysts (robustness for operation at high temperatures, lack of corrosion, and ease of separation of products) can be combined with the advantages of soluble catalysts (e.g., selectivity) by synthesis of structurally discrete, nearly uniform catalysts on supports. Our goal is to synthesize, characterize, and model such catalysts and their reactions thereby opening a door to unprecedented fundamental understanding of the properties of such materials. For a rhodium diethylene complex anchored to a zeolite underwent facile, reversible ligand exchange with a variety of ligands including N_2 , C_2D_4 , H_2 , and CO was observed. The supported complexes reacted

with CO to form rhodium gem-dicarbonyls, which, in the presence of ethylene, gave rhodium monocarbonyls. The facile removal of ethylene ligands from the complex in H₂-N₂ mixtures created coordinatively unsaturated rhodium complexes. The coordinative unsaturation was stabilized by the site isolation of the complexes, allowing reaction with N₂ to form rhodium complexes with one and with two N₂ ligands. The results also provide evidence of a new rhodium monohydride species incorporating a CO ligand or possibly a C₂H₄ ligand. The use of isotope labeling in combination with DFT calculations of the frequencies was critical to analyzing the experimental spectra and the observation of new intermediates. Ligand dissociation energies (LDEs) were calculated for the supported rhodium complexes with an accuracy of ±5 kcal/mol. For a complex zeolite-RhLL' (2 ligands bonded to Rh), the average Rh-L dissociation energies (in kcal/mol) are: $\Delta E(\text{H}) = 64 > \Delta E(\text{CO}) = 53 > \Delta E(\text{C}_2\text{H}_5) = 45 > \Delta E(\text{C}_2\text{H}_4) = 40 > \Delta E(\text{N}_2) = 28 \sim \Delta E(\text{H}_2) = 27$. The combination of all of the results provide a detailed picture of the intermediates of a heterogeneous catalytic process and unique insights into the behavior of such site isolated catalysts. Insertion reactions between lanthanide atoms and fluorinated methanes were theoretically studied using the DFT - B3LYP hybrid functional with the DZVP2 basis set for C, H, and F, and the Stuttgart RSC Segmented/ECP basis set for the lanthanides. Binding energies of these reactions were calculated for different reaction paths in all possible spin states to look at the trends and principles in the process of ligand binding on the lanthanide centers. Predictions were also made of structures and vibrational frequencies for IR matrix isolation assignments.

4. On the structure of the water dimer cation

Qianyi Cheng, UGA

Fourteen stationary points structures (1-14) of the water dimer cation on the electronic doublet state potential energy surface are characterized with the coupled cluster single and double excitations (CCSD) and CCSD with perturbative triple excitations [CCSD(T)] levels of theory, utilizing Dunning's correlation consistent polarized valence basis sets (cc-pVXZ and aug-cc-pVXZ, where X = D, T, Q). Two stationary points are found to be local minima, isomer 1 in C₁ point group symmetry with H₃O⁺ -OH character (hydrogen-bonded system), and isomer 7 in C₂ point group symmetry with H₂O⁺ -H₂O character (hemi-bonded system). Among the other stationary points, seven are transition states, and the remaining five are higher order saddle points. The energy difference of the fourteen water dimer cations ranges within 46.5 kcal/mol. The hydrogen-bonded transition states trans- and cis-Cs are within 1.0 kcal/mol of the corresponding minimum 1; this is due to the flat torsional potential connecting these three structures. Adiabatic ionization energies of (H₂O)₂ to 1 and 7 (H₂O)₂⁺ are determined to be 10.5 and 10.9 eV, respectively, which is in excellent agreement with the experimental value of 10.8 ~ 10.9 eV. The dissociation energies of 1 [(H₂O)₂⁺ → H₃O⁺ + OH •] is predicted to be 23.6 kcal/mol, while the dissociation energy of 7 [(H₂O)₂⁺ → H₂O⁺ + H₂O] is determined to be 40.5 kcal/mol. The hydrogen-bonded (1) and hemi-bonded (7) minima are separated

by 8.2 kcal/mol, with a barrier to inter-conversion of 16.0 kcal/mol with the cc-pVTZ CCSD(T) method.

5. *Insights into the Aluminum-Aluminum Bond From Sandwich Metallocenes*

Katie Compaan, University of Georgia

The structure and energies of the unusual aluminum sandwich compound, bis-penta-methyl-cyclo-penta-dienyl di-iodo-di-alane, are investigated using density functional theory (DFT) at the DZP B3LYP level, with an effective core potential (ECP) for iodine. This species is of interest as an Al(II) intermediate in the production of $(\text{Cp}^*\text{Al})_4$ from $[\text{Cp}^*\text{Al}(\mu\text{-I})]_2$, where Cp^* indicates the penta-methyl-cyclopenta-dienyl ligand. Although $(\text{Cp}^*\text{Al})_4$ was discovered in 1991, it was not until 2008 that this Al(II) intermediate was found for the Al(III) to Al(I) synthesis. It is also one of the few known species with an aluminum-aluminum bond. The barrier to rotation and heat of formation will be computed, as well as geometric and bonding parameters. We will also investigate the effects of replacing iodine with other ligands, such as chlorine, bromine, fluorine, or hydrogen. Preliminary results will be presented.

6. *Benchmarking Electron and Fluoride Affinities for 2nd and 3rd Transition Metal Compounds*

Raluca Craciun, University of Alabama

Electron affinities of the second and third row transition metal hexafluorides, MF_6 , were predicted by using density functional theory (DFT) and molecular orbital methods. Calculations were done up to the CCSD(T)/complete basis set limit with additional corrections. Molecular spin orbit corrections were needed to predict the electron affinities of the 3rd row transition metal hexafluorides and may need to be regularly included in predictions of transition metal cluster reactivity. The calculated adiabatic and vertical electron detachment and vertical electron attachment energies (ADE/VDE, VAE) are compared with the available experimental results. The performance of a wide range of DFT exchange-correlation functionals was benchmarked by comparing to the accurate CCSD(T) results. For the third row metals, the adiabatic electron affinities increase across the row. The introduction of correlation reduces the electron affinities contrary to expectation. A similar approach was used to predict the fluoride affinities of second and third row transition metal fluorides MF_n . The large values, ranging from 70 to 110 kcal/mol, show these compounds to be good Lewis acids. Fluoride affinities have also been calculated for groups IVB-VIIB oxides MOn , oxofluorides MOxFy , chlorides MCl_n , and mixed halides $\text{MCl}_x\text{-yF}_y$.

7. *Linear-Scaling Calculation of Time-Dependent Density Functional Theory with Non-Orthogonal Localized Molecular Orbital*

Ganglong Cui, Duke University

Time-dependent density functional theory (TDDFT) has broad applications in study of electronic response, excitation and transport. To extend such application to large and complex systems, a linear scaling formulation has been

developed based on the reformulation of the TDDFT equations in terms of non-orthogonal localized molecular orbital (NOLMO). NOLMO is the most localized representation of electronic degrees of freedom and has been used in ground state calculations. Its novel use in TDDFT leads to a very simple form of time propagation equations which can be solved with linear-scaling effort. In addition, fast NOLMO's construction in large-scale systems is also realized which removes the limitations of constrained optimizations in original one, resulting in unconstrained minimization. This opens up pathways for TDDFT applications to large bio- and nano- systems.

8. Bridge mediated two electron transfer pathways for generating free carriers from multi-exciton

Balamurugan Desinghu, Duke University

Multi-exciton generation in semiconductor nanoparticles is a process of great interest for enhancing the efficiency of solar energy conversion. The theoretical power conversion efficiency of solar cells with the multi-exciton generation is predicted to be greater than 40%. However, a current challenge is to extract free carriers from the multi-exciton state within the multi-exciton lifetime of about 100 picoseconds. We investigate donor-bridge-acceptor systems for achieving charge separation from multi-exciton. Our model assumes the creation of bi-exciton in a donor and describes the bridge mediated tunneling of two-electrons to the acceptor. The bridge-mediated two-electron transfer (2ET) tunneling matrix elements are expressed in terms of tunneling pathways using a many-electron Greens function projection technique and a Hubbard Hamiltonian. We find that the 2ET tunneling matrix element, and thus the rate of 2ET is predicted to grow non-linearly with the number of parallel bridge units linking donor to acceptor, or with the number of acceptor nanoparticles linked to a single donor through independent bridge units. The nonlinear enhancement of the 2ET tunneling matrix element with the number of bridge linkers is characteristic of 2ET, and distinguishes it from single-electron tunneling. Our findings suggest strategies for rapidly generating free carriers from the multi-exciton state.

9. Investigation of Criegee Intermediates: The Formation and Decomposition of Dioxirane

Bryson Dye, UGA

Carbonyl oxide (1), dioxirane (2), and methylenebis(oxy) (3) have been studied using multi reference ab initio methods. These three species are prototypical Criegee intermediates, which constitute important transient species in the ozonolysis of simple alkenes. Complete Active Space Self Consistent Field [CASSCF(6,4)] computations with 6 electrons in 4 molecular orbitals were carried out on 1, 2, and the transition state (TS1-2) connecting them through the formation of a new C-O bond. The active space was increased to CASSCF(6,6) for calculations on 2, 3, and the transition state (TS2-3) connecting them through the cleavage of the O-O bond. Multi reference configuration interaction (MRCI) calculations are currently being carried out on all stationary points. These will be followed by state-specific Mukherjee multi reference coupled cluster singles and

doubles (MkCCSD) optimizations. The MkCCSD results will provide the most accurate barrier heights for isomerization of these Criegee intermediates to date.

10. *Evolution of an Amorphous Carbon Surface due to Chemical Sputtering using Molecular Dynamics Simulations*

Marcel Fallet, Clemson University

Thermonuclear fusion experiments in magnetically confined reactor geometries damage the inner wall of the reaction vessel, which can lead to unpredictable chemical reactions, diminished material strength of the reactor wall, and instability of the confined plasma. It is determined from experimental data that the walls of the reaction vessel, often made of graphite or some other crystalline material, evolve to amorphous carbon in very short time frames. Chemical sputtering molecular dynamics simulations are therefore useful in studying the effect of constant, long-term impacts on various starting surfaces. Although it has been hypothesized that graphite surfaces will become amorphous after many impacts, a focused study has not yet been done, and the properties of this amorphous material are unknown. Using the Reactive Empirical Bond Order (REBO) and Adaptive Intermolecular REBO (AIREBO) potentials, both prepared amorphous carbon and crystalline graphite surfaces were impacted with neutral deuterium atoms with 100 eV and 20 eV translational energy for several thousand impacts at a substrate temperature of 750 K. The resulting sputter yields and the surface composition can then be analyzed and compared to experimental values. Here, we present early results of the evolution of these amorphous carbon and graphite surface simulations using the AIREBO and REBO potentials.

11. *Electron Correlation Effects and Spin Contamination in Electronically Excited States of Interstellar Radicals*

Ryan Fortenberry, Virginia Tech

The decades-old collaboration between theory and experiment in astrophysics has resulted in the identification of dozens of molecules in interstellar and circumstellar media, primarily via comparisons between predicted and measured microwave emission fingerprint spectra. However, theory has been less fruitful for the comparable task of prediction of electronic spectra- especially of the many radical species likely to exist in interstellar space- because of the greater sensitivity of such spectra to electron correlation effects, basis set completeness, spin-contamination, etc. In this work, we examine the ability of coupled cluster methods to produce accurate simulations of the electronic spectra of two sets of radical chain species: $C_{2n}H$ and $SiC_{2m}+1H$. Both families of molecules have been implicated in interstellar chemistry, and their electronic spectra exhibit a number of interesting complications, including spin-contamination and vibronic effects. We will specifically consider the ability the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method as compared to the more complete CC3 approach, which includes the effects of connected triples, to provide electronic excitation energies that are invariant to the choice of reference wave function.

12. *Modeling Charge Transferred Distribution in Buckminster fullerene*

Jacob Fosso-Tande, University of Tennessee

We study the distribution of charge transferred from Calcium (Ca) to Buckminster fullerene (C60). The quantum mechanical electrostatic potential and the partial charge distribution difference between Ca@C60 and C60 gives neither an excess charge within the volume of C60 nor on the surface of C60. Molecular orbital analysis shows a transfer of two electrons from Ca to the LUMO of C60: about 61% of the electrons reside on the surface and the remaining 39% reside in the volume of C60. Charge transfer in C60 is not a quantum mechanical electrostatic process but a molecular orbital interaction process.

13. *Nonadiabatic dynamics and tunneling in large reactive systems using coordinate/polar wavefunction representation*

Sophya Garashchuk, University of South Carolina

Quantum-mechanical effects in molecular dynamics -- zero-point energy, tunneling and non adiabatic dynamics -- are essential for accurate description and understanding of reactions in complex molecular systems. Since the exact solution of the Schrödinger equation for such systems in full dimension is neither feasible nor necessary, the trajectory-based approaches have special appeals: (i) Monte Carlo sampling of a wave function circumvents the exponential scaling of the conventional quantum methods; (ii) all degrees of freedom can be treated on equal footing avoiding the quantum/classical separation issues; (iii) classical description is cheap and appropriate for dynamics of heavy particles such as nuclei. In order to include quantum effects into trajectory dynamics, the de Broglie-Bohm formulation of the Schrödinger equation is used to formulate a trajectory ensemble method; the quantum force, which when approximated in a practical in high-dimensions manner, introduces dominant quantum effects in semi classical systems. The 'hard' quantum effects - nonadiabatic dynamics and tunneling - are included by combining this trajectory approach with the complex coordinate space amplitudes transferring 'population' between the reaction channels. The approach is applied to O(3P,3D)+H₂ reaction treated in three-dimensions on four electronic states coupled by the spin-orbit interaction. The wave packet reaction probabilities are in good agreement with the quantum-mechanical results. Intersystem crossing is found to have negligible effect on reaction probabilities summed over final electronic states.

14. *Prediction of Thermodynamic Properties for H₂ Spent Fuel Regeneration Schemes and Heats of Formation of IOOX Compounds*

Edward Garner, The University of Alabama

Critical issues for the use of H₂ as a fuel for fuel cells in the transportation sector include the development of efficient and safe H₂ storage materials. Chemical hydrogen storage is a storage approach which eliminates issues such as high pressure and low temperature, as the hydrogen is stored in chemical bond and is delivered via a chemical reaction. For any such hydrogen storage system to be practical, it is equally important that the spent fuel material be

reprocessed/recycled efficiently. Unlike combustion, where the spent fuel is ejected into the atmosphere, we need to recycle the spent fuel so that it can be used for a very large number of cycles. We have used computational chemistry methods to predict the energetics of a range of regeneration reactions using density functional theory and molecular orbital theory relevant to hydrogen storage issues. The thermodynamics of these reactions need to be for the liquid phase for use in process simulations and to predict the overall thermodynamic efficiency. The gas phase heat of formation can be calculated directly or by using isodesmic reactions. The heat of vaporization was obtained from the calculated boiling point obtained by using the COSMO-RS approach at the BP/TZ2P level using the ADF program and the rule of Pictet and Trouton with $\Delta H_{\text{vap}} = T_{\text{BP}}\Delta S$, where T_{BP} is the calculated boiling point and $\Delta S = 22$ or 25 cal/mol-K. The unknown dispersion element specific parameters of COSMO-RS were optimized by fitting to experimental boiling points of known compounds while the solvation radii were left at the default of 1.17 times the Van der Waals radii. The calculated boiling points using the optimized parameters were in good agreement with experimental data when it was possible to test them. An example of a regeneration scheme is presented as well as one for first fill. Since Molina and Rowland's paper on the role of chlorine atoms in the destruction of ozone in the stratosphere, there has been substantial interest in the nature of halogen oxides and their potential impact on stratospheric ozone. High level ab initio electronic structure calculations at the coupled cluster level with a correction for triples (CCSD(T)) extrapolated to the complete basis set limit have been made for the thermodynamics of the IOOX isomers, for X a halogen. Corrections for atomic spin orbit, scalar relativistic effects, and zero point energy were added to the weighted core complete basis set binding energies for higher accuracy. The calculated heats of formation of the XOOY isomers exhibit different trends which apparently depend on the oxidation state of the central atom.

15. *Accurately Characterizing the pi-pi Interaction Energies of Indole-Benzene Complexes*

Yue Geng, Georgia Institute of Technology

Noncovalent interactions play a significant role in determining the structures of DNA, RNA, and proteins. Among the most prevalent are pi-pi interactions, which occur as favorable van der Waals forces between the aromatic subunits of biochemical molecules. Tryptophan and phenylalanine are commonly modeled with indole and benzene, respectively. We have utilized the spin-component scaled second-order Moller-Plesset perturbation theory (SCS-MP2) method to compute all T-shaped interaction energies and sandwich shaped 3-D potential energy surfaces (PESs). The trend of the T-shaped interactions has been rationalized via an electrostatic potential mapping of indole. The 3-D PESs suggest the minimum occurs when the center of the benzene is over the nitrogen of indole (disagreeing with previous results by other groups). Furthermore, the coupled-cluster of single and double excitations with the perturbative treatment of triple excitations, CCSD(T), method (the "golden standard") has been used to obtain interaction energies at each local minima confirming the T-shaped N-H/ π

interaction to be the global minimum and the sandwich shaped minimum to be over the nitrogen (agreeing with SCS-MP2 results).

16. Structure and Heats of Formation of the Krypton, Iodine and Xenon Fluorides and the Respective Closed Shell Ions from CCSD(T) Electronic Structure Calculations and Reliable Prediction of the Sterical Activity of the Free Valence Electron Pair in ClF_6^- , BrF_6^- , KrF_6^- , IF_6^- , and XeF_6^- .

Daniel J. Grant, The University of Alabama

Because of the general interest in the bonding in noble gas compounds and the lack of experimental data coupled with large discrepancies, reliable theoretical calculations are very important for the prediction of their structures and thermodynamics. A key part of the more recent efforts to identify new molecules containing noble gas atoms has been the use of computational chemistry in the analysis of structural and spectroscopic data and thermodynamic properties. The use of modern computational chemistry approaches for the prediction of the properties of noble gas compounds has come about due to the confluence of advances in theory, algorithms, software, and high performance computer architectures. Atomization energies at 0 K and heats of formation at 0 K and 298 K are predicted for MF_n , $\text{MF}(n-1)^+$, and $\text{MF}(n+1)^-$ ($n = 2, 4, 6$) for $M = \text{Kr}$ and Xe and MF_n , $\text{MF}(n+1)^+$, and $\text{MF}(n+1)^-$ ($n = 1, 3, 5, 7$) for $M = \text{I}$ from coupled cluster theory (CCSD(T)) calculations. To achieve chemical accuracy ($\text{\AA}\pm 1$ kcal/mol), three corrections were added to the complete basis set binding energies: corrections for core-valence, scalar relativistic, and atomic spin-orbit effects. Vibrational zero point energies were computed at the CCSD(T) level where possible. The calculated heats of formation are in good agreement with available experimental data and allow for the prediction of F^+ and F^- affinities, and F_2 dissociation pathways. We predict correctly the steric activity of the free valence electron pair on the central atoms in KrF_6^- (Oh), XeF_6^- (C3v), IF_6^- (C3v), BrF_6^- (Oh), and ClF_6^- (Oh).

17. Understanding Nerve Agent Antidote Specificity via Molecular Dynamics Simulations

Steven Gwaltney, Mississippi State University

The potential use of nerve agents by either terrorist groups or rogue states remains a significant threat to national security. Currently, war fighters carry with them antidotes to nerve agent poisoning. However, developing a broad spectrum and fast acting reactivator remains a priority for the United States and other friendly militaries. This poster chronicles our recent work simulating the interactions of next-generation reactivators with enzymes that have been poisoned with the nerve agents sarin and tabun. Nerve agents are organophosphates, which bind covalently to the active sites of cholinesterases, leading to overstimulation of the nervous system. Currently, oximes are used as reactivators. The role of the oxime is to attack the organophosphate bound to the cholinesterase active site and remove it from the enzyme. Two of the oximes under consideration for deployment in the near future are obidoxime and HI-6. However, none of the reactivators are effective against all nerve agents. To

better understand the cause of this, we have built models of human acetylcholinesterase and human butrylcholinesterase inactivated by sarin and by tabun. To each of these models we have docked obidoxime and HI-6. Based on the docked structures, we have performed explicit solvent molecular dynamics simulations to determine the interactions of the oximes with the enzymes. In this poster we present the results of these simulations. In addition, we discuss possible causes of the differences in potency against sarin and tabun between obidoxime and HI-6.

18. *On the Mechanism of Proton Transport in Model Perfluorosulfonic Acid Systems: Ab initio Molecular Dynamics Simulations*

Bradley Habenicht, University of Tennessee, Knoxville

Proton exchange membrane fuel cells (PEMFCs) have the potential to provide a clean and efficient source of energy through the electrochemical conversion of hydrogen and oxygen into water. Current difficulties in the optimization of these systems include operating temperatures below 100 °C, high humidity conditions, and catalyst poisoning. Furthermore, the phase separation that occurs when the membranes are hydrated creates an extremely complex and inhomogeneous system. Understanding the connections between structure and proton transport has therefore been difficult. A detailed understanding of this disordered network is required for the development of ionomers capable of efficient proton transport under conditions of high temperature and low hydration. Ab Initio molecular dynamics (AIMD) allow the study of proton diffusion and transport on the nanometer scale with no empirical parameters or force fields. AIMD does not require assumptions about the mechanisms or structures of proton transport and may reveal surprising reaction dynamics and pathways. As carbon nanotubes (CNT) are very structurally defined on a nanometer length scale, they provide a scaffold for investigating effects of acidic group density and distribution on proton transport. The CNT allows for the study of transport that is nearly one-dimensional and also Zundel or Eigen ion formation, and the effects of minimal hydration on transport. The AIMD simulations were performed using the Vienna Ab Initio Simulations Package (VASP). The simulation cells were constructed with periodic boundary conditions along the length of the CNT and 6 Å of vacuum in the perpendicular directions. The geometry was optimized to its minimum energy structure and the system was then heated to 300K using repeated velocity scaling. Once the cells were thermalized, 10 to 20 ps trajectories were obtained in the microcanonical ensemble for the calculation of diffusion coefficients and the analysis of ion formation.

19. *Non-adiabatic Scattering Wave Functions in a Simple Born-Oppenheimer Model*

George Hagedorn, Virginia Tech

We describe mathematical results, obtained in collaboration with Professor Alain Joye of the Institut Fourier, that concern non-adiabatic transitions in a simple molecular dynamics model. We study scattering theory for the time-dependent molecular Schrödinger equation:

$$i\varepsilon^2 \frac{\partial \psi}{\partial t} = -\frac{\varepsilon^4}{2} \frac{\partial^2 \psi}{\partial x^2} + h(x)\psi$$

in the small ε (Born-Oppenheimer) limit.

We assume the electron Hamiltonian $h(x)$ has finitely many levels and consider the propagation of coherent nuclear states with sufficiently high total energy. We further assume two of the electronic levels are isolated from the rest of the electron Hamiltonian's spectrum and have an avoided crossing with a small ε -independent gap. We compute the leading order behavior for the nuclear wave function associated with the non-adiabatic transition that is generated as the nuclei move through the avoided crossing. This component is of order $(-C/\varepsilon^2)$. It propagates asymptotically as a free Gaussian in the nuclear variables, and its momentum is shifted. The total transition probability for this transition and the momentum shift are both larger than what one would expect from a naive approximation and energy conservation.

20. *Non-Covalent Interactions between a Polycyclic Aromatic Diol Epoxide and DNA Base Pairs*

Jacqueline Hargis, University of Georgia

The interaction of a mutagenic and tumerogenic polycyclic aromatic diol epoxide (PADO) with DNA base pairs has been studied using the M05-2X DFT functional. PADO is a metabolite of benzo[a]pyrene, a renowned carcinogenic component of soot. The ultimate aim of this work is to delineate factors determining sequence selectivity in the intercalation of PADO into DNA. A large number of low-lying complexes of PADO with the GC and AT base pairs have been located. The interaction is modulated by a combination of hydrogen binding between the base and the hydroxyl and epoxide groups of PADO and pi-stacking interactions between the bases and the aromatic core of PADO. The global gas phase minimum energy geometry is congruent with an experimental structure of a PADO-DNA adduct determined via two-dimensional NMR.

21. *Effects of Hetero-atoms on pi-pi Interactions: Benzene-Pyridine and Pyridine Dimer*

Edward Hohenstein, Georgia Institute of Technology

Hetero-atoms are found in many non-covalent complexes which are of biological importance. The effect of hetero-atoms on pi-pi interactions is assessed via highly accurate quantum chemical computations for the two simplest cases of interactions between aromatic molecules containing hetero-atoms, namely, benzene-pyridine and pyridine dimer. Benchmark quality estimated coupled-cluster through perturbative triples [CCSD(T)] binding energies are computed near the complete basis set limit. Comparisons to the benzene dimer are made to determine the contributions from hetero-atoms. The presence of a heteroatom reduces the spatial extent of the pi-electron cloud and polarizability of pyridine as compared to benzene. As a result, the magnitude of the dispersion, exchange and induction interactions in benzene-pyridine and pyridine dimer are generally reduced as compared to the benzene dimer. Benzene-pyridine and pyridine dimer bind more strongly than the benzene dimer

in several configurations, and in contrast to the benzene dimer, parallel-displaced configurations can be significantly preferred over T-shaped configurations. Hydrogens para to a heteroatom are more effective "pi hydrogen bond" donors, but aromatic rings with hetero-atoms are worse "pi hydrogen bond" acceptors.

22. Carbon-Isotope Fractionation Factors and the Reactivity of CO₂ in H₂O

Virgil Jackson, University of Alabama

¹²C, ¹³C isotopic fractionation between gaseous CO₂(g), the aqueous carbonate species [CO₂(aq), HCO₃⁻(aq), CO₃²⁻(aq)], and the common carbonate minerals (calcite, dolomite, and aragonite) is fundamental to a variety of geochemical processes involving the carbon cycle. Quantum chemical calculations on large super-molecular carbonate-water and carbonate mineral clusters are used to predict equilibrium constants for ¹³C, ¹²C isotope-exchange reactions between CO₂(g), aqueous carbonate species, and the common carbonate minerals. For the aqueous species, we evaluated the influence of the size and conformational variability of the solvation shell, the exchange-correlation functional, and the basis set. There is a mixing of the modes of the ion with the solvent leading to more than the minimal number of vibrational modes in the ion being important in determining the isotope fractionation factor. Carbon-isotope fractionation factors for gas, aqueous and mineral phases can now be integrated into a single theoretical/computational framework. Because of the broad geochemical significance of the carbon cycle, controlled, in part, by aqueous carbonate species, we have been studying the reactions in the aqueous carbonate system. The reaction of CO₂ in H₂O leads to a range of reactions relevant to carbon sequestration or to CO₂ clathrate formation. We are focused on the formation of carbonic acid, H₂CO₃ in aqueous solution. Although a consensus has emerged on the active involvement of a water cluster n(H₂O), rather than a water monomer (n = 1), in CO₂ hydration, there has been a debate on the actual number of participating water molecules and the modes of their catalytic action. Using our CCSD(T)/CBS formalism with the COSMO self consistent reaction field approach to treat solvation, we have calculated the potential energy surface for H₂O + CO₂ with up to 4 water molecules. For n = 1, a high energy barrier of ~50 kcal/mol is predicted. For n = 2, a trimeric six-member cyclic transition state with a barrier of ~33 (gas phase) and a free energy barrier of ~31 (solvation) kcal/mol was found. We found 6 transition states with 3 H₂O molecules reacting with CO₂ and 2 low energy reactive pathways are predicted. TS3-3-1 has all 3 water molecules involved in H transfer in an eight-member cycle. This transition state leads to formation of a structure like an (HCO₃⁻/H₃O⁺) ion pair. In TS3-2-1 the third water molecule is not directly involved in the hydrogen transfer but solvates the n = 2 transition state. In the gas phase, TS3-3-1 and TS3-2-1 have comparable barrier heights of ~15 kcal/mol relative to separated reactants. TS3-3-1 is favored in aqueous solution by ~5 kcal/mol based on the free energy as it has a larger dipole moment. Bulk solvation reduces the free energy barrier of the first path by ~10 kcal/mol for a free energy barrier of ~22 kcal/mol at 298 K relative to the complex. There are a wide range of possible structures for n =4 for reactant complexes and transition states. The

energetics are similar to those for the $n = 3$ potential energy surfaces. The results for $n = 4$ show that participation of more water molecules beyond $n = 3$ in the cyclic transition will not lower the barrier and could be counter-productive.

23. *Equilibrium Structures of the Two Most Stable Conformers of Alanine*

Heather Jaeger, University of Georgia

Accurate equilibrium structures have been determined for the two lowest-energy conformers, Ala-I and Ala-IIA, of the neutral form of the natural amino acid L-alanine (Ala). The best estimates of the Born-Oppenheimer equilibrium structures of these conformers of Ala were obtained from ab initio electronic structure calculations at the frozen-core CCSD(T) / cc pVTZ level. The semi-experimental equilibrium structures of the same conformers have been determined from a least-squares fitting of structural parameters to a large set of equilibrium rotational constants. These constants were obtained from measured effective rotational constants by correcting them with lowest-order vibration-rotation interaction constants determined at the MP2(FC) / 6-31G(d) level. Due to the large number of structural parameters (altogether 33) and the insufficient number of observed rotational constants (data are available for 10 isotopologues for both conformers), certain structural parameters were constrained to their ab initio values during the fitting. Accurate relative energies were obtained using the focal point analysis approach, revealing that the lowest-lying conformers of Ala are nearly iso-energetic.

24. *Optimizing Single Molecule Conductivity of Conjugated Organic Oligomers with Conjugated Carbodithioate Linkers*

Shahar Keinan, Duke University

A challenge presented by single molecule conductance is to define the relative influence of the molecular "core" and the molecular "interconnects" on the observed currents. Much focus has been placed on designing conductive, conjugated molecules. However, the electrode-molecule contacts can dominate the responses of metal-molecule-metal devices. We have experimentally and theoretically probed single molecule conductances in phenyleneethynylene molecules terminated with thiol (DTS) and carbodithioate (CTS) linkers, using respective STM break-junction and non-equilibrium Green's function methods. Experimental data demonstrate that the carbodithioate linker not only augments electronic coupling to the metal electrode relative to thiol, but also reduces the barrier to charge injection into the phenylene-ethynylene bridge. The theoretical analysis shows that the nature of sulfur hybridization provides the genesis for the order-of-magnitude increased conductance in carbodithioate-terminated systems relative to those that feature the thiol linker. We have analyzed the conductance of CTS and DTS in the two limiting regimes: deep tunneling and resonant transport. Our calculations suggest that the experimental data can be explained in the weak coupling limit, and we predict that the trend of higher conductances for CTS relative to DTS will be retained in general for other metal/inorganic electrodes (beside gold) which couple weakly with the molecule. Collectively, these data emphasize the promising role for carbodithioate-based connectivity in

molecular electronics applications involving metallic and semi-conducting electrodes.

25. Computational Studies of Alcohol Oxidative Dehydrogenation and Dehydration Reactions Catalyzed by Transition Metal Oxide Clusters

Shenggang Li, University of Alabama

Transition metal oxides (TMOs) form an important class of materials widely employed as industrial catalysts and catalyst supports. Catalytic transformations of alcohols to more useful products such as alkenes and aldehydes are important industrial processes as alcohols can potentially be efficiently derived from natural gases, renewable bio-feedstocks, or even carbon oxides. We use density functional theory (DFT) and coupled cluster theory (CCSD(T)) methods to study these reactions as catalyzed by group VIB TMO clusters. Potential energy surfaces (PES) for these reactions were calculated up to the CCSD(T)/CBS level with additional corrections. Our studies show that the catalytic oxidative dehydrogenation (ODH) and dehydration reactions follow similar initiation steps: a Lewis acid-base addition followed by proton transfer to a μ -oxo group to form metal alkyloxy. This is followed by an endothermic reduction via α -H transfer for the ODH reaction, and by an endothermic β -H transfer step for the dehydration reaction. The catalyst is regenerated by the exothermic oxidation of the reduced metal oxide cluster for the ODH reaction, and by water elimination for the dehydration reaction. We discuss the effects of the metal, the cluster size, and the type of alcohol on the reaction energetics. In addition, we benchmark a large number of DFT exchange-correlation functionals for the calculations of the PES.

26. B3LYP functional Calculations of spin densities of aromatic radicals

Liyuan Liang, The University of South Carolina

B3LYP functional and a variety of UHF related ab initio methods with or without elimination of spin contamination are used to calculate H-, C-13, O-17, and N-14 isotropic hyperfine coupling constants for p-benzosemiquinone, nitrobenzene, and benzyl radicals. Four basis sets with escalated sophistication and flexibility are investigated for the purpose of constructing a reliable as well as economical basis set for spin density calculations of large molecules. The performances of delta-function operator and the Rassolov-Chipman operator are examined. Overall, the B3LYP yields the most accurate results with quantitative predictability. The solvent effect including hydrogen bonding on spin densities is studied using three different solvation models. It shows that B3LYP, combined with the SS(V)PE solvation model, is able to interpret the spin redistribution in solutions.

27. Diphosphene and Diphosphinylidene

Tongxiang Lu, University of Georgia

The equilibrium structures of P_2H_2 isomers and the associated isomerization transition states have been investigated systematically starting from self-consistent-field theory and proceeding to coupled cluster methods using

a wide range of basis sets. For each structure the geometry, energy, dipole moment, harmonic vibrational frequencies, and infrared intensities have been predicted. The global minimum has been confirmed to be planar trans-HPPH diphosphene, lying 3.2 kcal/mol below cis-HPPH with the aug-cc-pVQZ CCSD(T) method upon inclusion of zero point vibrational energy corrections.

Diphosphinylidene, which has the connectivity PPH₂ and C_{2v} symmetry lies 25.2 kcal/mol above the global minimum. The trans-cis isomerization reaction occurs via internal rotation with a barrier of 35.2 kcal/mol using the cc-pVQZ Mk-MRCCSD (2e/2MO) method. This transition state exhibits multi-reference character and consequently properties were evaluated using CASSCF, MRCI, CASPT2, and Mk-MRCCSD methods with various basis sets. At the aug-cc-pVQZ CCSD(T) level, the transition state for the isomerization reaction between trans-HPPH and diphosphinylidene (planar PPH₂) was predicted to be non-planar with a torsional angle of 101.1 degree. The corresponding barrier is estimated to be 48.2 kcal/mol.

28. Potential Energy Curves for Cation- π Interactions: Side-on Configurations are also attractive

Michael Marshall, Georgia Institute of Technology

Accurate potential energy surfaces for benzene-M (M = Li⁺, Na⁺, K⁺, and NH₄⁺) are obtained using coupled-cluster theory through perturbative triple excitations, CCSD(T). Our computations show that side-on cation- π interactions, where the cation is in the same plane as the benzene, can be favorable and may influence molecular recognition. These side-on interactions retain 18-32% of their π -face interaction energy in the gas phase, making their bond strengths comparable to hydrogen bonds.

29. Insight into density functional theory: delocalization error, static correlation error, and beyond

Paula Mori-Sánchez, Duke University

Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions are unified and extended to states with both fractional charge and fractional spin to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of all known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems.

30. The C₃H₅ Potential Energy Surface

Beulah Narendrapurapu, University of Georgia

The C₃H₅ Potential Energy Surface (by Beulah Narendrapurapu, Andrew C. Simmonett and Henry F. Schaefer III) The potential energy surface describing C₃H₅ isomers encompasses many molecules of importance in combustion chemistry, including propyne, acetylene, allyl radical, methane and the propargyl radical. Many of the interconversions occurring on this surface have been studied extensively due to their important roles as elementary steps in combustion processes. A recent theoretical kinetic study performed by Miller and co-workers [1] considered 10 minima and 15 transition states on the surface using density functional theory geometries, renealed by QCISD(T) energies, which were extrapolated to remove basis set error. A number of the barrier heights required small adjustments to match the available experimental data. Here we provide preliminary results from our study of this surface, which aims to elucidate the energetics of the various isomers, and the barriers between them, to unprecedented accuracy. As the global minimum on the C₃H₅ surface, the complex electronic structure of the allyl radical presents some interesting questions regarding choice of reference function, which is discussed in detail. [1] J. A. Miller, J. P. Senosiain, S. J. Klippenstein, and Y. Georgievskii, *J. Phys. Chem. A* **112** 9429 (2008).

31. *The vibrational band origins and potential energy surface of fluorine isocyanate and its isomers*

Frank Pickard, University of Georgia

The isomerisation pathways of fluorine isocyanate (FNCO) have been studied using coupled-cluster theory incorporating all single and double excitations (CCSD), along with the perturbative inclusion of connected triple excitations [CCSD(T)]. These calculations employed large one particle correlation consistent basis sets (cc-pVQZ). The final potential energy surface (PES) of this system was computed using valence focal point extrapolations[1]. Accurate vibrational band origin (VBO) predictions were made for all minima on the PES. Excellent agreement was found between the predicted and observed VBOs for FNCO. The VBO predictions for the heretofore unsynthesized high energy isomers of FNCO should assist in their eventual experimental characterization. The calculated PES also demonstrates that several high energy isomers should be viable synthetic targets.

[1] Császár, A. G.; Allen, W. D.; Schaefer, H. F. J. *Chem. Phys.* 1998, 108, 9751.2. Jacobs, J.; Juelicher, B.; Schatte, G.; Willner, H.; Mack, H. G. *Chem. Ber.* 1993, 126, 2167.

32. *Energy landscapes analysis of disordered proteins: A case study of histone tail dynamics*

Davit Potoyan, University of North Carolina at Chapel Hill

Histone tails mediate and maintain nucleosomal packaging in chromosome and, thus, significantly contribute to chromosomal remodeling and gene activation processes. Despite their key importance in chromatin regulation, the structural mechanism of their action has remained elusive. Some of the difficulties stem from histone tails being highly disordered, thus, challenging the

classical paradigm of structural molecular biology, that biological function strictly follows from well defined three-dimensional structure. In our work, we have carried out several microsecond long explicit solvent molecular dynamics simulations of all three histone tails to gain fundamental understanding of physics of natively disordered proteins and link our understanding of histone tail dynamics to chromosomal organization. Subsequently, we constructed two-dimensional free energy landscapes of various histone tails, as a function of physically motivated order parameters, such as the number of hydrogen bonds and the radius of gyration. This approach, combined with principal component analysis, revealed a co-existence of ordered and disordered structural basins, that, in turn, shed light on the multitude of functional roles performed by histone tails. We carried out additional analysis, borrowing some ideas from disordered magnetic systems, to classify dominant structural forms for all three histone tails.

33. Towards multi-scale modeling the chromatin fiber: Renormalization-Group-based coarse-graining technique applied to double-stranded DNA and electrolyte solutions.

Alexey Savelyev, The University of North Carolina at Chapel Hill

DNA is compacted a million-fold into a highly organized structure in eukaryotic cells called chromatin. Understanding the mechanism of chromatin folding is of great biological importance, since it controls important DNA-templated processes, such as gene expression, recombination and repair. All-atom Molecular Dynamics (MD) simulations could provide crucial insights into the electrostatic and structural mechanisms of chromatin folding. However, because of the enormous size of even short chromatin fiber segment and long folding time-scales, all-atom MD simulations will remain computationally impractical in the foreseeable future. Our long-term aim is to build an accurate coarse-grained (CG) model of the chromatin, derived systematically from all-atom simulations of its smaller parts. As a first step toward achieving this goal, we have developed CG model of a linear DNA chain, playing the role of a linker DNA segment in the chromatin. We accurately derived CG inter-DNA electrostatic potential, instead of relying on the standard models of continuum electrostatics which are inadequate at small separation distances. In addition, we used the ideas of renormalization group theory to build an optimization scheme for the obtained CG force field. This novel approach is designed to accurately reproduce correlations among various CG molecular degrees of freedom. The implementation of these correlations was left as an open question in the prior studies of polymer models. We also applied our RG-based optimization scheme to accurately describe the bulk properties of monovalent electrolyte solutions by systematically integrating out the solvent degrees of freedom (water) from the corresponding all-atomistic system. In particular, we were able to accurately capture the structural behavior of ions at their small separations, associated with hydration effects, at very low computational cost. Mobile ions, characterized by the obtained CG force-field, may be incorporated into the CG model of DNA chain to capture coupling between DNA dynamics and the dynamics of surrounding salt. Similarly, obtained ionic parameters may be used to incorporate ions into CG simulations

of other complex biomolecular systems, where both long-range electrostatics and short-range hydration effects have to be considered.

34. Sequence Dependence of Ion Distributions Around Nucleic Acids as Examined by Molecular Dynamics Simulations

Latsavongsakda Sethaphong, NC State University

Nucleic acids are highly charged biological macromolecules that are often associated with a cloud of monovalent and divalent ions. Others have been shown that ion interactions with nucleic acid complexes are required for proper function. This work examines the electrostatic environment constructed by the sequence arrangement of nucleic acid residues in loop-loop conformations as found in "kissing-loop" and helical structures. It is hypothesized that specific residue patterns correlate with observed ion distributions to consequentially affect biological function.

35. Benchmarking Water Clusters with Local Correlation Methods

Benjamin Shepler, Emory University

A new fully flexible ab initio potential energy surface (PES) for water including 1, 2, and 3-body terms has been developed in our group. Testing of how this surface describes water clusters requires accurate ab initio benchmark calculations that become extremely computationally demanding as the size of the water clusters grows larger. Local correlation methods are a less expensive alternative to conventional correlation treatments. Local MP2 and CCSD(T) methods (as implemented in the MOLPRO suite of electronic structure programs) have been compared with their conventional counterparts and the newly developed PES for small (H₂O)_n [n=2-6] clusters. In addition to the computational savings, local correlation methods are largely free of basis set superposition error (BSSE) which can be quite large for these molecular clusters effecting not only the interaction energies, but also their structures and harmonic frequencies.

36. Investigation of DNA Film Structure and Growth Dynamics via MD Simulation

Stacy Snyder, North Carolina State University

We investigate the self-assembly of single-stranded DNA oligomers into thin, multilayered films, which have been prepared by depositing DNA strands in a layer-by-layer technique [A. P. R. Johnston, H. Mitomo, E. S. Read, and F. Caruso, "Compositional and Structural Engineering of DNA Multilayer Films" , *Langmuir*, Vol. 22, No. 7, 2006, pp. 3251-3258]. Films are assembled on a base layer such as polyT, with additional layers of oligo-nucleotides having a structure which allows both hybridization with the existing film and a non-hybridizing tail for hybridization of the subsequent layer. The effects of nucleic acid strand length and the number of layers on film growth and structure are studied using molecular dynamics simulations. We monitor the dynamics and conformation of successive DNA oligonucleotides as a film is grown in order to explain experimental results, including anomalous changes in growth efficiency with strand length. We found that a minimum oligonucleotide length of approximately twenty nucleotides is required for film growth, due to the increased probability of

self-hybridization and triple helix structures for shorter strands. Insight into the observed decrease in growth efficiency for 60-mer strands is gained by monitoring the probability of crossover or hybridization of neighboring strands in the film. Clearer understanding of the self-assembly process is expected to make possible the algorithmic self-assembly of nucleic acid thin films for applications in drug delivery and biological sensing.

37. Isomers of OCNO revisited: comparison of theoretical and experimental vibrational assignments

Lucas Speakman, University of Georgia

The radical-radical reaction of $\text{CN} + \text{O}_2$ plays a crucial role in combustion, atmospheric, and astronomical chemistry. The main product channel produces $\text{OCN} + \text{O}$, in which the cyanato radical is a key intermediate in the rapid removal of nitrogen oxides (RAPRENOx). A more exothermic channel produces $\text{CO} + \text{NO}$ through a bent OCNO intermediate. It has been suggested that the determination of the OCNO radical in interstellar space could be used to derive the abundance of the infrared inactive nitrogen molecule. Two independent matrix isolation experiments claimed to observe the bent OCNO radical structure. Both Jamieson et. al.[1] and Wu and Le[2] used experimental and computational isotopic substitution techniques to confirm their CO stretch of OCNO to be 2113 and 2045 cm^{-1} , respectively. To help clarify these contradictory vibrational assignments, ab initio computations are necessary to elucidate the OCNO potential energy surface. Geometries have been optimized with restricted open shell coupled cluster with single, double, and perturbative triple excitations [ROCCSD(T)]. Second order vibrational perturbation theory using cc-pVQZ CCSD(T) data yielded fundamental frequencies and isotopic shifts for several isomers on the potential energy surface. Wu and Lee's experimental isotopic shifts agree with our computed OcCNO frequencies and isotopic shifts, while we have been unable to match any of our structures to Jameison et. al. frequencies and shifts. Focal-point extrapolations with correlation-consistent basis sets, cc-pVXZ (X= D, T, and Q), with coupled cluster single and double excitations (CCSD), perturbative triple excitations [CCSD(T)], and full triple excitations ascertained the most comprehensive potential energy surface to date.

[1] C. S. Jamieson, A. M. Mebel, and R. I. Kaiser, *Phys. Chem. Chem. Phys.* 7 (24), 4089 (2005).

[2] Y. J. Wu and Y. P. Lee, *J. Chem. Phys.* 123 (17), 6 (2005).

38. Molecular dynamics simulations of evolving kissing loop motif formed between the TAR RNA element of HIV-1 and aptamer

Abhishek Singh, NCSU

Kissing loops(KL) found in nature have significant role in viral transcription and building block for nano-devices. The molecular architecture of RNA culminates in kissing loops that are hydrogen bonded motifs comprising of at least two hairpins. Molecular dynamics using Amber 9, investigates the fundamental study of the formation of kissing loops in terms of the directional

hydrogen bonding and ionic environment which allows hairpin molecules to conform to the minimum energy states. Individual components of the KL were simulated separately under identical conditions. The stabilized single chains were subjected to the targeted molecular dynamics technique that reveals the development of KL from the individual components. The self assembled stable structure with estimated molecular dynamics parameters was used as a reference for the simulations. This study has impact on health and nanotechnology.

39. *Semi-Empirical Quantum Mechanics-Based Simulations Investigating the Interfacial Phase Stability in a Series of TiV Multi-Laminate Thin Films*

Amanda Stott, The University of Alabama

Phillip B. Abel (NASA Glenn Research Center), Guillermo H. Bozzolo (Loyola College of Maryland) and David A. Dixon (The University of Alabama)

Economically viable methods for energy production to replace the combustion of carbon-based fuels are arguably one of the greatest challenges of the 21st Century. Nickel metal-hydride (Ni/MH) batteries are promising materials for improving energy production while reducing carbon emissions. TiV-based alloys for NiMH batteries exhibit a V-based bcc solid solution phase as well as a C14 *hcp* Laves phase. The *bcc* phase is the major hydrogen absorbing phase, while the *hcp* phase is a catalyst for the electrochemical hydrogenation and dehydrogenation process. The influence of the interfacial energy on phase stability is investigated for a series of TiV multi-laminate thin films. Experiments reveal that at higher layer thicknesses, the *hcp* phase is the stable phase. As the laminate thickness is reduced, a phase transformation from *hcp* to *bcc* occurs. Atomic-scale characterization and semi-empirical quantum mechanics-based atomistic simulations confirm the phase transformation, and indicate it is an interface-mediated process.

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40. *From Small Molecule Using Quantum Method to Large Molecule using QM/MM Method*

Zhigang Sun, Duke University

Previously I was doing dynamics process simulation using full quantum wavepacket method, such as numerical simulation of photodynamics and spectroscopy theory involving pulse lasers, reactive scattering processes on adiabatic PES and reactive scattering on PES with diabatic coupling and spin-orbit coupling. Now I am doing with large molecule with QM/MM method. I am just at the beginning stage of this transformation process, your advice and experience are welcome.

41. *Appropriate Approximations to Model the Al(Cl)-Salen Catalyzed Cyanide Addition Mechanism*

Tait Takatani, Georgia Institute of Technology

The salen [bis(salicylaldehyde)ethylene-diamine] ligand with various metal centers comprise a highly active class of synthetic complexes. Unfortunately, recent research indicates that density functional theory (DFT) methods do not reliably describe the metal-salen electronic structure; in some cases, even using different DFT functionals yield qualitatively contradicting results. These failures are attributed to the large degree of multi-reference character present in transition-metal complexes, where even some ab initio methods fail because they are based on single-reference formalisms. For the Al-Salen complex, however, it is predicted that DFT methods should be reliable due to the lack of degenerate occupied d-orbitals. Moreover, since obtaining reaction mechanisms would greatly aid ongoing experimental research, it is useful to explore the appropriateness of all approximations utilized to reduce the computational costs. The B3LYP and BP86 functionals were benchmarked against high-level complete-active space results. The effect of reducing the sizes of the salen ligand and linkers as well as the reliability of the solvent models, SCRF and COSMO, were studied. Results indicate that both DFT functionals perform rather well and that truncating the Al-salen complex to its smallest model will yield qualitatively accurate results for mechanistic studies. Both solvent models predict similar results when comparing the effects of counter-ions and therefore the inexpensive SCRF method should be sufficient. Indeed, the Al-salen complex is 'well-behaved' compared to its transition-metal counterparts, and further research on the Al(Cl)-salen catalyzed cyanide addition reaction will be one of few reliable mechanistic studies involving metal-salen complexes.

42. *Acidity and basicity for azole.xBH₃ compounds for chemical hydrogen storage*

Monica Vasiliu, The University of Alabama

Critical issues for the use of H₂ as a fuel in the transportation sector include the development of efficient and safe H₂ storage materials. Chemical hydrogen storage is a storage approach which eliminates issues such as high pressure and low temperature, as the hydrogen is stored in chemical bond and is delivered via a chemical reaction. One can consider the use of chemical bonds for storing energy as a compact way to store electrons in contrast to batteries or ultra-capacitors as the density of electrons that can be stored in a bond can be quite high. Because of their high weight percent capacity of hydrogen, boron-nitrogen compounds are being extensively studied to meet the U.S. Department of Energy's goals for on-board transportation systems. Proton affinities and acidities (kcal/mol) have been predicted for chemical hydrogen storage candidates: azoles.xBH₃ (pyrrole, pyrazole, imidazole, 1(H),2,3-triazole, 1,2(H),3-triazole, 1(H),2,4-triazole, 1,2,4(H)-triazole, 1(H),2,3,4-tetrazole and 1,2(H),3,4-tetrazole) at the DFT and G3MP2 levels and in some cases at the CCSD(T)/CBS level. The proton affinities of the azoles are slightly less than NH₃. By adding BH₃ groups to these azoles the proton affinities are predicted to decrease making these compounds poor bases. The calculations show that the gas phase acidities of the BH₃ adducts are lower than the corresponding azole. The azole-borane adducts are very strong gas phase acids. The lowest acidity of

the azoles adducts with 2N is 281 kcal/mol, with 3N is 258 kcal/mol, and with 4N is 266 kcal/mol. These are very strong acids, as strong if not stronger than the strongest known, $(\text{CF}_3\text{SO}_2)_3\text{CH}$ with an acidity of 274 kcal/mol. In aqueous solution, the predicted pKa for $(\text{CF}_3\text{SO}_2)_3\text{CH}$ is -17.4 so we expect the BH_3 adducts to be very strong acids in solution.

43. *Reaction rates by quantum trajectory formalism*

Tijo Joseph Vazhappilly, University of South Carolina

The calculation of accurate reaction rates has been always a challenging goal in chemistry. These reactions rates are often greatly influenced by quantum mechanical (QM) effects such as zero-point energy, tunneling and non-classical reflections. The full quantum mechanical treatment of the system is expensive and increases with the complexity of the reaction. The quantum trajectory formalism is an alternative approach to include QM effects in the time evolution of the system which is more efficient and cheap compared to other quantum mechanical approaches in high dimensions. In this work, we are interested in the calculation of quantum mechanical rate constants. For this purpose, we introduced analytical expression for the flux operator eigenfunctions and eigenvectors in terms of delta functions. The method is tested for the transmission probability through one-dimensional Eckart barrier.

1. Sophya Garashchuk and Vitaly A. Rassolov, *J. Chem. Phys.* **120**, 1181(2004).
2. Sophya Garashchuk, *J. Chem. Phys.* **126**, 154104 (2007).
3. Sophya Garashchuk and Vitaly A. Rassolov, *J. Chem. Phys.* **129**, 024109 (2008).

44. *Effect of conformational fluctuations on charge transport in peptide nucleic acids*

Ravindra Venkatramani, Duke University

We investigate conductance and charge transfer rates of a synthetic analog of DNA the peptidenucleic acid (PNA). Molecular dynamics (MD) simulations coupled to quantum chemical (QC) methods and charge transport calculations were applied to single and double stranded PNA fragment sequences to sample the charge transfer rate and conductance across an ensemble of geometries and electronic structures. Transport properties vary considerably across the ensemble with coherent tunneling transport competing with thermally activated carrier injection and incoherent hopping transport. Our studies show that conformational fluctuations can bias individual members of an ensemble toward one mechanism or another and we estimate the contributions of different transport mechanisms to the overall charge transfer kinetics of the ensemble. Implications of our observations on ongoing electrochemical and STM break junction experiments of nucleic acid monolayers will be discussed.

45. *Computational Studies of the Reaction of TiO_2 Nanoclusters with Water*

Tsang-Hsiu Wang, University of Alabama

There is recent interest in using transition metal oxides as photocatalysts to control chemical transformations for energy production and to minimize

environmental impact. One of the most important applications is the use of photoactivated nanoclusters of titanium dioxide to split water to make hydrogen and oxygen molecules. We are using density functional theory and coupled cluster theory to study the initial steps of water activation on small nanoclusters of TiO_2 to understand these reactions. Our recent calculations show great variations in the first adiabatic excitation energies for the low-lying isomers of the $(\text{TiO}_2)_n$ ($n= 1-4$) nanoclusters. For example, three low-lying isomers of Ti_4O_8 have the first adiabatic excitation energies ranging from 2.02 to 3.53 eV. We calculated the potential energy surfaces for the reactions of water on both singlet and triplet TiO_2 nanoclusters. The potential energy surfaces are qualitatively the same for the first addition of H_2O . H_2O adds in a Lewis acid base reaction followed by proton transfer to a $\text{Ti}=\text{O}$ μ -oxo bond. This can occur on the singlet surface with barriers between 5 and 15 kcal/mol depending on the cluster size and isomer. The reaction of a second water can occur with comparable, to much higher barriers. The reactions on the triplet surface which serves as model for the photo-excited state are higher in general than those on the ground state singlet surface. Thus, H_2O can readily be split without a photon and, in fact, the photon may actually impede the reaction. Why is the photon needed? Water splitting to form H_2 and O_2 is an endothermic process requiring 116 kcal/mol to produce two H_2 and one O_2 from two H_2O . Thus the photon provides the energy to overcome the endothermicity of the reaction and break the metal hydroxide bonds. Approximately two 500 nm photons are needed to overcome just the reaction endothermicity for the two H_2O molecules. Work is ongoing to probe the release reactions.

46. A computational study of the keto-enol equilibria of catechol in gas and aqueous solution phase

Yuhe Wang, Wake Forest University

Keto-enol equilibria in catechol have been studied using ab initio methods and density functional theory. Six structural isomers of $\text{C}_6\text{H}_6\text{O}_2$ were fully optimized in gas phase at HF and B3LYP levels of theory in combination with the 6-311++G** basis set. Self-Consistent Reaction Field Polarizable Continuum Model was used to investigate the effect of an aqueous solvent on the extent of tautomerisation at the two above mentioned model chemistries. In addition, gas phase electronic and Gibbs free energies for the six molecules were computed using the CBS-QB3 method, and the G3 approach to evaluate highly accurate relative energies. It was found that the two dienol isomers are always lower in energy than the other species and predominate. Resonance stabilization arising from aromaticity in these six-member cyclic systems is posited, and is understood on the basis of Huckel theory. Confirmation of the findings is provided by comparison of the simulated vibrational spectra of catechol with the measured infrared spectrum in gas phase.

47. The Study of Pendant Side Chain Effects on Hydrated Morphologies with Dissipative Particle Dynamics Simulations

Dongsheng Wu, University of Tennessee in Knoxville

The hydrated morphologies of two structurally related bis[(perfluoroalkyl)sulfonyl]imide-based ionomers materials have been investigated through dissipative particle dynamics (DPD) simulations as a function of ionomer equivalent weight (EW) and degree of hydration. The studied imide-based ionomers contain different terminal groups: phenylsulfonic acid and phenyl. For the convenience of description, the two ionomers will be denoted as PSA-ionomer and P-ionomer, respectively. Coarse-grained mesoscale models were constructed by dividing the hydrated ionomer into components consisting of a common polytetrafluoroethylene backbone bead, an ionomer specific backbone bead, bis[(perfluoroalkyl)sulfonyl]imide bead, a terminal side chain bead and a water bead consisting of a cluster of six water molecules. Flory-Huggins χ -parameters and repulsion parameters between all DPD beads were calculated. Equilibrated morphologies were then determined for the PSA-ionomer with EW of 988 and P-ionomer with EW of 908. The hydration level was varied in both systems with water contents corresponding to 6, 12, 18 and 24 H₂O/NH (H₂O per imide acid group). Water contour plots reveal that as the hydration level is increased, the isolated water clusters present at the lower water contents increase in size eventually forming continuous regions. The connectivity of the water in P-ionomer, however, requires a higher water content to achieve than observed on the PSA-ionomer. The morphology can be mapped to the ionomers' conductance behaviors and illustrate why the ionomers show especially low conductance at low hydration levels. Water-water particles' radial distribution functions (RDFs) were also evaluated and the average size of water clusters at lower hydration levels were estimated.

48. *Inelastic charge transfer in a molecular interferometer*

Dequan Xiao, Duke University

Inelastic charge-transfer kinetics is expected to be sensitive to bridge-localized vibronic interactions. Using a vibronic Hartree-Fock Hamiltonian, we show how inelastic charge transfer may be controlled (turned on and off) in a double-slit type experiment that uses a molecule as an interferometer. We describe donor-acceptor interactions in terms of interfering vibronic coupling pathways that can be actively selected (“labeled”) when pathway-specific vibrations. Thus, inelastic charge transfer may be actively controlled. Based on this controlling mechanism of charge transfer, we suggest schemes for building molecular scale quantum interferometers and switches.

48. *Calculating Solution Redox Free Energies with Ab initio QM/MM Minimum Free Energy Path Method*

Xiancheng Zeng, Duke University

A quantum mechanical/molecular mechanical minimum free energy path (QM/MM-MFEP) method was developed to calculate the redox free energies of large systems in solution with greatly enhanced efficiency for conformation sampling. The QM/MM-MFEP method describes the thermodynamics of a system on the potential of mean force (PMF) surface of the solute degrees of freedom. The MD sampling is only carried out with the QM subsystem fixed. It

thus avoids "on-the-fly" QM calculations and overcomes the high computational cost of the direct ab initio QM/MM molecular dynamics (MD) needed for sampling. The enhanced efficiency and uncompromised accuracy of this approach are especially significant for biochemical systems. The QM/MM-MFEP method thus provides an efficient approach to free energy simulation of complex electron transfer reactions.

49. *Comparison of one-electron and many-electron approaches for computing charge transfer integrals*

Jinmei Zhang, Virginia Tech

The electronic coupling ("transfer integral") between charge-localized (diabatic) states is one of the key quantities for studying charge transport in molecular level. A common assumption is to neglect the many-electron relaxation (i.e. use Koopman's theorem), which allows to use the one-electron Hamiltonians and orbitals instead of their many-electron counterparts. In this picture the diabatic states are described by the monomer HOMOs, and the transfer integrals are computed directly using the Fock operator of the neutral dimer (see Valeev et al, *J. Am. Chem. Soc.* 2006, 128, 9882). Here we investigate how accurate is such one-electron approximation for computing hole transfer integrals. The transfer integrals are computed for several simple dimers in the one-electron approximation using the Hartree-Fock as well as Kohn-Sham DFT Hamiltonians. We demonstrate that the basis set needs to include diffuse functions to compute the coupling accurately when the separation of monomers becomes large. Within the same basis set, the coupling shows the expected exponential decay with the inter monomer distance. Comparison with the benchmark diabatic couplings computed at the EOM-IP-CCSD and full CI levels (Peniazek et al, *J. Chem. Phys.* 2007, 127, 164110) suggests that the Hartree-Fock method produces electronic couplings accurate to few percent, whereas the KS DFT methods surprisingly give poorer agreement, which becomes even worse for larger dimers (for example, C₂H₄ dimer). We conclude that the diabatic couplings can be very accurately computed within the one-electron approximation at the Hartree-Fock level, whose modest cost will allow charge transport studies in realistic model systems.

50. *Monte Carlo Study of Modulated Phases Using Thermodynamic Integration*

Kai Zhang, Duke University

Patterns or microphases can form under the competition of short-range ordering forces and long-range frustrating interactions. Such Systems undergo a nucleation process during which the thickness or the scale of the patterns grows as the temperature increases. The nature of the interactions vary in cases. Some simple models of this kind include: 1) ANNNI model in which the neighboring Ising ordering interaction competes with the next-nearest neighbor disordering interaction in one axial direction; 2) Ising-Coulomb model in which the Ising

interaction competes with the long-range Coulomb force. Many theoretical and simulation works have been done to understand these systems. We propose a systematic simulation method--the thermodynamic integration--to calculate the free energy of all possible phases in a finite system and thus determine the phase diagram and phase transition accurately. The ANNNI model is extensively studied, and some attempts have been done to attack the Ising-Coulomb system.

51. Molecular Noise of Capping Protein Binding Induces Macroscopic Instability in Filopodial Dynamics

Pavel Zhuravlev, UNC

Capping proteins are among the most important regulatory proteins involved in controlling complicated stochastic dynamics of filopodia, which are dynamic finger-like protrusions used by eukaryotic motile cells to probe their environment and help guide cell's motility. They attach to the barbed end of a filament and prevent polymerization, leading to effective filament retraction due to retrograde flow. When we have simulated filopodial growth in presence of capping proteins, qualitatively new dynamics emerged. We discovered that molecular noise due to capping protein binding and unbinding leads to macroscopic filopodial length fluctuations, compared with minuscule fluctuations in the actin only system. Thus, our work shows for the first time that molecular noise of signaling proteins may induce growth-retraction cycles in filopodia. When capped, some filaments eventually retract all the way down to filopodial base and disappear. This process endows filopodium with a finite lifetime. We have also developed an accurate mean field model which provides qualitative explanations of our numerical simulation results. Our results are broadly consistent with experiments, in terms of predicting filopodial growth retraction cycles and also the average filopodial lifetimes.

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