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Adding Dynamical Insight to X-ray Images by Solution and Crystal Molecular Dynamics Simulation

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X-ray crystallography is the most robust technique for protein structure determination. However, crystal packing may select a conformation unrepresentative of the dominant solution form of a protein. Here we compare solution and crystal lattice molecular dynamics (MD) simulations of the dimeric λ Cro transcription factor to add dynamical insight to the interpretation of its various X-ray images, which range from a closed DNA-free conformation to an open DNA-bound form. Free energy profiles reporting on the conformational space sampled in solution reveal that closed and semi-open states are accessible. The fully open form lies higher in energy, indicating that it is stabilized by DNA or crystal contacts. Subsequent crystal MD simulations yield quantitative estimates of the strength of packing interfaces to show the effect of the crystal form and mutation in stabilizing different dimer conformations. Our results will help to improve the interpretation of other protein X-ray structures in establishing structure-function relationships.

Probing Peptide-Water Coupled Motions in Crystalline GAL Peptide with Terahertz Spectroscopy

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The far-infrared Terahertz radiation spanning the region 0.1 to 1 mm is exquisitely sensitive to coupled motions of protein and water.¹ Coupling of water to protein global modes can enhance dipole moments and yield strong THz signals. It is therefore possible to selectively study biological water using THz spectroscopy. In our on-going THz studies of model peptide-water systems we have utilized THz spectroscopy and quantum mechanical calculations to probe coupling of peptide-water interactions in GAL tripeptide. From X-ray diffraction studies it is known that the GAL peptide can be grown in an α -helical conformation² with three crystallographic waters per peptide bond. Weight measurements indicate that two of the three waters are lost due to dehydration which leaves behind a highly crystalline monohydrate. Calculated Terahertz spectra computed using density functional theory favorably compares with the experimental spectra. Free energy analysis suggests that the dehydration is driven by phonon energy differences.³

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3. S. Chaturvedi, K. Go, R. Pathasarathy, *Biopolymers*, 1991, 31, 397-407
4. Zeeshan Ahmed, Shin G. Chou, Karen Siegrist and David Plusquellic, "State-resolved THz spectroscopy and dynamics of crystalline peptide-water systems" *Faraday Discuss.*, 2011, 150, 1-18

Growth Mechanisms of Gold Nanoparticles

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Nanoparticles have a number of important technological applications in biolabeling, cancer therapy, catalysis, and sensing. Although these particles have been synthesized for over two decades, very little is known about their growth mechanisms.

The growth mechanisms of gold nanoparticles are investigated using density functional theory. The growth mechanisms of gold-phosphine and gold-thiolate nanoparticles are found to be quite different. Gold-phosphine growth is studied starting from the precursor AuClPR_3 ($\text{R}=\text{H}$, Me and Ph) up to clusters containing four gold atoms. For gold-phosphine nanoparticles, addition of electrons leads to Au-Au bond formation and to spontaneous dissociation of ligands. Chloride dissociation is preferred over phosphine dissociation, although both are observed. Most reactions involved in gold-phosphine cluster growth are exothermic. A wide variety of products are observed in agreement with experiment.

In contrast, addition of electrons to gold-thiolate oligomers leads to the formation of isolated Au^- ions and $\text{Au}_{n-1}(\text{SR})_n^-$ chains. On the other hand, addition of a hydride ion to gold-thiolate oligomers leads to products such as free thiols and compounds that contain both Au(0) and chain-like oligomers $\text{Au}_n(\text{SR})_{n+1}^-$ ($n=1-6$), which are plausible intermediates for gold nanoparticle growth.

A Quantum Dynamic Investigation of Proton-Coupled Electron Transfer Reactions in Solution

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A variety of complex systems relevant to renewable energy research involve proton-coupled electron transfer (PCET) reactions. Understanding the mechanism of PCET is, for instance, central to the design of artificial photosynthetic systems, the design of efficient water-splitting catalysts, and the generation of hot electrons and subsequent energy storage in organic semiconductor technology for solar cells. This class of reactions has been studied extensively and poses a significant challenge to theoretical methods requiring accurate simulations of the coupled electronic and nuclear dynamics. In addition, experimental investigations are limited by their ability to fully discriminate between and quantify the effects of wide range of factors that determine the mechanism of PCET such as, but not limited to, the relative strengths of interactions between the electron, proton, and solvent coordinates and the nonadiabaticity of electron and proton transfer reactions. PCET reactions can be broadly classified into those that occur via a concerted mechanism, where the proton and the electron transfer simultaneously, and those that occur via a sequential mechanism, where a single charged particle transfers first resulting in a favorable energy bias that facilitates the subsequent charge transfer event. We construct a simple model for one-dimensional PCET reaction in solution that can be parameterized to tune between the concerted and sequential mechanisms. We present quantum rates obtained for the PCET reaction as well as the individual electron and proton transfer reactions in these model systems. These calculations employ an exact quantum-mechanical path integral method that has previously been used to obtain quantum rates for electron transfer between transition metal ions.¹ Comparison of the quantum rates across a range of parameter space for our model system yields mechanistic insights. Finally, we investigate the accuracy of our recently developed PI-ST formalism (for exact quantum statistics of nonadiabatic systems) combined with semiclassical dynamics² in the calculation of thermal rates for PCET both in this model system and others that are inaccessible to fully quantum-mechanical simulations.

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2. N. Ananth and T. F. Miller III, *J. Chem. Phys.* 133, 234103 (2010).

Toward an Understanding of the Specific Ion Effect Using Density Functional Theory

Marcel D. Baer, Gregory K. Schenter and Christopher J. Mundy

Although it is now accepted that some anions adsorb at the air-water interface following a reverse Hofmeister series¹ the nature of the microscopic interactions driving ions to interfaces is currently the subject of active research.² We use extensive density functional theory (DFT) based interaction potentials to study the free energy of transfer of iodide from the interior to the surface in both a cluster and the extended air-water interface. Our research supports a picture that empirical polarizable interaction potentials may overestimate surface adsorption for the halides. These results, in conjunction with previous theoretical and experimental studies on iodide solvation³ have implications toward the necessary interactions that give rise to the specific ion effect at the air-water interface.⁴

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Adsorption of Lysine and 5-Aminovaleric Acid on Montmorillonite Surfaces: A Comparative Study

Peter Balliet, Aman Chugh and Lorena Tribe

The interactions of small biological molecules with mineral surfaces are at the heart of phenomena of fundamental importance in areas as diverse as drug delivery systems, soil remediation, fate of herbicides, catalysis, and origins of life theories. In each of these cases moieties of the molecules will either be attracted to or repelled by areas of the surfaces - and occasionally by ions - causing adsorption or desorption processes. Molecule – surface complexes can have many configurations depending on the nature and distribution of the intermolecular forces which come into play. The combination of surface structures, presence or absence of water molecules, interlayer ions, and moieties of the biological molecules leads to a rich variety of structural possibilities. Anchoring of molecules to the surface may enable reactions which would not happen in solution, serve as a template, and favor decomposition mechanisms. In addition to the structure of the system, dynamics also depend on the nature of the surface complexes and the surrounding environment.

In this project the interactions of lysine and 5-aminovaleric acid with clay surfaces will be studied. Theoretical calculations of the vibrational infra red and Raman spectra of amino acids surface complexes will be carried out, using the results in conjunction with experimental data from the literature to provide a detailed map of the most likely surface complexes in each case. Density Functional Theory calculations will be performed on portions of a clay surface and a series of amino acids with the software package Gaussian 09. The structural differences between both amino acids will be correlated with the differences in surface complex formation.

Construction and Application of a New Time-Dependent Current-Density Functional Theory

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In recent years, single-molecule spectroscopy and non-linear techniques have become the prime choice for probing complicated intermolecular and intramolecular processes. New or improved methods are required in order to calculate quantities such as the magnetic properties of large molecules. The paramagnetic current-density must be properly incorporated into magnetic theories¹ for a complete microscopic description. The delicate balance between a gauge-invariant energy and continuity of the charge-density must also be preserved in the single-particle scheme. We show that the classical continuity equation is violated for gauge-variant meta-Generalized Gradient Approximations (mGGAs) within the adiabatic approximation. The solution for preserving this conservation is presented and directly connected to restoring gauge-invariance in the energy expression through introduction of the paramagnetic current-density.² We also derive and apply a new adiabatic, time-dependent current-density functional response theory using our modified approximation for the exchange-correlation energy. We applied this new formalism, in conjunction with the non-empirical mGGA of Tao, Perdew, Staroverov, and Scuseria,³ to compute the optical rotations of a set of structurally rigid chiral molecules. The performance of our method is compared to other popular density functionals and CCSD.⁴ The prospects for extension of this formalism to computation of non-linear optical properties are also discussed.

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Generalized Quantum Master Equations for Electronic Energy Transfer

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System-bath models are ubiquitous in chemical physics problems ranging from electron transfer in solution to defect tunneling in solids. Because most approximate analytical solutions of such models are perturbative in some parameter, the so-called 'intermediate coupling' regime, where all energy scales are similar in magnitude, provides a challenge to analytical theories. Motivated by recent computational and experimental investigations, we explore the performance of a variety of generalized quantum master equations describing electronic energy transfer in systems epitomizing this intermediate coupling regime. In particular, we analyze the time-local and time-nonlocal weak system-bath coupling approaches which go beyond the Markovian limit of the celebrated Redfield theory, often yielding qualitatively different dynamics in the intermediate coupling regime. We additionally present results for more advanced master equations which employ analytical resummation techniques to improve convergence, resulting in rate constants and population dynamics in excellent agreement with exact numerical approaches.

Lattice Density-Functional Theory for the Hubbard Model of Graphene Nanostructures

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This poster describes a local lattice density-functional theory (LDFT) for the Hubbard model of poly-aromatic hydrocarbons, such as graphene nanostructures, with nearest neighbor distance and bond order dependent couplings. The exchange correlation functional follows the example of Ijas and Harju [Phys. Rev. B 82, 235111 (2010)], and the bond distance and bond order dependence of the Hamiltonian follows the example of Wohlthat, Reimers, and Hush [Phys. Rev. B 81, 195125 (2010)]. Our model was parameterized using the bond lengths, electron affinities, and ionization energies of a set of forty representative aromatic hydrocarbons calculated using B3LYP/6-31+G*. The quality of our model is compared to a similarly parameterized Hartree-Fock mean field treatment of the same Hamiltonian. The final LDFT model allows for calculations to be carried out on systems whose size prevents the application of typical quantum chemistry methods.

Post-Hartree Fock, Generalized Gradient, and Dispersion-Corrected Atomic-Centered Potential Approaches for Atom Tunneling through Nanoporous Membranes

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A single graphene sheet is impermeable to gases even as small as helium; pores are required for the transmission of atoms or molecules. Because a nanoporous graphene barrier is thin, quantum tunneling plays a role in the transmission of atoms through the barrier, even at room temperature. Tunneling calculations rely on accurate barriers, but barrier evaluations must account for the complex interplay between dispersion interactions and computational tractability with increasing system size. We benchmarked potential energy barriers calculated with an atomistic post-Hartree Fock MP2/cc-pVTZ model chemistry,¹ a plane-wave pseudopotential PBE approach based on density functional theory (DFT), and plane-wave calculations with an additional empirical dispersion-corrected atom-centered potential (DCACP).² In each case, the tunneling probability is calculated using the finite-difference method. Helium, neon, argon, and krypton are used as a model system for tunneling calculations due to their chemical inertness, periodic trend in radii, and lack of internal degrees of freedom. The permeability of periodic and non-periodic porous graphene nanostructures to these atoms is measured with reference to their potential energy barriers. These calculations allow us to predict the selective permeability of graphene to each of these atoms and provide a benchmark for the treatment of dispersion interactions in these systems.

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Enhancing Tracer Diffusivity By Tuning Interparticle Interactions and Solvation Shell Structure

James Carmer, Gaurav Goel and Thomas Truskett

We present results of a computer simulation study exploring the relations between a particle's solvation shell structure in a dense fluid state, its interactions with neighboring particles, and its dynamic properties. We find that the long-time diffusivity of the particle can be significantly enhanced if a soft repulsion is added to its effective interactions, which disrupts the cage structure of its neighbors. We demonstrate how excess entropy scalings not only predict this behavior but also can suggest how the effective interactions of a tracer nanoparticle in a dense fluid suspension can be "tuned" to increase its diffusivity. Finally, we argue that similar physics can be used to understand some of the dynamic behaviors ions in liquid water.

Accelerating Path Integral Molecular Dynamics with a Generalized Langevin Equation

Michele Ceriotti, David E. Manolopoulos and Michele Parrinello

With the steady improvement of the description of the interactions between atoms by both first-principles and empirical methods, it becomes more and more important to include explicitly the effects of the quantum nature of lighter nuclei in order to make atomistic simulations even more accurate and predictive. Path integrals are the technique of choice to treat nuclear quantum effects accurately, but they involve an overhead of an order of magnitude or more when compared to classical simulation techniques. Here it is shown how – by introducing a correlated noise term on top of path integral molecular dynamics – it is possible to greatly accelerate the convergence to a full quantum mechanical description of the nuclear degrees of freedom. Computational savings between a factor of four and a factor of ten can be expected. This approach promises to greatly extend the range of systems for which nuclear quantum effects can be properly accounted for.

Noble Gases on Metal Surfaces: New Insights on Adsorption Site Preference

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Experiments have previously found that noble gases (Kr, Xe) adsorb on low-coordination atop sites on several different metal surfaces, rather than on high-coordination hollow sites. This unexpected preference for low-coordination sites has been previously ascribed to reduced Pauli repulsion mostly due to exchange energy at the atop site, based on density functional theory calculations within the local density approximation (LDA). In contrast, our calculations using non-local van der Waals (vdW-DF) density functional show that site preference is due to a delicate balance between the electrostatics which favor the hollow site and kinetic energy which favors the atop site; exchange-correlation energies has a very little role. Moreover, we find, using LDA, GGA, and vdW-DF functionals, that the hollow site is a saddle point of index 1 or 2 (stationary points with 1 or 2 imaginary frequencies, respectively) on the 2-dimensional potential energy surface, while the atop site is the only true minimum. Therefore, the reason that hollow site occupation is not observed is that it is a transition state and so has a very short life-time. We show that this phenomenon holds for noble gas adsorption on close-packed Pt(111), Pd(111), Cu(111) surfaces, as well as the non-close-packed Cu(110) surface. Our results show that the inclusion of non-local vdW interactions is crucial for obtaining results in quantitative agreement with experiments for adsorption energies, equilibrium distances, and vibrational energies.

An Empirical Potential for Electronic Excitations using Charge Equilibration

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We present an empirical potential that models multiple electronic states with the same parameters and is suitable for both atomistic and coarse-grained force fields. Atoms or fragments are described as open quantum systems coupled together by a common charge reservoir, and can hence exchange charge. Unlike existing fluctuating-charge models, our new model uses multiple charge reference states, and smoothly interpolates between the strongly interacting and noninteracting limits. We present numerical results for donor-acceptor systems, developing a model for the ground state surface of lithium fluoride that also predicts reasonable charge transfer excitations in the dissociation limit. We also present a potential for benzene dimer that can be fit accurately to both the neutral and monocation curves simultaneously.

The Effect of Grain Boundaries Based on the (311) Surface of Y Doped BaZrO₃ on Proton Conduction Pathways

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Perovskite oxides have attracted much interest due to their possible use in proton conducting fuel cells. Our objective is to understand grain boundary structure and how it affects preferred proton conduction pathways in the doped perovskite oxide BaZrO₃. Prior studies have shown the O terminated (311) BaZrO₃ surface to be the most energetically favored surface.¹ Twist and tilt boundaries based on this surface are considered. The grain boundaries are optimized using density functional theory with the PBE functional. Binding sites and transition states are found on the optimum grain boundary. These are used to construct a graph for conduction across a grain boundary. Graph theory methods are used to find all probable conduction pathways across the boundary as in our earlier studies in bulk systems.²

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² M. A. Gomez, M. Chunduru, L. Chigwesh, L Foster, S. J. Fensin, K. M. Fletcher, and L. E. Fernandez, "The effect of yttrium dopant on the proton conduction pathways of BaZrO₃, a cubic perovskite," *J. Chem. Phys* 132 (2010) 214709; M. A. Gomez, M. Chunduru, L. Chigweshe, K. M. Fletcher, "The effect of dopant at the Zr site on the proton conduction pathways of SrZrO₃: An orthorhombic perovskite," *J. Chem. Phys.* 133 (2010) 064701.

The Thickness of a Liquid Layer on the Free Surface of Ice as Obtained from Computer Simulation

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Molecular dynamic simulations were performed for ice Ih with a free surface by using four water models, SPC/E, TIP4P, TIP4P/Ice, and TIP4P/2005. The behavior of the basal plane, the primary prismatic plane, and of the secondary prismatic plane when exposed to vacuum was analyzed. We observe the formation of a thin liquid layer at the ice surface at temperatures below the melting point for all models and the three planes considered. For a given plane it was found that the thickness of a liquid layer was similar for different water models, when the comparison is made at the same undercooling with respect to the melting point of the model. The liquid layer thickness is found to increase with temperature. For a fixed temperature it was found that the thickness of the liquid layer decreases in the following order: the basal plane, the primary prismatic plane, and the secondary prismatic plane. For the TIP4P/Ice model, a model reproducing the experimental value of the melting temperature of ice, the first clear indication of the formation of a liquid layer, appears at about -100 °C for the basal plane, at about -80 °C for the primary prismatic plane, and at about -70 °C for the secondary prismatic plane.

Heat Dissipation from the Catalytic Center of Human Heart Lactate Dehydrogenase

Ardy Davarifar and Steven Schwartz

We examine if the rate promoting vibration of lactate dehydrogenase (hLDH) is a preferred axis of thermal energy transfer. It seems plausible that such a mechanistically important motion is also a favored direction of energy transfer, but no previous study has directly addressed this question. It is possible that the promoting vibration, while catalytically important, has no different thermal properties than any other axis in the protein. Resolution of this issue is important for two reasons: First, if energy is transferred along this axis in a preferred fashion, it shows that the protein is engineered in a way that transfers excess thermal energy into a motion that is coupled to the chemical step. Second, the discovery of a preferred direction of thermal transfer provides a potential route to experimental verification of the promoting vibration concept. Our computational experiments are specifically designed to mimic potential laser experiment with the deposition of thermal energy in an active site chromophore with subsequent measurement of temperature at various points in the protein.

Regulation of Telomerase Activity by Macromolecular Crowding

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Human telomerase is a ribonucleoprotein complex responsible for maintaining telomeres. Precise regulation of telomerase activity in cells is essential for human health. Up-regulated telomerase activity is associated with cell immortality and cancer, whereas down-regulated activity has been linked to dyskeratosis congenita and aplastic anemia.

A central element of the RNA component of telomerase (hTR) is a conserved pseudoknot domain, which can exist in two alternative conformations, a pseudoknot (PK) and a hairpin. Mutations that either increase or decrease the stability of the PK result in a reduction in telomerase activity. Hence, inter-conversion between the PK and hairpin conformations is deemed essential for telomerase function.

In our poster, we present results of a simulation study of the hTR pseudoknot domain in a crowded environment using a new model, which accurately reproduces the experimental thermodynamic properties of different conformations of this domain. We find that crowding agents shift the thermodynamic equilibrium towards the PK conformation. The computed changes in the PK stability due to crowders are smaller than typical variations associated with disease-related mutations. Nevertheless, given the extreme sensitivity of enzyme activity to the stability of the PK, the effect of crowding on telomerase function is substantial. We estimate that the activity of telomerase can be up- or down-regulated by more than two-fold, by simply modulating the density of crowders in the cellular environment. This raises the possibility that local environment is an important factor in telomerase function.

Using Force-Matching of Ab Initio Molecular Dynamics Trajectories to Derive Empirical Water Models and to Understand the Differences Between Density Functionals

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Classical force fields that replicate properties of ab initio molecular dynamics (AIMD) simulations allow long-time trajectories to be efficiently obtained. In this study, a force-matching method is applied to three AIMD trajectories of water to obtain corresponding classical force fields. The AIMD trajectories are generated within the CP2K Born Oppenheimer dynamics framework by density functional theory using BLYP, BLYP plus Grimme dispersion correction, and HCTH density functionals. A comparison of the resulting models and calculated properties demonstrates that the Grimme correction has a non-trivial influence on the pairwise potentials. These results help in understanding the origins of different results from different density functionals.

Silicon Quantum Dots for Solar Cells

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Silicon quantum dots (QDs) encounter a large interest in various fields of applications, from biological markers to electronic devices. The size of the particles permits the silicon nanoparticles to benefit from the quantum confinement, giving them a direct band gap and a strong blue luminescence. Silicon QDs show high light conversion efficiency due to the bandgap and enhanced absorbed wavelengths, that makes them a strong candidate for solar cells applications.

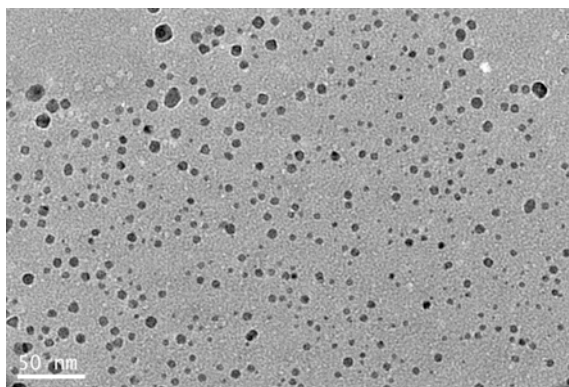


Fig: Amine terminated silicon quantum dots

We are investigating new surface modification on silicon quantum dots. A solution route has been used to synthesize the Silicon QDs. The composition of the nanoparticles and the attachment of the capping molecule were characterised by FTIR and ¹HNMR analysis. The shape and size repartition has been characterised by TEM.

Transition Path Sampling Study of the Reaction Catalyzed by Heavy Enzyme Purine Nucleoside Phosphorylase

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The connection between enzyme dynamics and transition state formation in Purine Nucleoside Phosphorylase (PNP) has been explored through our previous studies in collaboration with Schramm group. To further elucidate the mechanism of barrier crossing in enzymatic reaction, the effect of a “per-labeled” enzyme is being studied experimentally. To facilitate the understanding of the experimental findings, QM/MM transition path sampling (TPS) was applied to the phosphorolysis of guanosine catalyzed by heavy PNP in the explicit solvent followed by committor analysis. The TPS study of the heavy enzyme confirms the previous reaction mechanism in PNP catalysis, and provides insight into how the vibrational structure of the protein affects the catalytic efficiency.

Thermal Gaussian Molecular Dynamics: A Practical Approach for Quantum Dynamics in the Condensed Phase

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A new method, called Thermal Gaussian Molecular Dynamics (TGMD), for simulating the dynamics of quantum many-body systems has recently been introduced. As in the Centroid Molecular Dynamics (CMD), in TGMD the N-body quantum system is mapped to an N-body classical system. The associated effective potential and the effective force are computed within the Variational Gaussian Wavepacket (VGW) method. The TGMD is exact for the high-temperature limit, is accurate for short times and preserves the quantum canonical distribution. For a harmonic potential it provides exact time correlation functions $C_{AB}(t)$ for operators $A = A(\mathbf{x})$ and B a linear combination of the position, \mathbf{x} , and momentum, \mathbf{p} , operators. While conceptually similar to CMD and other Quantum MD approaches, the great advantage of TGMD is its computational efficiency. We introduce the many-body implementation and demonstrate it on the benchmark problem of calculating the velocity time autocorrelation function for liquid para-hydrogen.

Application of Effective Fragment Potential Method to the Redox Potential of Green Fluorescent Protein

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Green fluorescent proteins (GFP) can be considered as a model for fluorescent dyes and are of importance in photovoltaic materials. It exhibits bright green fluorescence when exposed to blue light and has been an extremely powerful tool as non-invasive marker in living cells and extensively used in molecular and cell biology. The understanding of the underlying electronic structure of these proteins and its chromophore is therefore crucial to the understanding of the mechanism for its optical properties.

The chromophore of the GFP is p-hydroxybenzylidene-imidazolinone (HBDI) and is embedded in the center of the β barrel of the GFP. Calculating redox potential of this chromophore is a challenging problem, especially in diverse solvents and protein environment. It is possible to carry out high-level accurate ab-initio calculation of ionization potential or electron affinity of the microsolvated chromophore or the bare chromophore. But, it is not possible to extend these calculations to bulk solvents due to the high computational cost. Effective fragment potential (EFP)[1,2] method gives us a convenient tool to understand such systems.

In our work, we have benchmarked the ionization energy and electron affinity of the microsolvated GFP chromophore calculated by combined EOM-IP-CCSD/EFP and EOM-EA-CCSD/EFP with the EOM-IP-CCSD and EOM-EA-CCSD calculations of the oxidized and reduced forms. We have carried out similar EFP-EOM-IP-CCSD and EFP-EOM-EA-CCSD calculations of ionization potential and electron affinity of GFP chromophore in bulk solvent generated by ab-initio molecular dynamics simulations.

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Time Resolved Photoelectron Spectroscopy from First Principles Simulations: Nonadiabatic Dynamics of Photoexcited Butadiene

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Time resolved photoelectron spectroscopy (TRPES) is a suitable tool to probe both the nuclear and electronic dynamics that occurs during ultrafast photochemical processes. However, the interpretation of TRPE spectra is not always clear, particularly in situations where multiple electronic states are populated and have overlapping photoelectron spectra. Nonadiabatic molecular dynamics simulations can aid in unraveling photochemical mechanisms and we present our approach to simulating TRPE spectra from first principles within the framework of the Ab Initio Multiple Spawning method with electronic structure treated at the multi-state complete active space second-order perturbation theory level (MS-CASPT2). As an application of our method, we have simulated the TRPES of photoexcited s-trans-1,3-butadiene and find good agreement with experiment, affording a detailed mechanistic picture of the photochemical dynamics.

Validation and Application of SCC-DFTB to the Study of Proton Transport in Aqueous and Biological Systems

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Water-mediated proton transfer (PT) plays an important role in many biological processes as well as in important industrial applications such as fuel cells. Despite numerous studies, there remain fundamental questions concerning factors that limit the rate and directionality of PTs in various biological and artificial systems.

The specific subjects of interest to our study include identifying the proton loading site (also referred to as proton storage site) in prototypical proton pumps, bacteriorhodopsin and cytochrome c oxidase (CcO), and elucidating the gating principles of vectorial proton pumping in CcO. To effectively address these challenging mechanistic questions, we have also carried out extensive benchmark calculations and improvements to the approximate density functional theory (SCC-DFTB) approach used in our QM/MM studies by investigating various gas-phase and condensed phase problems. Collectively, our studies of both aqueous and biomolecular systems illustrate that while there is ample room for further developments, the SCC-DFTB based QM/MM framework can effectively complement experimental studies to reveal novel insights into the mechanism of proton transport in complex systems.

Specifically, we first illustrate the accuracy and limitations of the current SCC-DFTB parameterizations with results for protonated water clusters, bulk water and proton transport in bulk water. Next, we discuss an “intermolecular proton bond” model for the proton storage site in bacteriorhodopsin and show that the model is consistent with many available experimental data including the temperature dependence of the so-called continuum band in infrared spectra. Finally, preliminary results concerning the gating principles in CcO will also be presented.

Adsorption in CuBTC MOF

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CuBTC, $\text{Cu}_3(1,3,5\text{-benzenetricarboxylate})_2$, the metal-organic framework (MOF) compound with coordinatively unsaturated metal sites, is one of the most studied MOFs for adsorption and separation of gases. The structure and properties of MOFs depend in general on a delicate balance of various energy contributions, including covalent, electrostatic, and van der Waals (vdW) interactions. A reliable description of all these energy contributions put great demands on the quality of methods used for modeling of MOFs. A density functional theory (DFT) is the most common method used for the description of materials in general. However, a failure of DFT to describe the vdW interactions accurately limits the applicability of DFT method in modeling MOFs severely.

A recently developed density functional theory/coupled cluster method (DFT/CC), based on the pairwise representability of DFT error (mostly the lack of dispersion interactions), has provided reliable results for molecular crystals, zeolites, and graphite. The DFT/CC correction scheme was extended and applied for the description of the MOF framework and MOF interactions with adsorbates.¹

The interaction of small molecules (H_2O , CO , CO_2 , hydrocarbons) with coordinatively unsaturated sites in CuBTC has been investigated. Calculated adsorption enthalpies were in very good agreement with experimental data. The DFT/CC results were also used for obtaining accurate interaction potentials for subsequent GCMC simulations of adsorption isotherms.

¹ Grajciar, L.; Bludsky, O.; Nachtigall, P. J. *Phys. Chem. Lett.* 2010, 1, 3354-3359.

Ultrafast Vibrational Spectroscopy of Water in Hydrated Lipid Multi-Bilayers

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The vibrational spectroscopy of hydration water in dilauroylphosphatidylcholine (DLPC) multi-bilayers is investigated using molecular dynamics simulations and a mixed quantum/classical model for the OD stretch spectroscopy of dilute HDO in H₂O. We suggest a simple two-population model for hydration water and investigate the slow exchange of molecules between these two populations. This model is then used to determine best-fits for the vibrational lifetimes T_1 for each population by comparing the population relaxation decay to recent experimental results. We then calculate the FTIR absorption spectra, rotational anisotropy decay, and 2DIR and peak-shift spectra as a function of the hydration level of the lipid multi-bilayer. Our theoretical FTIR absorption spectra successfully reproduce the experimentally observed red-shift with decreasing lipid hydration, and we interpret this shift in terms of the hydrogen bonding of water to the lipid phosphate group. From the anisotropy decay, we find that the reorientational motions of water molecules slow significantly as hydration decreases, with water bound in the lipid carbonyl region undergoing the slowest rotations. For each spectroscopic observable, we also investigate the effects of making various approximations in our theoretical treatment, and we discuss the role of these approximations in the interpretation of the anisotropy decay and 2DIR spectra

Development of a Charge-Perturbed Particle-In-A-Sphere Model for Nanoparticle Excitation Energies

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The complex surface structure of gold-thiolate nanoparticles is known to affect the calculated DFT excitation spectra. However, as the nanoparticle size increases, it becomes unpractical to calculate their excitation spectrum using DFT, so other methods need to be developed. Perturbation theory is a useful procedure that has been widely used to determine the energies of complex systems. One of the difficulties in this method is to determine the form of the perturbation involved for a specific system. Sometimes, more than one perturbation is necessary to get reliable energy values. In this study, perturbation theory is used to determine the energy levels of the $[\text{Au}_{25}(\text{RS})_{18}]$ nanoparticle. Its structure was determined by Heaven et al. to be a Au_{13} core protected by six $[(\text{RS})_3\text{Au}_2]$ “staples”. A particle-in-a-sphere model is used to treat the core. The “staples” are treated with point charge perturbations. As more perturbations are added, the degeneracy of the energy levels decreases. The main transitions are analyzed to predict the excitation spectrum. This model can be applied to larger nanoparticles with quasi-spherical geometry and a wide variety of ligands.

Milestoning with Transition Memory

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Milestoning is a method used to calculate the kinetics and thermodynamics of molecular processes occurring on time scales that are not accessible to brute force molecular dynamics (MD). In milestoning, the conformation space of the system is sectioned by hypersurfaces (milestones), an ensemble of trajectories is initialized on each milestone, and MD simulations are performed to calculate transitions between milestones. The transition probabilities and transition time distributions are then used to model the dynamics of the system with a semi-Markov process, where a long trajectory of the system is approximated as a succession of independent transitions between milestones. This approximation is justified if the transition probabilities and transition times are statistically independent. In practice, this amounts to a requirement that milestones are spaced such that trajectories lose position and velocity memory between subsequent transitions. Unfortunately, limiting the number of milestones limits both the resolution, at which a system's properties can be analyzed, and the computational speedup achieved by the method. We propose a generalized milestoning procedure, Milestoning with Transition Memory (MTM), which accounts for memory of previous transitions made by the system. When a reaction coordinate is used to define the milestones, the MTM procedure can be carried out at no additional expense as compared to conventional milestoning. To test MTM, we have applied it to the toy model of a polymer chain undergoing Langevin dynamics in solution and computed the mean first passage time for the chain to attain a cyclic conformation. We found that the number of milestones that can be used by MTM without incurring significant errors in the first passage time is at least 8 times that permitted by conventional milestoning. Moreover, we demonstrate that unlike conventional milestoning, MTM permits milestones to be spaced such that transitioning trajectories do not have enough time to lose velocity memory.

Theoretical Investigations of Proton-Coupled Electron Transfer in Ni(P₂N₂)₂ H₂ Oxidation Catalysis

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In this work we investigate the H₂ oxidation mechanism catalyzed by proton relays in the Ni(P₂N₂)₂ class of molecular electrocatalysts. Experiments indicate that these complexes can oxidize H₂ to 2H⁺ with turnover frequencies as large as 50 s⁻¹, the fastest reported for a molecular H₂ oxidation catalyst.^{a,b} A critical step in the proposed oxidation pathway involves electrochemical oxidation of the Ni complex and proton transfer between an amine ligand and the Ni center.^a The mechanism of this step could be a sequential electron-proton transfer, with either the electron or proton transferring first (ET-PT or PT-ET, respectively), or a concerted electron-proton transfer (PCET). The concerted PCET mechanism may be favorable because it can potentially avoid high-energy intermediates. Here we investigate the possible mechanisms for this critical step within a Marcus theory framework extended to electrochemical PCET. We use density functional theory to calculate redox potentials and pK_as to determine the driving forces as well as the inner-sphere reorganization energies. We also use dielectric continuum theory to calculate the solvent reorganization energies for PT and for electrochemical ET and PCET. After obtaining potentials for the transferring proton, we treat the proton as a quantum mechanical wavefunction, and the reactions are described in terms of nonadiabatic transitions between electron-proton vibronic states. We examine the relative free energy barriers for these possible mechanisms and calculate standard rate constants as well as kinetic isotope effects for comparison to experimental data from our collaborators in an Energy Frontier Research Center on Molecular Electrocatalysis.

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^bJ. Y. Yang *et al. Chem. Commun.* 46, 8616 (2010).

QM/MM Studies of Phosphoryl Transfer Reactions in Alkaline Phosphatase Superfamily

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Alkaline Phosphatase (AP) superfamily contains a set of evolutionarily related enzymes that catalyze the hydrolytic reactions of various phosphates and sulfates. In particular, AP catalyzes the hydrolytic reaction of phosphate monoesters but also exhibit promiscuous activity for the hydrolysis of phosphate diester and sulfate ester; similarly, although the main function of Nucleotide Pyrophosphatase/Phosphodiesterase (NPP) is to hydrolyze phosphate diester, it can also cleave phosphate monoesters and sulfate ester with lower efficiency. By employing QM/MM method, we studied the hydrolysis reaction of 4-nitrophenyl methyl phosphate which is a cognate substrate of NPP while promiscuously catalyzed by AP, and its thio analog, in solution and enzymes. Our results agree with available experimental data and confirm that the hydrolysis reaction in solution proceed via a concerted pathway; in enzymes, the similar mechanism is adopted, supporting the hypothesis that instead of altering transition state (TS) structure, AP superfamily catalyze phosphoryl transfer reactions by recognizing and stabilizing TSs similar to those in aqueous solution. In addition, the thio analogy calculation supports an alternative explanation of substrate binding orientation and caution the interpretation of experimental data.

Accurate DFT Redox Potentials for Transition Metal Complexes: Application to the Catalytic Cycle of Single Site Ruthenium Oxygen Evolving Complex

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The mechanism of water oxidation by a single site ruthenium oxygen evolving complex is investigated using fully unrestricted pseudo-spectral B3LYP with the effective core potential LACV3P in continuum solvent with some quantum mechanical waters. Guess wavefunctions have been used that allow greater flexibility in sampling different electronic configurations of the complex. In agreement with results from the literature, the challenging $4e^-$ and $4H^+$ oxidation of water is accomplished using a mechanism that features threeproton coupled electron transfers, one electron transfer, one atom proton transfer, and one ligand exchange. Calculations on a large and diverse database of transition metal complexes allows us to benchmark the computation of reduction half potentials and offer a systematic correction scheme for predicting redox properties with DFT, for example as in investigating ligand variations and their effect on the reaction mechanism. Errors in computed reduction half potentials compared to experiment are generally smaller for the water oxidation ruthenium complexes than for other kinds of complexes. The atom proton transfer and ligand exchange steps are found to be rate limiting with free energy barriers of 19.27 kcal/mol and 19.53 kcal/mol respectively, which is in excellent agreement with the ~ 20 kcal/mol barrier obtained from experimental rate constants.

Accurate Thermochemistry from a Parameterized Coupled Cluster Singles and Doubles Model (pCCSD)

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The major characteristics of traditional single reference coupled cluster (CC) theory are size-extensivity, invariance under orbital rotations of the occupied and virtual space, and exactness for 2 electron systems in the case of CCSD, 3 electrons for CCSDT and so forth. One may ask whether or not CC theory is the only theory which displays these desirable properties and if the traditional CC approach is actually the best choice.

We have recently introduced a continuous class of methodologies that are closely related to CCSD and are inspired by the coupled electron pair approximations (CEPA). The motivation is to develop an accurate and economical methodology that, when coupled with a robust local correlation framework, is suitable for large scale thermochemical applications for sizeable molecular systems (50-100 atoms). It is demonstrated that this parameterized version of CCSD or pCCSD is a significant improvement upon the standard CCSD approach and that it often approaches the accuracy of CCSD(T) for the calculation of reaction energies. This approach has been implemented within the framework of an efficient and accurate local correlation methodology based on Local Pair Natural Orbitals, in the ORCA quantum chemistry package of Frank Neese and coworkers at the University of Bonn. The LPNO based methodology allows routine applications to intermediate sized (50-100 atoms) molecular systems and provides a viable alternative to MP2 and DFT for the accurate prediction of reaction energies.

Iterative Linearized Density Matrix Propagation for Modeling Coherent Energy Transfer in Photosynthetic Light Harvesting

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We present results of calculations [1] that employ a new mixed quantum classical iterative density matrix propagation approach (ILDMM, or so called Is-Landmap) [2] to explore the survival of coherence in different photosynthetic models. Our model studies confirm the long-lived quantum coherence, while conventional theoretical tools (such as Redfield equation) fail to describe these phenomena [3,4]. Our ILDM method is a numerical exact propagation scheme and can be served as a benchmark calculation tool [2]. Results from ILDM and from other recent methods have been compared and show agreement with each other [4,5]. Long-lived coherence plateau has been attributed to the shift of harmonic potential due to the system-bath interaction, and the harvesting efficiency is a balance between the coherence and dissipation [1]. We use this approach to investigate the excitation energy transfer dynamics in various light harvesting complexes including Fenna-Matthews-Olsen light harvesting complex [1] and Cryptophyte Phycocyanin 645 [6].

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Semiquantum Molecular Dynamics Simulation of Liquid Water

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Many important chemical and biochemical reactions take place in liquid water, and many classical and empirical water models have been proposed to achieve better agreement with experimental results. On the other hand, the quantum mechanical simulations of liquid water have not yet established. Rigorous quantum calculations are too complicated to be applied to a complex and large condensed system, so various semiquantum approaches such as centroid molecular dynamics (CMD) and ring polymer molecular dynamics (RPMD) have been developed and applied in recent years.

We have developed the new semiquantum water (SQW) molecular dynamics (MD) simulation method. [1] Here, the wave packet (WP) approach was for the first time applied to study condensed bulk water structure and dynamics. In order to account for nuclear quantum effects such as the zero point energy and WP delocalization, we described each hydrogen atom as a three-dimensional Gaussian WP basis function. Our SQW MD simulation requires only the additional equations of motion for the WP width and its momenta, and the computational cost is much cheaper than other semiquantum approaches. Moreover, our SQW simulation successfully reproduced the major properties of CMD and RPMD, namely that quantized water is less structured, that the diffusion coefficient is larger than is seen in classical simulations, and that the IR spectrum of the OH stretching mode is red-shifted. Furthermore, we found a new peak above the OH stretching peak set which corresponds to the WP beating motion. This could be a direct evidence of the hydrogen quantum effect in the liquid water.

Anomalous and complex behaviors of liquid water are closely correlated to the dynamical rearrangements of the hydrogen-bond network (HBN). Our SQW MD simulation made it possible to directly view the WP dynamics in the liquid water, and have demonstrated that WP dynamics play an important role in the HBN dynamics. [2] For example, we found that WP dynamics accelerates the memory loss of the HBN and makes the HBN dynamics more complicated and manifold ; the SQW exhibits an almost complete $1/f$ power spectrum of the HBN dynamics, indicating the presence of multiple timescale dynamics. We also found significant correlations between the WP dynamics and large displacements of a water molecule such as a cage breakout in liquid water; as the WP grows, the HBN connecting to the water molecule weakens and simultaneously induces a significant rearrangement of the HBN around the molecule. These results provide new physical and chemical insights into the HBN dynamics in condensed liquid water. These are important not only for describing the liquid water dynamics but also for understanding conformation dynamics and chemical reactions of biomolecules in liquid water.

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Can DFT Predicts the First Ionization Energy of Thymine in Water?

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We have simulated ionization of thymine in the explicit bulk water environment and discrete solvation shells. Geometrical configuration were sampled from the classical and first principles molecular dynamics simulations. Extensive Density Functional Theory (DFT) calculations have been carried out in order to obtain a meaningful analysis of the merits of a number of popular functionals. Obtained results were validated against reference hybrid IP-EOM-CCSD/EFP calculations. Pure GGA functionals tend to be very unreliable, significantly underestimating vertical ionization energies (VIE). However, functionals incorporating a larger fraction of exact exchange, range separation, and van Der Waals correction tend to drastically improve the calculated VIE values. Artifacts as a cation hole delocalization and spillage to the water surface would be also discussed.

Quantum Mechanical Studies of Cuprous Oxide for Photocatalysis

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Photocatalytic processes have the potential to provide sustainable fuels, by using absorbed solar energy to catalyze reactions that produce fuels such as hydrogen, alcohols, or small hydrocarbons. To improve the viability of photocatalysis as an economically competitive source of fuel, efficient and low-cost photocatalytic materials must be developed. One attractive material is cuprous oxide (Cu_2O), an abundant, inexpensive, and non-toxic semiconductor that exhibits some photocatalytic activity for water splitting.¹ Cu_2O also shows potential for CO_2 reduction, containing a Cu(I) oxidation state that has been identified as the crucial active site in CO_2 reduction with Cu-based catalysts.²

We evaluate the photocatalytic potential of pure Cu_2O by studying its properties using quantum mechanical calculations. By using hybrid density functional theory (DFT) to calculate its band gap center and the many-body Green's function G_0W_0 approximation to calculate its photoemission/inverse photoemission band gap, we can accurately reproduce measurements as well as predict that its conduction band edge potential is positioned favorably to catalyze reduction reactions. DFT+U theory is used to study the low index surfaces of Cu_2O , identifying the (111) surface as the most stable. Gas phase reactions of H_2O and CO_2 on the (111) surface are studied using DFT+U theory, where we calculate free energy differences associated with possible reaction mechanisms and determine adsorption geometries of intermediates. Embedded correlated wavefunction methods are used for further refinement in a localized picture of surface reactions and excitations.

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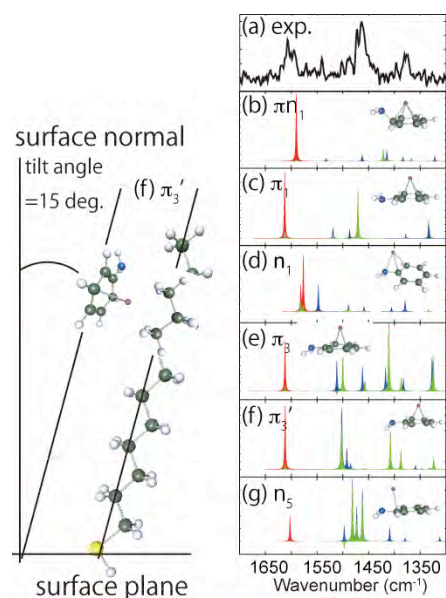
Theoretical Investigation of Infrared Reflection Absorption Spectra of a Titanium-Aniline Complex Soft-Landed in Alkanethiol Self-Assembled Monolayer

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Infrared reflection absorption spectroscopy (IRAS) is an informative tool regarding the molecular geometry and orientation at a surface. The selection rule at surface is different from in gas phase because the electric field at a surface mainly lies along the surface normal due to the interference between the induced and reflected light. We present (1) a theoretical method to calculate the IRAS spectrum and (2) an application to an open-sandwich Ti(aniline) complex. The complex is synthesized in gas phase and then soft-landed into an alkanethiol self-assembled monolayer matrix for characterizing its geometry and electronic state. The IRAS spectra are calculated as follows. At first, geometric structures of a modeled system of Ti(aniline)-C₃H₈ are optimized at the DFT(B3LYP/def2-TZVP) level, where an alkyl chain is modeled as C₃H₈. Then the normal mode derivatives of the dipole moment of the system are projected onto the surface normal direction. This projection accounts for the selection rule of IRAS. We assume the tilt angle of SAM to be 15 degrees. In the IRAS spectra shown in the figure, red, green, and blue represent the vibrations of NH₂, C₆H₅Ti, and C₃H₈, respectively. From the comparison, Ti(aniline) in CH-SAM is concluded to be a triplet state with the Ti-phenyl ring bond.



Coherent Resonance Energy Flow Dynamics in Soft Environments

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Recent experimental and theoretical studies suggest that natural photosynthetic complexes utilize the quantum coherence in a positive manner for efficient and robust flow of electronic excitation energy. Clear and quantitative understanding of such suggestion has significant implication in identifying the design principles behind efficient flow of excitons in soft environments, which may be adapted for the design of synthetic soft photovoltaic systems. Addressing these issues requires theoretical means to provide quantitative and reliable description of energy flow dynamics in such soft photovoltaic systems. While the theories by Förster and Dexter have been successful in describing various types of energy transfer processes for many decades, they are often inadequate for describing the energy transfer processes in soft and multichromophoric photovoltaic systems. One of the major issues is that conformational fluctuations and vibrational relaxations need to be treated on the same quantum mechanical footing as the energy transfer dynamics. The other issue is moderate or strong electronic coupling between energy donor and acceptor, which makes the simple rate picture of energy transfer invalid. This poster presents new theories[1-5] addressing these issues and the application of the theories to natural photosynthetic systems[1-2] and organic pi-conjugated systems[6]. These elucidate the sensitivity of quantum coherence on details of how electronic excitations are coupled among themselves and to their environments, and also suggest ways to utilize them for enhancing the efficiency of energy flow dynamics.

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Low-Temperature Kinetics from Parallel-Tempering Brownian Dynamics Simulations

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We develop a method to extrapolate the kinetics of the conformational dynamics at one temperature from the parallel tempering simulations using the stochastic path integral weight. In parallel tempering, the system is occasionally transported to different temperatures to access the whole configuration space more efficiently satisfying the detailed balance condition. We obtain an equilibrium time correlation function from the entire trajectory at multiple temperatures using a modified path integral weight, where the probabilities of the attempt and acceptance for switching the temperature are incorporated. The relative weights of the high-temperature trajectories are computed with a new time step, which is scaled with the same factor as the temperatures. We demonstrate the validity of this method beginning with a simple classical system of one-dimensional double well potential at two temperatures. To improve the statistical efficiency of this reweighting scheme, the resampling of the path integral weights is carried out. We discuss the extension of this method to the general parallel tempering simulations at three or more temperatures.

Ab Initio Study of Electron and Hole Transport in Pure and Doped MnO/ZnO Alloys

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Transition metal oxides (TMOs) such as MnO/ZnO alloys are intriguing materials for photocatalytic (PC) and photovoltaic (PV) devices because they are predicted to absorb visible light, their band edges are suitable for water splitting and CO₂ reduction, they are corrosion-resistant, and their elemental abundance makes them economical [1]. However, the MnO parent material and MnO/ZnO with up to 10% ZnO are known to have relatively low hole conductivity while their electron conductivities have been studied to a much lesser extent (in the case of MnO) or not at all (in the case of MnO/ZnO). Understanding what controls transition metal oxide conductivity is an important step towards harnessing solar energy effectively in such materials. N-type or p-type doping can increase carrier concentrations, thereby dramatically improving conductivity, but nanoscale understanding of how dopants affect these materials is still lacking. To elucidate this point, we investigated charge transport in MnO and MnO/ZnO, focusing on the effects of various (n-type dopants) Y, Gd, Ga, In, Sc as well as Li (a p-type dopant) using ab initio embedded cluster calculations and the polaron model. Our results based on relative transport barriers suggest Sc, In, and Ga will act as traps, while Y and Gd improve conductivity by donating carriers without becoming recombination centers or changing the electron transport pathway. The key advantage of Y and Gd over other n-type dopants lies in the stability and larger radii of their 3+ ions relative to their 2+ counterparts. We also find Li is a favorable p dopant that shifts the transport pathway from a Zn/Mn hopping pathway to an O hopping one. In summary, doping with Y-, Gd- (n-type), or Li- (p-type) should increase the conductivity of MnO/ZnO, making doped MnO/ZnO a competitive candidate for PC/PV devices.

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Preferential Adsorption of Surfactants to Nanoparticle Surfaces

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Cadmium selenide (CdSe) nanoparticles grown in organic solvent in the presence of the surfactants trioctylphosphine oxide (TOPO) and hexylphosphonic acid (HPA) have been found to form spherical nanoparticles with no HPA or low concentrations of HPA, nanorods at intermediate concentrations of HPA, and a variety of tapered rod-like shapes at high concentrations of HPA. The goal of this work is to understand why specific shapes of nanoparticles form in the presence of certain surfactants by calculating binding free energies, including solvent effects, for both TOPO and HPA to the solvent-accessible faces of CdSe particles. We performed Monte Carlo simulations using a generalized Born model for non-aqueous solvent to estimate the solvation free energy to obtain a large set of low free energy surfactant-crystallite structures. An energy screening window was identified, and only the solvation free energies of the structures in this range were refined using the solution to Poisson's equation. The calculated binding free energies for TOPO to each of the solvent-accessible CdSe faces were very similar, while the magnitude of the calculated binding free energy for HPA to the (001) face was significantly less negative than those of HPA to the other solvent-accessible faces. This is consistent with the formation of CdSe nanospheres in the presence of TOPO alone and the formation of CdSe nanorods in the presence of HPA. The calculated single surfactant binding free energies are an effective way to predict the relative growth rates of CdSe nanocrystal faces in the presence of surfactants.

Towards a Full-Dimensionality Semiclassical Treatment of the Helium Atom

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Semiclassical calculations for the electronic structure of atoms and molecules hold out the prospect of elucidating basic chemical and physical concepts while allowing an exact treatment of electron correlation. However, such calculations are extremely difficult for systems having more than a single electron because of the divided nature of the classical phase space, the existence of very strongly chaotic motion, the occurrence of classical autoionization at all energies, and the singular nature of the Coulomb potential. In particular, the presence of more than two degrees of freedom in such systems makes it unfeasible to apply semiclassical methods that require the enumeration of periodic orbits such as Gutzwiller's trace formula and techniques based on the semiclassical zeta function. As a result, despite the great interest in this subject since the days of the Old Quantum Theory, modern semiclassical calculations of atoms have been limited to reduced-dimensionality models for two-electron systems. To allow full-dimensionality treatments of atomic energies we have recently developed a semiclassical initial value approximation for the trace of Green's function. This method does not require a search for periodic orbits and is especially efficient for systems with homogeneous potential energy functions such as atoms and molecules. We present a description of the method and some preliminary computations for the helium atom that illustrate the technique and indicate the accuracy of the semiclassical approximation for this system.

Study of Solvation in Coarse-Grained Model of Room-Temperature Ionic Liquids via Molecular Dynamics Simulation

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We study solvation dynamics in a room temperature ionic liquid, 1-ethyl-3-methylimidazolium hexafluorophosphate (EMI⁺PF₆⁻), with a diatomic solute pair as a probe molecule by performing molecular dynamics simulations on a coarse-grained model. For a diatomic solute pair, two different state of charge distribution are used, a neutral pair (NP) and a ionic pair (IP) with each atom have opposite unit charge e and $-e$. We calculate the normalized time-dependent Stokes shift function in a non-equilibrium solvation dynamics simulation, using a concept of isoconfigurational ensemble to explore the effect of structure in solvation dynamics, after Frank-Condon transition from NP to IP and vice versa, especially in case of $\Delta E_{i \rightarrow f}$ equals to $\langle E_{i \rightarrow f} \rangle$. $\Delta E_{i \rightarrow f}$ is defined by difference of total energy of RTIL-solute system, where i and f mean initial and final solute state. We also perform similar simulation in case of red edge condition and blue edge condition to find specific reasons of dynamic heterogeneity of solvation dynamics.

Reduced Dynamic Heterogeneity of the East Model in Higher Dimensions

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We use kinetically constrained models to investigate a dimensional dependence of dynamic heterogeneity in supercooled liquid systems. Higher dimensional generalizations of East models are used as representative fragile liquid systems. We first investigate how the breakdown of the Stokes-Einstein (SE) relation changes with the system dimensionality. The scaling $D \sim \tau^{-\xi}$ reveals that there is still significant Stokes-Einstein violation at $d=4$ and higher dimensions, although its extent weakens as d increases. Our result is consistent with recent molecular dynamics simulation studies performed on supercooled liquid systems. Dimensional dependence of quantified dynamic heterogeneity in East models is analyzed both in time and length scales. By calculating persistence functions and the dynamic susceptibility, it is revealed that system is getting homogeneous as the spatial dimension is increased. Further, spatial correlator of the local persistence function and corresponding structure factor are computed. The correlation length and related dimension dependent scaling exponents are obtained from structural correlation functions.

Time Evolution, Equations of Motion, and Random Phase Approximation for Matrix Product States

Jesse M. Kinder, Claire C. Ralph and Garnet Kin-Lic Chan

Minimizing the action over a restricted space of variational wave functions provides a method for simulating the time evolution of an arbitrary quantum system. When the wave function is restricted to Hartree-Fock states (i.e. single Slater determinants), this approach yields the Dirac-Frenkel variational approach to time-dependent Hartree-Fock theory (TDHFT). Matrix product states (MPS) are an analog of Hartree-Fock states for strongly correlated systems and underlie the variational flexibility of the density matrix renormalization group. Drawing on analogies with TDHFT, we develop a theory of time-dependent matrix product states (TDMPS). In contrast with existing approaches to TDMPS, approximate projections of the wave function are replaced by analytic equations of motion. Further extending the analogy with TDHFT, we present an MPS analog of the RPA that gives the approximate excitation spectrum and response properties of an MPS ground state wave function.

Defining Reactive Forcefields from Condensed Phase Ab Initio Simulations

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Typical molecular mechanics forcefields assume a fixed bonding topology throughout the simulation, which prevents the modeling of reactive events coupled to the breaking and formation of chemical bonds. It would thus be highly advantageous to have a general methodology to parameterize reactive force fields using data from condensed phase ab initio simulations, where variable bonding topologies are naturally accounted for. When properly parameterized, these empirical reactive models would extend the time and length scales of the original ab initio simulations at a fraction of computational cost, while at the same time reproducing the thermodynamic and dynamic properties of the system. This work will discuss the application of a force matching algorithm to develop multistate empirical valence bond models for the hydrated proton and hydroxide ion based on ab initio molecular dynamics simulations.

This work was supported by the U.S. Dept. of Energy under Contract DE-AC02-06CH11357.

Low-Spin Excited States Through Spin Purification of Non-Aufbau Solutions to the Kohn-Sham SCF Equations

Tim Kowalczyk and Troy Van Voorhis

The Δ SCF approach to excited states in DFT is straightforward to implement within ground state DFT codes and affords excited states at similar computational cost to ground states. Δ SCF excited states are self-consistent solutions to the Kohn-Sham equations with a prescribed non-Aufbau occupation of the one-electron orbitals.

We recently presented benchmark linear response TDDFT and Δ SCF calculations of low-lying singlet excitations in large organic dyes.¹ Despite the *ad hoc* nature of the Δ SCF approach, Δ SCF and TDDFT excitation energies proved to be similarly accurate (RMSD approx. 0.3 eV) with the best functionals. As a partial justification of the similar performance of the two methods, we demonstrated that Δ SCF densities are stationary densities in linear response TDDFT within the adiabatic approximation. However, singly excited Δ SCF states of closed-shell molecules are by construction an admixture of singlet and triplet spin states, and thus require spin purification to obtain the singlet energy.

In this context, we consider two approaches to spin purification for Δ SCF states. The Ziegler sum rule obtains the singlet energy from energies of the spin-contaminated ("mixed") and triplet states. The restricted open-shell Kohn-Sham (ROKS) approach instead enforces a singlet spin state self-consistently at the level of the wavefunction. We present a variational two-layer SCF approach to ROKS, including an implementation for the lowest singlet excited state of closed-shell molecules within the Q-Chem package. We will also consider advantages and disadvantages of these spin purification approaches with respect to alternative spin adaptation techniques.

¹Kowalczyk, T.; Yost, S. R.; Van Voorhis, T. *J. Chem. Phys.* 134, 054128 (2011)

Approximately Size Extensive Local Multireference Singles and Doubles Configuration Interaction

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Multireference Configuration Interaction (MRCI) is known to accurately predict a variety of properties, such as bond dissociation energies, for small molecules. Unfortunately, MRCI methods cannot be applied to large molecules for two reasons: the computational cost scales badly with molecule size and MRCI methods are not size extensive. We have developed a local approximately size extensive MRCI method which addresses both these concerns. Computational cost is reduced by truncating long-range electron correlation in a local orbital basis in combination with efficient processing of two-electron integrals via Cholesky decomposition (CD) and integral screening. The multi-reference averaged coupled-pair functional provides approximate size extensivity by modification of the energy functional (CD-LMRACPF). We have also investigated using Davidson-type corrections to local MRSDCI to achieve approximate size extensivity. The Davidson-Silver and Pople corrections both produce quite accurate a posteriori corrections over a large range of molecular size. We have found CD-LMRACPF is slightly more expensive than using a Davidson-type correction, but provides superior results. CD-LMRACPF produces accurate bond dissociation energies and can handle up to 50 heavy atoms.

Polarizable, Classical Description of the Solvation Shell of Aqueous Divalent Metal Ions

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Aqueous solutions of divalent alkaline earth ions, like Mg^{2+} and Ca^{2+} , and transition metal ions like Cu^{2+} , play an important role in both biological and geological systems. Previously we have developed a polarizable model for water, POLIR, specifically optimized for IR spectroscopy. It is shown that POLIR, combined with new polarizable water-ion potentials for the indicated cations, yields a comprehensive classical description of the spectroscopy, energetics, and structure of the hydrating waters, including the case of Cu^{2+} , where they might be considered ligands held by intermediate-strength chemical bonds. Calculations of the thermodynamics of solvation are in progress.

Advances in Polarizable Continuum Models

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Polarizable continuum models (PCMs) are a family of implicit solvent methodology that provide an efficient means to incorporate bulk solvent effects into quantum chemical calculations. This is accomplished by placing a given solute molecule inside a cavity in a continuum dielectric and finding an apparent charge density, which resides on the cavity surface, that simulates the reaction field response of the solvent. Doing so for arbitrary shaped cavities requires a boundary element discretization of the cavity and surface charge density, yet a straightforward pointwise discretization can lead to numerical problems that may hinder commonplace quantum chemical applications. Recently, we have introduced a discretization scheme, called the Switching/Gaussian (SWIG) method, which amends these numerical problems.

Furthermore, SWIG provides an avenue to explore two new developments in the context of Debye screened PCMs (i.e. PCMs that solve the linearized Poisson-Boltzmann equation for solvents of non-zero ionic strength). Firstly, SWIG allows us to establish and test the first analytic implementation of the screened version of Integral Equation Formalism PCM (IEF-PCM). Secondly, we reformulate the conductor-like PCM (C-PCM) such that we are able to derive a generalization for non-zero ionic strength, which we dub the Debye-Huckel-like Screening Model (DESMO).

We demonstrate the versatility of SWIG with several examples, exhibit the accuracy of our implementation of screened IEF-PCM and DESMO, and report an efficient linear scaling parallelization of our code.

Correlation Between Pathway Heterogeneity and Folding Mechanism in Protein Folding Kinetics: A Lattice Model Approach

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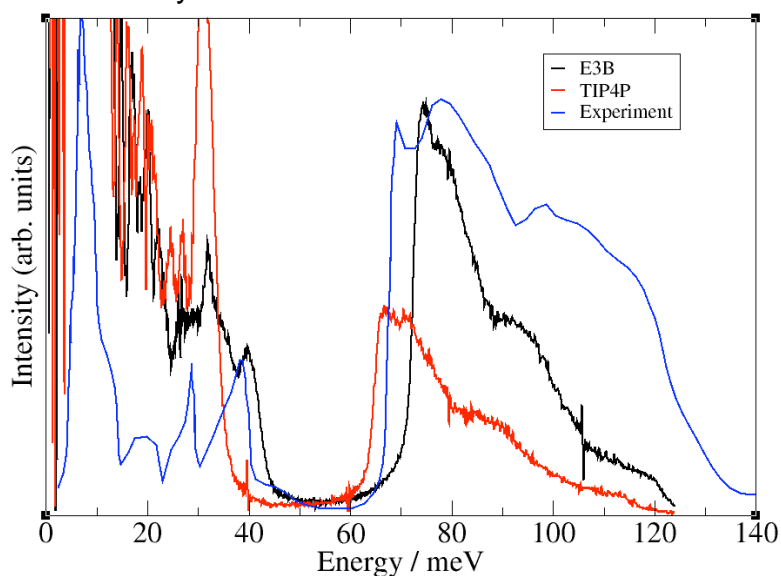
In the field of a protein folding science, energy landscape theory gives novel insight to multiple pathways in the protein folding, and many experimental and theoretical studies support heterogeneous intermediates and transition states. However, due to the diversity of protein sequences and their various folding mechanisms, pathway heterogeneities of protein folding also differ from each other. In this study, in order to find the correlation between pathway heterogeneity and the folding mechanism, we use the Muñoz-Eaton (ME) model which is a native-centric, one-dimensional spin model. The transfer matrix formalism offers the exact solution of the ME model and gives the free energy profiles versus the number of protein native bonds. Three representative proteins, known to show different folding kinetics, are used. Free energy calculations of three proteins clearly show that BBL, ubiquitin, and λ -repressor are downhill, two-state, and intermediate folder, respectively, which are consistent with previous experimental results. We also performed non-equilibrium Monte-Carlo simulations using ME Hamiltonian to study kinetics of transitions from a non-native to a native structure of proteins. Pathway deviations calculated from MC trajectories show that BBL has more heterogeneous pathway than ubiquitin below their folding mid-temperatures. Calculations of two-point correlation functions exhibit that BBL shows stretched exponential kinetics while ubiquitin shows single exponential kinetics, which also support heterogeneities of folding pathways. Moreover, analysis of four-point correlation functions provides the folding mechanism. In the case of BBL, the formation of tertiary structure drives the complete folding of the protein, and this process is often called a collapse mechanism. On the other hand, folding of ubiquitin has a nucleation mechanism that the specific secondary interactions act as nuclei of protein folding. λ -Repressor, unlike other systems, shows temperature-dependent folding mechanisms and heterogeneities. From above results, we conclude that large pathway heterogeneity comes from the loosely bounded interactions of a collapsed structure, while the relatively small pathway heterogeneity comes from the compact secondary structure of a nucleus.

Hydrogen Bond Strength in Ice

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Incoherent inelastic neutron scattering, which exploits the exceptionally large incoherent neutron cross-section of hydrogen, provides rich information about the hydrogen bond stretch strength in the region of 20 to 50 meV. However the interpretation of the presence of two peaks at ~30 and 40 meV in ice Ih is controversial^{1,2}. Some suggest that these results from two kinds of hydrogen bonds in ice Ih. In this presentation, we formulate a theoretical model to calculate the incoherent inelastic neutron scattering spectra in the hydrogen bond stretch region. We perform the calculations on proton-disordered ice Ih, using two water models, the popular TIP4P water model and a newly-developed water model (E3B) with explicit three-body interactions^{3,4}. Our results show that the high frequency peak shown below at about 40meV might arise from the three-body interactions.



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- [4] C. J. Tainter, P. A. Pieniazek, Y.-S. Lin and J. L. Skinner, *in preparation*.

Epitaxial Two Dimensional Ice Confined by Mica and Graphene Surfaces: An Ab initio Molecular Dynamics Simulation Study

Hui Li and Xiao-Cheng Zeng

Because of the template effect of the substrate and the intermolecular hydrogen bonding, interfacial water can form special ice structures on surfaces. Numerical kinds of ice structures formed by the surface water have been observed on various metal and nonmetal surfaces. Previous theoretical studies have also predicted several new forms of ice structures on surfaces. For example, bilayer hexagonal ice and monolayer ice clathrate structures confined to hydrophobic surface, such as graphene or the Lennard-Jones wall, have been predicted via classical Molecular dynamics (MD) simulation.^{1, 2} Recently, water adlayers on mica (muscovite) surface were carefully studied by using atomic force microscopy (AFM) at ambient conditions.³ It has been found that the thicknesses of single and double layers of water confined by mica (001) and graphene are the same as monolayer and bilayer of ordinary ice (ice I_h). This system provides an idea model to study the 2D ice/water structure confined by one hydrophobic side (graphene) and the other hydrophilic side (mica).

In this study, we employed an ab initio MD simulation method based on density functional theory (DFT) with dispersion correction. This method can provide more reliable description of structure and interaction between mica and water molecules. The simulation models contain mono, double, and triple layers of I_h -ice confined between mica(001) and a free standing graphene. The perfect epitaxial ice structure has been found on mica, as shown in Fig. 1. The bottom water molecules can form strong hydrogen bonds with the oxygen on mica, and with the top water layer, which exhibits no dangling hydrogen bonds, due to the confinement by the graphene layer. The ab initio MD simulations show that the melting point for the I_h -ice with graphene confinement is between 300 and 340 K; however, the melting point of the I_h -ice without graphene confinement is less than 300 K. Hence, we can conclude that the hydrophobic confinement side is important to the stabilization of the ice structure. The binding energy and free energy were also computed for this system.

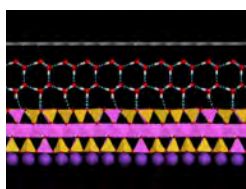


Fig. 1. A snapshot of 2D bilayer ice confined between a graphene on mica surface. The system is constructed by 3 layers: the top layer is graphene, the middle layer is ice, and the bottom layer is mica I. The blue dashed lines denote the hydrogen bonds.

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Hydrolysis Reaction Mechanism of NaBH₄ from First-Principles

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Complex hydrides of light elements are promising hydrogen storage materials due to their high gravimetric and volumetric densities. Hydrolysis of NaBH₄ is of importance for niche hydrogen storage applications, such as portable power generation. It is well-known that NaBH₄ is fairly stable in water, despite the very exothermic reaction to form NaB(OH)₄ and H₂ and that this reaction can proceed to completion with aid of acids or metal based catalysts. However, recent experimental work by Matthews et al. has shown that catalyst-free hydrolysis can take place with both fast kinetics and high extent of reaction under technical conditions by using steam deliquescence of NaBH₄. The catalysis-free reaction pathway offers significant advantages over acid-catalyzed hydrolysis. However, the reaction mechanism has not been elucidated. We use first-principles density functional theory to compute possible reaction pathways of catalyst-free hydrolysis of NaBH₄. We have observed reactions between NaBH₄ and water to generate H₂ and intermediate products NaBH₃OH and NaBH₂(OH)₂ on picosecond time-scales in multiple *ab initio* molecular dynamics simulations. These condensed phase simulations provide information on the elementary reaction steps for catalyst-free NaBH₄ hydrolysis.

Efficient First-Principles Electronic Dynamics

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An efficient first-principles electronic dynamics method is introduced in this article. The approach we put forth relies on incrementally constructing a time-dependent Fock/Kohn-Sham matrix using active space density screening method which reduces the cost of computing two-electron repulsion integrals. An adaptive step-size control algorithm is developed to optimize the efficiency of the electronic dynamics while maintaining good energy conservation. A select set of model dipolar push-pull chromophore molecules are tested and compared with the conventional method of direct formation of the Fock/Kohn-Sham matrix. While both methods considered herein take on identical dynamical simulation pathways for the molecules tested, the active space density screening algorithm becomes much more computationally efficient. The adaptive stepsize control algorithm, when used in conjunction with the dynamically active space method, yields a factor of ~3 speed-up in computational cost as observed in electronic dynamics using the time dependent density functional theory. The total computational cost scales nearly linearly with increasing size of the molecular system.

A Novel Application of ONIOM to Elucidate Structural Information Obtained from High Resolution NMR Investigations

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A novel approach to enhancing the information from high resolution NMR of ligand binding in large protein structures is undertaken. Molecular mechanics docking programs have long been used to probe likely regions for binding of ligands to large biochemical systems. NMR methods have been developed to extract detailed information about the chemical environment of bound ligands relative to a solution phase environment. X-ray structural information is considered to be the "gold standard" of structure/function relationships. Primarily this gold standard is based on having x,y,z co-ordinates of the atoms. NMR by itself cannot produce this amount of information. The purpose of this investigation is to explore the use of ONIOM to provide insight into the details of ligand binding in protein structures. Using a combination of experimental and theoretical NMR chemical shift information, it is proposed that detailed structural information can be obtained.

CO₂ Activation Using Middle Transition Metal Catalysts: A Computational Study

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The mechanism of the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) was investigated using the 3d transition metal complexes $\text{L}'\text{M}$ ($\text{M} = \text{Fe}, \text{Mn}$ and Co , $\text{L}' =$ parent β -diketiminato). The thermodynamics and reaction barriers of the elementary reaction pathways were studied with the B3LYP density functional and two different basis sets: 6-311+G(d) and aug-cc-pVTZ. Plausible reactants, intermediates, transition states and products were modeled, with different conformers and multiplicities for each identified. Different reaction pathways and side reactions were also considered. Reaction enthalpies and activation energies for all steps were determined for each transition metal. Calculations indicate that the most favorable mechanism involves mostly mono-metallic complexes. Among the three catalysts modeled, the Mn complex shows the most favorable catalytic properties, especially for the activation of CO_2 .

Effect of Biomolecular Structure on Energy Transfer Processes in Photosynthetic Light Harvesting Complexes: Implications for Designing Bio-Hybrid Solar Cells

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Energy transfer processes in photosynthetic light harvesting complexes are highly efficient and serve as a benchmark for evaluating the performance of artificial solar cells. These processes are largely governed by two factors: 1. The electronic coupling due to the orientation of the transition dipoles between adjacent chromophores, and 2. The relevant pigment-protein interactions due to fluctuations in the electrostatic environment. To study these processes in natural photosynthetic systems, such as visible light-absorbing dinoflagellates and infrared-absorbing green sulfur bacteria, we use a multiscale computational approach: 1. Molecular dynamics simulations to accurately predict biomolecular structure, and 2. Time-dependent density functional theory calculations to determine energies of excited states. Rates and efficiencies of energy transfer are then calculated using the Forster equation or Redfield equation, depending on whether the chromophores are determined to be weakly or strongly coupled, respectively. This work has been recently extended to the study of potential bio-hybrid solar cells, where photosynthetic light harvesting complexes are integrated with appropriate semiconductors for long-range energy propagation and/or charge separation. We discuss our progress in modeling the binding of these biological complexes to inorganic substrates, and calculations of energy transfer rates in these systems.

Theoretical Studies Linking Protein Dynamics, Structure, and Enzymatic Catalysis

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Protein dynamics on the timescale of enzymatic turnover plays a pivotal role in the catalytic cycles of many enzymes; however, recent evidence suggests that faster protein dynamics on the timescale of chemical change may also directly participate in some enzymatic reactions. To interrogate the role of these fast motions, termed promoting vibrations, in enzymatic chemistry, we are conducting complimentary, computational studies designed for confirmation by experimental counterparts on two enzymes: lactate dehydrogenase (LDH) and deoxynucleotide *N*-hydrolase (RCL). In LDH, an enzyme in which our group has previously identified a promoting vibration, we are attempting to disrupt the promoting vibration via *in silico* mutagenesis of residues involved in the promoting vibration. We will determine the effect of mutation on the enzymatic reaction coordinate and the chemical step using transition path sampling (TPS). Simultaneously, we are implementing statistical coupling analysis to determine if the residues of the promoting vibration are evolutionarily conserved. We will also perform TPS using RCL, a newly discovered enzyme with an abnormally small k_{cat} , to identify the reaction coordinate of the enzyme. We will then attempt to facilitate the chemical step by mutating key residues to intensify dynamic networks within the protein. Establishing the role of specific, fast protein motions in enzymatic chemistry will demonstrate that, in addition to active site geometry, protein architecture facilitates chemistry by acting as a scaffold for vibrational modes.

Using Mini-Proteins and Mixed QM/MD Simulations to Study Tryptophan Fluorescence

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Tryptophan fluorescence is widely used as a probe of protein structure and dynamics due to the sensitivity of quantum yield and emission spectrum to the surroundings; however, the factors that influence these properties remain poorly understood. To simplify this question we have measured fluorescence in a series of hairpin and Trp-cage peptides that fold into well-defined structures as observed by NMR. These peptides contain a single Trp residue with variable surrounding residues that can influence the fluorescence properties. In the hairpins, Trp fluorescence can be quenched by a Cys or protonated His, Asp or Glu residue near the Trp, probably by electron-transfer from the excited indole ring to the side chain of the quencher. Tyrosine and ornithine can quench by a different process that displays a deuterium isotope effect and thus likely involves proton transfer. The 20-residue Trp-cage peptides exhibit more variable emission energies and strong quenching, possibly by electron-transfer to the peptide backbone as Callis and coworkers have proposed for proteins. To aid in interpreting these results we are attempting to calculate fluorescence yields, emission spectra and dynamic Stokes shifts by hybrid quantum-classical MD simulations using modified versions of Warshel's QCFF/PI and Enzymix programs. The calculations include a quantum treatment of the Trp residue, its attached amide groups, and possible electron acceptors. The classical Enzymix program controls all the atomic coordinates and sends QCFF/PI the electrostatic potentials at the quantum atoms from atomic charges and induced dipoles of the peptide and solvent atoms. QCFF/PI then calculates energies, oscillator strength and charge-transfer properties and returns the charges of the quantum atoms to Enzymix. The relative simplicity of our system allows us to perform quantum calculations at each step of the MD trajectory and to extend simulations over the 10 ns time scale of fluorescence. Time-dependent Stokes shifts of an ensemble of molecules can be simulated by running multiple trajectories in the excited state, with excitation occurring from different starting points on the potential surface of the ground state. Though still being developed, our simulations reproduce some of the major quenching mechanisms and variations in energy.

In Silico Optimization of an Optical Sensor For Calcium

Brandon M. Mills and Lillian T. Chong

Although many strategies have been proposed towards the design of new protein switches, these approaches still involve significant trial-and-error. One encouraging design scheme, Alternate Frame Folding (AFF), has recently been used to convert calbindin into an optical sensor for calcium. Under the AFF strategy, two proteins are fused together in an end-to-end fashion such that they partially overlap in sequence. This causes the folding of the two proteins to become mutually exclusive, with a competition equilibrium that is sensitive to ligand binding and optically observable via the introduction of fluorophores. Since the AFF strategy involves partial unfolding, it is difficult to characterize the switch using high-resolution structural or kinetic studies, potentially limiting opportunities to rationally improve the design. These challenges have led us to employ coarse-grained molecular simulations to complement experiments in the analysis of the Calbindin-AFF protein switch. These simulations, which take less than a week, allow for the exploration of switching mechanisms and relative kinetics. These details may then be used to propose alterations that can improve signal response and switching rate. We believe these simulations can increase the success rate and efficiency of AFF switch designs for a minimum of additional time and cost.

The Geometry and Electronic Structure of the As-DNA Backbone

Arnošt Mládek, Jiří Šponer, Bobby G. Sumpter, Miguel Fuentes-Cabrera
and Judit E. Šponer

High level quantum chemical calculations have been applied to investigate the geometry and electronic properties of the arsenate analogue of the DNA backbone. The optimized geometries as well as hyperconjugation effects along the C3'-O3'-X-O5'-C5' linkage (X = P, As) exhibit a remarkable similarity for both arsenates and phosphates. This suggests that arsenates, if present, might serve as a potential substitute for phosphates in the DNA backbone.

Ab Initio Molecular Dynamics with the Analytical Multistate CASPT2 Nonadiabatic Coupling: Application to the Dynamics of the Rydberg State in Ethylene

Toshifumi Mori and Todd J. Martínez

Department of Chemistry, Stanford University

Ab initio molecular dynamics is a powerful tool to study photochemical reactions involving nonadiabatic transitions. The state averaged complete active space self-consistent-field (SA-CASSCF) method has been a workhorse on this field. However, the lack of an important feature in SA-CASSCF method, i.e., the dynamic electron correlation, has restricted its applicability. Moreover it is well known that, without the correlation effect, states with different characters, e.g., valence and Rydberg states, are often not well described, even qualitatively. Recently, it became possible to overcome this problem by the second order perturbation theory for SA-CASSCF method (MSPT2) after the introduction of the analytical MSPT2 energy gradient. However, the lack of nonadiabatic coupling has restricted the applications of MSPT2 method in the dynamics.

In this work we derived the analytical expression of the nonadiabatic coupling for the MSPT2 method. The method has been combined with the ab initio multiple spawning method to study the nonadiabatic dynamics using the MSPT2 method.

As an application, we studied the role of the 3s Rydberg (Ryd(3s)) state in ethylene. Our result shows that, the population initially excited to the $\pi\pi^*$ state undergoes a $\pi\pi^* \rightarrow \text{Ryd}(3s)$ transition only partly (~20%), in the first 10 fs. The populations on Ryd(3s) state then decays quickly back to a valence state within 50 fs (Fig. 1). On the contrary, when the trajectories were initially excited to the Ryd(3s) state, much slower decay of the excited states were observed (Fig. 2). This indicates that the two reactions proceed through different mechanisms.

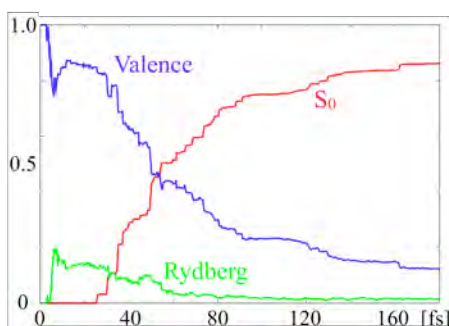


Fig. 1: Change of populations after excitation to $\pi\pi^*$ state

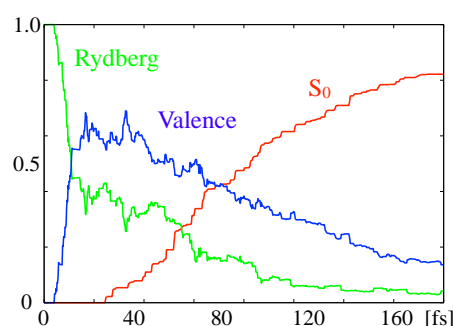


Fig. 2: Change of populations after excitation to Ryd(3s) state

Enhanced Multiple Time-Scale Molecular Dynamics Using Colored Noise

Joseph A. Morrone, Thomas E. Markland, Michele Ceriotti and B. J. Berne

Chemical systems typically involve interactions occurring on many time scales ranging from rapidly varying, but cheap to calculate, bonded interactions to slow, but expensive, long range electrostatics. Multiple time scale methods can be used to exploit this separation in time scales by updating the slow interactions less frequently than the fast interactions, in principle, allowing significant computational savings to be achieved. However, the maximum outer time step which can be obtained is in practice limited by resonances between the slow and fast modes. This poster will highlight our recent work where we have shown that this problem can be alleviated by using a simple colored noise thermostating scheme which selectively targets the high frequency modes in the system. Applications to flexible water and biological systems demonstrate that this allows the use of outer time-steps exceeding 20 fs while still obtaining accurate sampling and with minimal perturbation of the dynamics.

Effect of Jahn-Teller and Spin-Orbit Coupling on X²E Infrared Spectrum of CH₃O

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The alkoxy group of free radicals is one of the most important group of intermediates in atmospheric and combustion reactions. Apart from understanding their role in reaction dynamics, delving into their rovibronic structure is an on-going theoretical and experimental challenge. In this work, we study the vibronic structure of the simplest radical of the alkoxy family, namely the methoxy radical in the ground electronic state, by calculating its infrared spectrum. CH₃O has an unpaired electron mostly centered on oxygen atom, which gives rise to two degenerate electronic configurations (conical intersection) when the molecule belongs to the C_{3v} point group (equilibrium). However, the degeneracy is removed by Jahn-Teller coupling as we displace the molecule along any asymmetric mode of vibration. Spin-Orbit coupling plays an important role as well, since it removes degeneracy at the equilibrium itself and partially quenches Jahn-Teller coupling at displaced geometries, belonging to lower symmetries. Presence of a conical intersection has profound consequences on spectroscopy and vibrational dynamics of the molecule. For instance, the selection rules in calculating the infrared spectrum of the X state involve combining symmetries of vibrational and electronic degrees of freedom and are less straightforward. We calculate a 9-D dipole moment surface for x,y and z components using *ab initio* methods. The components of the vibronic dipole moment operator, obey transformation properties belonging to different symmetry species of the C_{3v} point group and based on group-theoretical arguments, we impose constraints on the allowed terms in the functional form. The arguments are similar to those made in construction of the vibronic Hamiltonian [1]. We construct the dipole moment surface solely using geometries of C_s symmetry, in a diabatic representation, using the two electronic states as diabatic basis. The vibronic states are calculated using a 9-D quartic force field as described in [1], where both Jahn-Teller and spin-orbit coupling are included. The Davidson and Lanczos iterative methods are used to calculate the transitions between the ground vibronic to the higher levels in the infrared spectrum and the calculated transitions are compared to experiment.

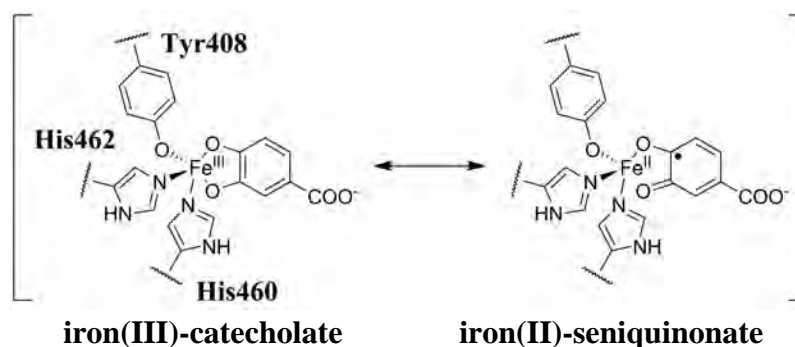
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A CASPT2 Study of Native Iron(III)-dependent Catechol Dioxygenase and its Functional Models: Dioxygen Activation Mechanism and Ligand-to-Metal Charge Transfer Excitation

Naoki Nakatani, Yutaka Hitomi and Shigeyoshi Sakaki

Iron(III)-dependent catechol dioxygenase activates dioxygen molecule to catalyze the aromatic bond cleavage of catechol derivatives. This activation reaction is of considerable interest because in general the high-spin iron(III) center does not react with dioxygen molecule. It is experimentally believed that the key of this reaction is a formation of iron(II)-semiquinonate species as a resonance structure through the ligand-to-metal charge-transfer (LMCT) from the catechol moiety to iron(III) center (Scheme 1). In fact, the LMCT excitation energy deeply relates to the reactivity of this enzyme and its functional models.

Scheme 1



We theoretically investigated the LMCT excitation energy of iron(III)-dependent catechol dioxygenase and its functional models with the CASPT2 level of theory to present theoretical understanding of the relation between the LMCT excitation energy and the reactivity.

Our CASPT2-calculated results agree well with experimental excitation energy. Interestingly, iron(II)-semiquinonate character is little involved in the ground state and we found that the charge transfer directly occurs from the catecholate moiety to the dioxygen molecule in the dioxygen activation process. From detailed analyses, we concluded that the reactivity relates to the LMCT excitation energy through the ionization potential of the catecholate moiety and the iron(III) center lifts the electron affinity of the dioxygen molecule to induce the direct charge transfer from the catecholate moiety to the dioxygen molecule.

Pfaffian Pairing Wavefunctions and Large Jastrow Factors for Strongly Correlated Systems

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The treatment of strongly correlated valence electrons remains one of the major unsolved problems in quantum chemistry. While this challenge has been overcome in some special cases through the density matrix renormalization group, notably in small systems and systems extended along one spatial dimension, accurate descriptions of strong correlation are lacking for arbitrarily large systems in two and three dimensions. We demonstrate that highly flexible many-body Jastrow factors coupled with a Pfaffian pairing wavefunction similar to the antisymmetrized geminal power can accurately describe strong correlation in large two dimensional systems. Regardless of the system's dimension, this wavefunction contains a polynomial amount of information and can be optimized in a polynomial amount of time using highly parallel quantum Monte Carlo algorithms. We discuss the structure of this wavefunction, the novel optimization approach we developed to handle millions of variational parameters, and results for strongly interacting model Hamiltonians and preliminary applications in quantum chemistry.

The Non-Equilibrium Spin-Boson Model: Current, Power Noise, and Fluctuation Relations

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We focus on the non-equilibrium-two-bath spin-boson model, a toy model for examining quantum thermal transport in many-body open systems. We examine the model in two limits: (i) in the strong coupling limit, adopting the NIBA approximation, (ii) in the weak coupling limit, for an unbiased case, using the Redfield approximation. In both cases we demonstrate the validity of the steady-state heat fluctuation relation. Furthermore, using the generating function, analytical expressions for the heat current and its power noise are obtained in the Markovian and non-Markovian limits.

Chemistry in Electrostatic Environments: Anion Stabilization

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We present a unified finite-difference quantum mechanics in an electrostatic environment approach for determining electronic structure properties. A key feature of our method is the use of arbitrary electrostatic kernels that include non-trivial effects such as screening and gate potentials. Excess charge stabilization of molecules in metallic environments is of particular importance for fields such as molecular electronics and surface chemistry. We study the energetics of benzene and its anion between two metallic plates. We observe that orientational effects are important in small inter-plate separation. This leads to benzene oriented perpendicular to the gates being more stable than the parallel case due to induced dipole effects. We find that the benzene anion, known for being unstable in the gas-phase, is stabilized by the plates at zero bias and an inter-plate distance of 21 Å. We also observe the effect of benzene under a voltage bias generated by the plates; under a negative bias, the anion becomes destabilized. We use the electron localization function to analyze the changes in electron density due to the bias. These findings suggest that image effects such as those present in nanoscale devices, are able to stabilize excess charge and should be important to consider when modeling molecular transport junctions and charge-transfer effects at the nanoscale [1].

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Properties of Ordered Structure of Ionic Liquids in a Bucky-Gel-Based Actuator

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Upon mixing with ionic liquids (ILs) based on imidazolium ions, carbon nanotubes (CNTs) form physical gels, called “bucky gels”[1]. Their versatile properties, such as flexibility and electrical conductivity, can be adopted as electrochemical devices, for example, sensors, capacitors, and actuators. While experimental studies have given a conjecture that π - π stacking between the imidazole rings of the cations of ILs plays an important role on the gel formation, the molecular-level understanding of their structure has not been provided. In this study, we present a structure of bucky gel composed of CNTs in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF₄) obtained via molecular dynamics simulations. It is found that imidazole rings of cations in the first solvation shell are mainly parallel to the CNT surface, indicating π - π stacking between the CNT and [EMIM]⁺ ions, which is consistent with our previous study[2]. Molecular ordering of ILs between the CNTs is also investigated with respect to the radial direction in variation with separation of the CNTs, i.e., concentration of the CNTs. Further, we explore the structural properties of bucky-gel-based electrochemical actuators [3] by modeling with two oppositely charged CNTs in [EMIM]BF₄ to show that bending of the actuator is induced by reorganization of ions around the CNTs.

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Hydration at the Nanoscale: Quantifying the Role of Water in Protein Interactions

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Quantifying the interactions of non-polar solutes in water (i.e., the hydrophobic effect) is essential for developing a molecular understanding of several biological self-assembly processes, including protein folding, membrane formation and molecular recognition. Macroscopically, the hydrophobicity of a surface is characterized by a droplet contact angle. However, this approach is not feasible at the nanoscale (e.g. to characterize a protein surface), and molecular measures of hydrophobicity are needed. We have developed a novel technique that uses biased molecular dynamics simulations to show that water density fluctuations (and not the average local density), specifically, the ease with which water can be displaced from the vicinity of a surface, is a quantitative measure of its hydrophobicity. Using this fluctuations-based measure, we demonstrate how the properties of water at interfaces influence the binding, folding, and dynamics of flexible molecules in interfacial environments. Since biomolecules are heterogeneous, rugged and occur in crowded cellular environments, we investigate how the hydrophobicity of a surface changes due to chemical patterning, curvature and proximity to other surfaces. Our results highlight the shortcomings of hydrophobicity-scale based methods and provide a computational tool for mapping the hydrophobicity of protein surfaces, with relevance to developing predictive strategies for biomolecular binding, recognition, and aggregation. Our results also have implications on a range of applications where solvation phenomena play an important role, ranging from the design of nanoporous materials for water purification, to protein interaction networks and drug discovery.

Calculating Anharmonic Vibrational States Without All the Pain: Progress Towards Moving Away from Pre-Existing PESs and Huge Basis Sets

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The accurate calculation of the vibrational states of highly fluxional molecules and clusters is complicated by both the need to first obtain the full-dimensional potential energy surface (PES) and the necessity of using a very large basis to fully capture the large anharmonicities. Although commonly exploited as a way around this problem, grid-based methodologies scale exponentially with system size while reduced dimensional approaches are highly system dependent, both in terms of the details of their application and in terms of their suitability. We report here our recent efforts to develop an algorithm capable of accurately calculating anharmonic vibrational energies, even for very floppy systems, without first obtaining a PES and using only a handful of basis functions per degree of freedom. More specifically, the potential energy and G-matrix elements are calculated via Monte Carlo integration over a set of points obtained from an importance sampling of configuration space based on the harmonic ground state wavefunction, a procedure that dramatically reduces the number of required electronic structure evaluations. The Hamiltonian matrix is then constructed using an evolving basis which, with each iteration, captures the effect of building \mathbf{H} from an ever-expanding basis despite the fact that the actual dimensionality of \mathbf{H} is fixed throughout the calculation. This latter property of the algorithm also greatly reduces the size of basis needed for the calculation relative to more traditional variational approaches. The results obtained from the application of our method to several test systems will be reported, along with its observed convergence properties.

A Time-Dependent Density Functional Theory Analysis of the Charge Transfer Properties in Dye-Functionalized Silsesquioxanes

Heidi Phillips, Shaohui Zheng, Alex Hyla, Eitan Geva and Barry Dunietz

The application of nano-devices in light harvesting and storage is a major focus in solar energy research. Specifically, there is interest in identifying molecular systems that possess enhanced absorption and charge transfer properties. Recently, large red-shifts in the emission spectra of chromophore-functionalized silsesquioxane nano-cages suggest photo-induced charge transfer.

In order to understand the charge transfer processes in such systems, *ab initio* electronic structure calculations (DFT/TDDFT) can be used to obtain the excited state energies. However, the limitations of DFT/TDDFT in describing charge transfer states are well known and can be addressed by use of range-separated hybrid functionals.

In this study, the excited state energies of chromophore-functionalized silsesquioxane were calculated using the B3LYP hybrid functional and the BNL range-separated hybrid functional. The absorption energies were compared to experimentally measured values. Inter-chromophore charge transfer excitations were also identified using both functionals. Implicit and explicit solvent models have been applied in order to compare calculated charge transfer energies to experimentally observed Stokes-shifted emission.

DFT Study of Cp₂Th and Cp₂U Catalysts for Hydrodenitrogenation (HDN) and Hydrodesulfurization (HDS)

Aaron W. Pierpont, Richard L. Martin, Enrique R. Batista, Jaqueline Kiplinger and Nicholas E. Travia

As our nation's supply of fossil fuels dwindles over the next century low-quality "dirty" petroleum feedstocks (from tar sands, oil shales, etc.) will serve as a bridge to alternative energy sources. However, these feedstocks typically contain N/S-containing hydrocarbons as impurities, and must be "cleaned" prior to burning via hydrodenitrogenation (HDN) and hydrodesulfurization (HDS). Despite the importance of these industrial processes, they have several drawbacks (ex. poor selectivity, harsh conditions required, etc.) that have encouraged inorganic chemists to develop better catalysts for each process.

In this project, DFT calculations are performed for the actinide systems Cp₂Th and Cp₂U. Experimentally, these systems exhibit a rich chemistry towards heterocyclic substrates (C-H/C-N activation, ring-opening, dearomatization). Computations will be performed to predict how well this chemistry extends to pyridine and thiophene ring opening, as these have been some of the most difficult contaminants to process via conventional HDN/HDS routes.

Thermodynamic Analysis of Nanoporous Membrane Separation Processes

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Reverse-osmosis desalination is becoming an increasingly viable solution to the lack of potable water which plagues a large portion of the world's population, causing death, disease, and international tension. Membrane desalination attempts to introduce a chemical potential gradient through decoupling solute and solvent transport in pressure-gradient induced volume flows. While the thermodynamic equilibrium cost of seawater desalination is fixed at $RT=0.7 \text{ kW-hr/m}^3 / (\text{Osm/L})$, carrying out the process at exactly the osmotic pressure is impossible due to back-flow from leaky membranes. Therefore, a theory capable of addressing the physical mechanisms responsible for irreversible entropy production is required to gain an understanding of energy loss in real devices. We show how nonequilibrium transport relations from local equilibrium theories connect to molecular simulations and are able to address the additional, Darcy's law fluid flow resistance. We present a novel, standardized flow resistance measure based on this theory and show biomimetic, self-assembled nanoporous materials recently developed at Sandia that achieve a three-fold decrease in excess energy consumption (compared to commercially available membranes) for brackish water desalination. Our theoretical results provide a strong framework from which to understand energy consumption beyond the local equilibrium approximation for coupled transport processes.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Finite-Temperature Auxiliary-Field Quantum Monte Carlo for Bose-Fermi Mixtures

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Rapid advances in ultracold atomic physics have paved the way toward experimentally emulating many of the fundamental models of condensed matter physics with fine control for the very first time. Past success emulating the superfluid-Mott insulator transition in Bose gases and Fermi pressure in Fermi gases has stimulated interest in Bose-Fermi mixtures. Analytical work suggests that Bose-Fermi mixtures possess a rich phase diagram, yet many of the phase diagram's most interesting features are beyond the reach of current computational techniques, which are limited to one-dimensional explorations. In this work, we outline how Bose-Fermi mixtures may be studied free of the sign and phase problems using finite-temperature auxiliary-field quantum Monte Carlo with the phaseless and constrained-path approximations. One of our key results is the derivation of a single-particle bosonic Green's function that enables simulation of bosonic systems in any number of dimensions, at any physical value of the temperature and chemical potential. We benchmark our Monte Carlo results against exact results for multidimensional bosonic systems and furthermore demonstrate the novelty of our method by studying the formation of "Bose-Fermi molecules."

The Balance between Efficiency and Accuracy of Representations of Molecular Interaction in Hydrogen-Bonded Systems

Gregory Schenter, Garold Murdachaew and Christopher Mundy

I will present efforts to better understand the balance between efficiency and accuracy of representations of molecular interaction in hydrogen-bonded systems. We have been developing a method to enhance the accuracy of efficient electronic structure methods such as density functional theory (DFT) and semi-empirical neglect of diatomic differential overlap (NDDO). We do this by supplementing the charge density with multipole polarization sources located on atomic sites with formation energies that are quadratic in their magnitude. This charge density is determined self-consistently (Self Consistent Polarization, SCP) through screened Coulomb interaction with the electronic structure system. Developments in the parameterization and applications of this approach will be discussed.

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A New Multi-Reference Configuration Interaction (MRCI) Method Which Efficiently Handles Large Active Spaces, Long Configuration Expansions, and Many Closed-Shell Orbitals

K. R. Shamasundar, Gerald Knizia and Hans-Joachim Werner

We present a new internally contracted MRCI method which, at the same time, efficiently handles large active spaces, long configuration expansions, and many inactive orbitals. This is achieved by applying the Celani-Werner internal contraction scheme [J. Chem. Phys. 112, 5546 (2000)] to the MRCI method and then using in-house domain specific computer algebra systems to semi-automatically derive, simplify, and implement the resulting enormously complex equation systems. The new MRCI program treats inactive orbitals as efficiently as a single-reference program and thus opens up the possibility to perform high-accuracy investigations for much larger molecules than before. We demonstrate the method with some applications to di-copper-oxygen complexes with different ligands, to spin-state-splittings of metallocenes, and other calculations which previously were infeasible.

Understanding Protein Energy and Interaction Landscapes Using a Relative Entropy Coarse-Graining Framework

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The development of accurate coarse-grained molecular models is central to many efforts in soft-condensed matter, materials, and biophysics that seek to understand large length and time scale properties. We recently proposed a broad new statistical-mechanical framework for such problems based the relative entropy, a phase-space functional measuring the “information” lost upon coarse graining and hence the (inverse) fitness of a given coarse-grained model [1]. We suggest that minimization of the relative entropy provides a universal variational principle for coarse-graining.

Here, we show how this approach provides a quantitative and systematic approach to the development of coarse-grained models of proteins. We first describe the development of stable, efficient, and robust numerical coarse-graining algorithms based upon relative entropy minimization [2]. In particular, these approaches are able to locate optimal models in very high dimensional parameter spaces. We show that the relative entropy framework offers exquisite control over coarse-graining errors, and is able to generate coarse peptide models whose structural correlations and folding behavior are in excellent agreement with more expensive all-atom simulations. We also demonstrate how these models are well-suited to large-scale simulations of peptide self-assembly.

Second, we show that the relative entropy approach provides an a priori prediction of coarse-graining errors (i.e., errors in the properties predicted by coarse-grained models), and gives a systematic strategy for designing coarse-grained models [3]. We use this theory to develop simple analytical energy-landscape models of protein folding. Here, an ensemble of predicted structures for a large protein is projected onto a coarse-grained funnel landscape, and the relative entropy predicts which structure is nearest to the true native structure. We present results on several model protein systems and from a recent community-wide blind structure prediction competition.

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Nonadiabatic Path Sampling

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Charge transfer mechanisms control prominent reactions in all branches of chemistry, physics, and biology. The prevalence of such reactions provides great motivation to further develop the methods by which they are studied computationally. Transition Path Sampling (TPS) has expanded the scope of reaction rate theory by eliminating the need to locate transition states and define reaction coordinates. Nonadiabatic Path Sampling (NAPS) seeks to generalize the TPS formalism to accommodate reactions involving multiple electronic and vibrational energy states. The molecular dynamics with quantum transitions (MDQT) surface-hopping algorithm equips us with the means to integrate such transitions into TPS. NAPS will enhance our understanding of charge transfer reactions in the condensed phase by allowing reactions to access excited electronic and vibrational states, model reaction timescales currently beyond the scope of molecular simulation, and identify specific molecular motions that influence or control the mechanisms and kinetics of charge transfer reactions. Once developed, this method will be validated against known model problems which have been studied extensively with a variety of other computational techniques.

Comparing the Hertz-Schlüter and Boltzmann-Planck Definitions of Microcanonical Entropy for Small Systems

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Thermodynamic quantities calculated using different ensembles may differ by terms of order N^{-1} . This poster examines differences between the canonical (constant NVT) and microcanonical (constant NVE) ensembles using two different definitions of the microcanonical partition function. The standard microcanonical definition of entropy due to Boltzmann and Planck is the logarithm of the number of states within an energy shell ($E, E+\Delta E$). This *surface entropy* is consistent with Shannon's information theory, but yields an entropy proportional to $N-1$ rather than N (not extensive, an error of order N^{-1}). A competing definition of the partition function due to P. Hertz (1910) and A. Schlüter (1948) is the number of states below the energy shell (*volume entropy*). This definition gives a size extensive entropy and agrees better with canonical ensemble calculations; however, the entropy is no longer an ensemble average of $-\rho \ln \rho$. The pluses and minuses in this century-long controversy will be highlighted, as well as misinterpretations that have appeared in the literature. I favor using the size-extensive Hertz-Schlüter entropy when finite system simulations are to be compared with experiments or with canonical ensemble results. For small systems, the disagreements are much smaller.

DNA Mechanics and Mechanical Modeling

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Experimental studies suggest that the mechanical properties of a given DNA sequence dictate its nucleosome positioning propensity, and therefore may play an important role in gene regulation (1). In particular, the nucleosome affinity of DNA sequences is higher in sequences that have dinucleotides (AA, TT, TA) repeated every 10 bp(2), while other sequences (Poly (dA:dT)(3) are known to disfavor binding of DNA to histone proteins. The mechanical properties of DNA have been of interest to modelers for decade but past work has not considered properties needed to describe 10 bp periodicities and other similar structures(4). With this mind, using 10 bp DNA sequences that have been modeled with Jumna (5) have been studied employing ab initio quantum mechanics (HF, MP2, DFT). One concern from this work is whether Amber and Charmm force fields are reliable for mechanical property studies. Preliminary results indicate that the hybrid meta-GGA family of functionals provide significant improvements over traditional density functionals in describing noncovalent interactions without deteriorating the results for hydrogen bonding in the systems. Some other aspects of the functionals with respect to computation of interaction, basis set dependence and important geometric parameters were considered and will be presented. All calculations were performed using QChem(6).

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Solvent Penetration in Photoactive Yellow Protein R52Q Mutant: A Theoretical Study

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An R52Q mutation of photoactive yellow protein creates a cavity mimicking an intermediate state in the wild-type. This mutation, of a positively charged arginine to a neutral glutamine, does not affect the spectral tuning of photoactive yellow protein. Contradicting explanations for this phenomenon suggest either water or hydronium occupation in the cavity. To solve this controversy, we have performed 3D-RISM calculations on the mutant structure examining the solvation structure. Our results show that while there is a high probability of hydronium in the cavity compared to bulk, there is still a relatively low occupation when considering realistic concentrations. Thus our findings suggest that while the cavity is clearly accessible by hydronium, it is mostly occupied by water molecules. We expect high-resolution neutron crystallographic analysis of the mutant to confirm our prediction.

Diabatization for Proton-Coupled Electron Transfer Reactions

A. Sirjoosingh and S. Hammes-Schiffer

The identification of charge-localized diabatic states is a crucial step in nonadiabatic proton-coupled electron transfer (PCET) theories. In PCET reactions, the proton transfer often induces electron transfer, and the transferring proton coordinate can be used as a tool to construct diabatic states. We implemented an adiabatic-to-diabatic transformation scheme to calculate diabatic electronic states for PCET reactions. In the case of one-dimensional proton motion, these states exactly satisfy the diabaticity condition of possessing zero first-derivative couplings along the proton transfer coordinate. We applied this methodology to the prototypical PCET self-exchange reaction between phenol and the phenoxyl radical. The resulting diabatic electronic states exhibit physically meaningful localized charge distributions that are relatively invariant with respect to the proton motion. Proton vibrational states can be calculated for each diabatic electronic state using grid-based methods. The electron-proton vibronic states relevant to nonadiabatic PCET reactions are products of a diabatic electronic state and an associated proton vibrational state. These vibronic states can be used within the framework of nonadiabatic PCET theories to calculate rate constants and kinetic isotope effects of experimentally studied systems.

Initial Steps in Methanol Steam Reforming on PdZn and ZnO Surfaces

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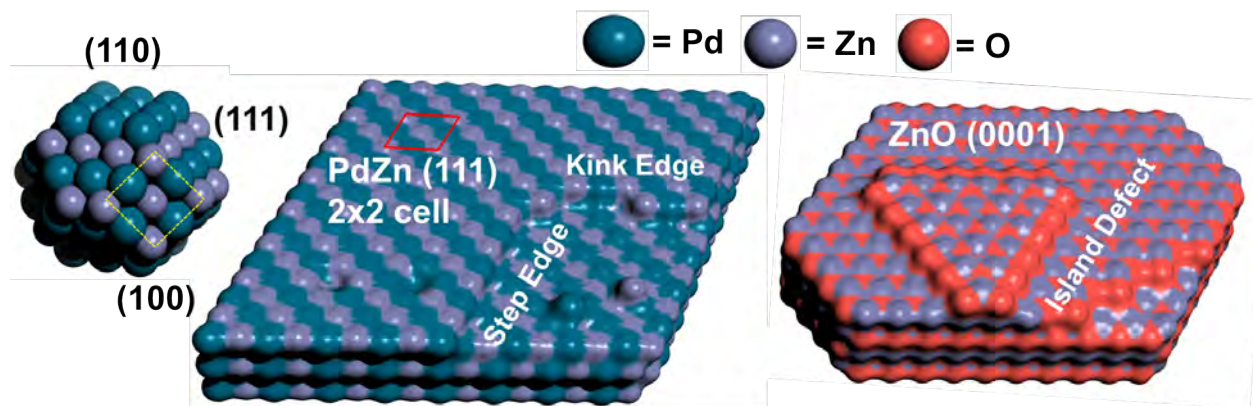
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Recent experiments suggested that PdZn alloy on ZnO support is a very active and selective catalyst for methanol steam reforming (MSR). To gain insight into MSR mechanism on this catalyst, plane-wave density functional theory calculations were carried out on the initial steps of MSR on both PdZn and ZnO surfaces. Our calculations indicate that the dissociation of both methanol and water is highly activated on flat surfaces of PdZn such as (111) and (100), while the dissociation barriers can be lowered significantly by surface defects, represented here by the (221), (110), and (321) faces of PdZn. The corresponding processes on the polar Zn-terminated ZnO(0001) surfaces are found to have low or null barriers. Implications of these results for both MSR and low temperature mechanisms are discussed.



Mechanistic Quantum Mechanical Study of Hydrogen-Evolving Catalyst $\text{Co}(\text{dmgBF}_2)_2$

Brian Solis and Sharon Hammes-Schiffer

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The promising catalyst $\text{Co}(\text{dmgBF}_2)_2$ (dmg = dimethylglyoxime) has been shown to electrochemically reduce H^+ through a Co-hydride intermediate in acetonitrile. The hydrogen-evolving elementary step can proceed monometallically, involving a single cobalt catalyst, or bimetallically, requiring two protonated catalysts. Density functional theory calculations of $\text{Co}(\text{dmgBF}_2)_2$ in several oxidation and protonation states, with and without acetonitrile ligands, were performed at the B3P86/6-311+G** level. The use of an isodesmic cycle was employed to ascertain relative free energies between pairs of states in the calculation of reduction potentials and pK_a s. Inner-sphere and outer-sphere reorganization energies were calculated with electronic structure methods and dielectric continuum solvent models. Free energy barriers for the electron transfer steps were determined using Marcus theory. These calculations provided insight into the relative probabilities of monometallic and bimetallic pathways as well as sequential and concerted electron-proton transfer mechanisms.

Mechanistic Study of the 2-Thienylmethyl + HO₂ Reaction

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The ab initio potential energy surface for the reaction of the 2-thienylmethyl radical with the HO₂ radical has been presented. Sixteen product channels associated with either addition/elimination or direct hydrogen abstraction mechanisms were revealed for the first time. The association paths of the two radical reactants are barrierless with the formation of three adducts, as distinguished by the radical centers of the 2-thienylmethyl radical. The addition is exothermic by 37 ~ 55 kcal mol⁻¹ and these excess energies are available to promote further decomposition or rearrangement of the adducts, leading to the nascent products such as H, OH, H₂O, CH₂O. The results suggest that the formation of OH via a simple OO bond fission is the dominant channel in view of the barriers height and exothermicity. Moreover, direct hydrogen abstraction may take place on both the singlet and triplet surfaces, forming molecular oxygen. The barrier for singlet abstraction is approximately 10 kcal/mol while that for triplet is essentially zero with respect to the initial reactants. The mechanisms are compared to the analogous 2-furanylmethyl + HO₂ and benzyl + HO₂ reactions.

High-Level Quantum Mechanical Studies of the Singlet Carbenes HCXH (X=O, S, Se)

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Carbenes of the form HCXH (X=O, S, Se) exist in both *cis* and *trans* isomer forms in the ground singlet state, as well as in a skewed configuration in the lowest triplet state. Hydroxycarbene, HCOH, has received a great deal of recent experimental and computational scrutiny as an isomer of formaldehyde, H₂CO, and is thought to play a role in H₂CO photochemistry and in the reaction of C atom with H₂O. Thiohydroxycarbene, HCSH, has been previously suggested as a possible product formed in the atmosphere of Jupiter as a result of the collision of Comet Shoemaker-Levy 9 with the planet in 1994. HCSH is also involved as an intermediate in the reaction of C atom with H₂S. To the best of our knowledge, there have been no experimental or computational studies of the structure or properties of the selenium-containing analog, HCSeH. In this work, computational studies at the CCSD(T)/cc-pVTZ level and higher have been performed in order to elucidate key features of the potential energy surfaces of HCXH. In particular, the barrier for conversion from *cis*- to *trans*-¹HCXH has been computed for each of the analogs, and results have been compared with previous computational results where available. The results indicate that the barriers to rotation are rather high for what would nominally be considered rotation about a C-X single bond, ranging from 26-38 kcal/mol depending upon the level of theory. The origin of the barriers to rotation for conversion between the *cis* and *trans* forms of HCXH has been explored in detail using a variety of techniques.

The Langevin Hull - NPT Dynamics Without Periodic Boundary Conditions

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We present a new method for carrying out isobaric-isothermal (NPT) molecular dynamics on non-periodic systems. Previous affine-transform methods for sampling this ensemble cannot be used without periodic boundary conditions, and have known problems when used on heterogeneous systems with different compressibilities. Our new method, the Langevin Hull, avoids both of these issues. The method uses an external pressure and temperature bath interacting with the surface atoms defined by the convex hull of the particle positions. We have tested the method on gold nanoparticles as well as SPC/E water clusters and heterogeneous mixtures. The Langevin Hull does not cause appreciable dewetting at the surface of the SPC/E water clusters. Experimentally determined features in the pressure dependence of the O-O radial distribution function are also preserved in the water clusters. The Langevin Hull has also been applied to gold nanoparticles embedded in SPC/E water and shows promise for applications to other heterogeneous biomolecular systems.

Proton Transport in [NiFe]-Hydrogenase

Isaiah Sumner and Gregory A. Voth

Hydrogenases belong to a family of biological redox enzymes that are known to reversibly catalyze the reduction of protons and the oxidation of molecular hydrogen. Current interest in these enzymes is focused on understanding the catalysis in order to develop hydrogen-based fuel cells and photosynthetic cells for hydrogen production. A key step in the hydrogenase catalytic cycle and the focus of this work is proton transport (PT) to and from the active site. We study the (PT) mechanism of the enzyme using molecular dynamics simulations of the full protein and we allow the excess proton to reactively transfer via the Grotthuss mechanism using the multi-state empirical valence bond (MS-EVB) method. We find several pathways connecting the bulk and the active site that suggest participation by several protonatable residues. We also calculate free energy surfaces to differentiate the pathways.

Three-Body Simulation Model for Water and the Vibrational Sum-Frequency Spectrum of the Water Surface

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Water potentials that assume a pairwise additive form have been very successful in reproducing many properties of liquid water at ambient conditions and are therefore widely used.^{1,2} However, these models begin to fail at non-standard conditions and especially in heterogeneous environments such as the liquid/vapor interface. This has led to the parameterization of a simulation model that explicitly includes three-body interactions.³ Herein, we reparameterize this model, fitting to a wider range of experimental quantities. The robustness of the model was determined by comparing many other properties to experimental data, including the vibrational sum-frequency (VSF) spectrum of the liquid/vapor interface. VSF spectroscopy is a surface sensitive technique that can provide orientational information about the structure of an interface. While pairwise additive potentials fail to reproduce quantitatively the VSF spectrum, our three-body model is in excellent agreement with experimental data. These results emphasize the importance of many-body interactions in simulations, especially in heterogeneous environments.

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Simulation of Reactive and Non-Reactive Rate Processes in Liquid Solutions: Vibrational Energy Relaxation of Liquid HCl and DCl and Solvent Effects on the Dynamics of 1,3,5-cis-Hexatriene Isomerization

Surma Talapatra and Eitan Geva

Understanding the rates and mechanisms of energy transfer in condensed phase chemical reactions is a crucial problem in chemical dynamics. Study of vibrational energy relaxation of molecules in solutions is important in this context as it provides direct information about solute-solvent energy exchange process. Vibrational energy relaxation (VER) of liquid HCl is interesting because of high quantum effects in the process. Calculating the rate of VER in systems like HCl using molecular dynamic (MD) simulations requires one to account for quantum effects in the simulation that can be far more expensive and complicated than classical MD simulations. We have calculated the rate of VER for a system of neat liquid HCl and DCl at 188K and have estimated the possible mechanism of energy relaxation using linearized semi-classical (LSC) quantum simulation methods. The LSC method gives the rate of VER in terms of the Fourier transform, at the transition frequency, of the autocorrelation function of the fluctuating force exerted by the bath modes on the relaxing mode. The results indicate that the LSC method can predict VER rate constant fairly accurately. In addition, by looking into the various contributions to the autocorrelation function of force, we could conclude that the Coulombic contribution to the force plays a central role in VER. The possible reason, as we have hypothesized, is quantum delocalization that brings the H closer amplifying the Coulombic repulsion.

The ring opening reaction of 1,3-cyclohexadiene (CHD) is important because it is analogous to the reaction of 7-dehydrocholesterol to form pre-vitamin-D. Previous experimental studies on the multistep reaction reveal that the ring opening of CHD is followed by the isomerization of cis-1,3,5-hexatriene (Zt-HT) from cis to trans conformer (cZt-HT to tZt-HT). Detailed experimental studies on this last step reveal that the rate of isomerization in different alcohols and alkanes do not follow the η^{-1} dependence predicted by Kramers theory. We have investigated the isomerization reaction using molecular dynamics simulations to develop a molecular level explanation for this interesting trend of reaction rates in alcohols and alkanes. Using a number of alcohols (methanol, ethanol, propanol, butanol) and a number of alkanes (cyclohexane, n-hexane, n-heptane, cycloheptane) as solvents, the isomerization reaction rate constant was calculated at various temperatures ranging from 280K to 320K. The rate constant was calculated using the reactive flux correlation function and transition state theory. In order to explain the results seen, thermodynamic properties of the reaction were calculated, including changes in free energy, entropy and enthalpy as the cZt-HT goes to the transition state. The results reveal that the rate of isomerization in alcohols is indeed slower than in alkanes. The calculated entropy changes indicate that the faster reaction rates in alkanes can be attributed to the structural difference of the alkane solvents from alcohol solvents.

Time-Dependent Importance Sampling Method for Semiclassical Time Correlation Functions

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We developed a new time-dependent importance sampling Monte Carlo method for the evaluation of time correlation functions using the full semiclassical (SC) initial value representation (IVR) methodology. This new sampling method takes both initial and final phase points of a trajectory into account, while at the same time avoiding being trapped into a local region in phase space, therefore only those phase points which contribute to the time correlation function significantly are being sampled more efficiently. Numerical results for some benchmark systems demonstrate the high efficiency of this method. This new sampling method, in combination with recent developments for the SC-IVR theory in our group and others, makes it possible to understand molecular quantum dynamics in realistic large systems to an unprecedented level.

Proton Transfer in Malonaldehyde Monitored with Infrared Spectroscopy of C-D Labels

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Malonaldehyde is a useful model compound for understanding proton transfer in biological contexts. Vibrational spectroscopy is an ideal tool for monitoring proton transfer events because of its superb subpicosecond time resolution. However, such experiments would require a suitable vibrational probe. Density functional theory (DFT) calculations in the gas phase have shown that deuteration of one of the carbonyl/enol carbon atoms in malonaldehyde provides $\sim 150 \text{ cm}^{-1}$ of sensitivity to the proton transfer event. Mixed quantum mechanics/molecular mechanics simulations employing the self-consistent-charge density functional tight binding (SCC-DFTB) method of malonaldehyde in aqueous solution are the starting point to computing linear and two-dimensional infrared line shapes in solution.

GVVPT2 and MRCISD Molecular Gradients

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Generalized van Vleck perturbation theory (GVVPT) is an ab initio method that generates accurate potential energy surfaces for molecules that possess complicated multiconfigurational electronic structures. Using a Lagrangian based approach, codes were developed that analytically calculate molecular gradients using the GVVPT2 and MRCISD electronic structure methods. The mathematical background and benchmark calculations are presented in this poster. Using the same formalism, codes can be developed to calculate GVVPT2 and MRCISD nonadiabatic coupling coefficients.

Stochastic Coupled Cluster Theory

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Instead of treating Coupled Cluster theory in the full space of amplitudes, it is possible to discretize the equations and represent the solutions as a series of particles moving in excitation space according to simple rules whose time-average represents the Coupled Cluster Amplitudes and thus the wavefunction[1]. This dramatically reduces the storage requirements of the theory, and slashes the complexity of the code (with arbitrary levels of truncation in excitation space) to some very simple stochastic steps. An additional advantage of this simplicity is a great ease of parallelization of the calculations over many compute nodes with relatively little communication. We show the general theory and demonstrate the usefulness of this method over deterministic Coupled Cluster theory with some calculations on atoms and small molecules, as well as applications to some extended systems.

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Computational Refinement of the Syn-Anti Interconversion Potential for Cyclopropane Carboxaldehyde

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Dian, *et al.* [1] have reported highly accurate measurements of the dynamic rotational spectrum of cyclopropyl carboxaldehyde. Their analysis rests in part on the values of the relative energies of the *syn* and *anti* isomers and the energy barrier opposing interconversion. Their B3LYP/6-31+G(d,p) calculations place the *anti* isomer 46 cm⁻¹ more stable than the *syn* isomer and estimate the barrier as 2200 cm⁻¹. CBS-4 values [2] are 85 and 1910 cm⁻¹ respectively. These values enter into the phenomenological Bloch equations that describe the isomerization under irradiation and also into the RRKM estimates of the rate for isomerization induced by irradiation of the 2822 cm⁻¹ vibrational absorption of the *syn* isomer. The reported rate of *syn* to *anti* interconversion (3.08×10^9 sec⁻¹) and its reverse (2.52×10^9 sec⁻¹), are about 16× smaller than the RRKM value, 9.09×10^{10} sec⁻¹. The authors attribute this discrepancy to a shortcoming in the assumption of RRKM of purely statistical distribution of energy among modes, that is to say instantaneous energy exchange among degrees of freedom.

Since the height of the barrier and the vibrational frequencies are so central to the predictions of the RRKM model – a modest increase in the height of the barrier would depress the estimated rate significantly – we have embarked on a study of the *syn* – *anti* interconversion potential surface. Our best results so far place the energy difference in the range 70 to 93 cm⁻¹ and the barrier in the range 2048 to 2260 cm⁻¹. We will report the results of our efforts to model the details of the cyclopropyl carboxaldehyde vibrational-rotational spectrum in the regions relevant to the experiments by Dian *et al.*

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Use of Many-Body Methods to Calculate Accurate Electron Binding Energies of $(\text{H}_2\text{O})_n^-$ Clusters

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The calculation of accurate electron binding energies of $(\text{H}_2\text{O})_n^-$ clusters is a challenging theoretical problem as it requires large basis sets and treatment of high-order correlation effects. In this work, the equation-of-motion coupled-cluster-singles-doubles (EOM-CCSD) and second-order algebraic diagrammatic correction (ADC(2)) methods, are employed to calculate the electron binding energies (EBEs) of $(\text{H}_2\text{O})_n^-$ clusters as large as $n=24$. These results are used to test the Drude model approach that was developed in our group. Overall the Drude model does an excellent job at reproducing the *ab initio* results, although for a subset of the clusters it considerably overbinds the excess electron. The reasons for this discrepancy are explored.

Continuous Constant pH Molecular Dynamics in Explicit Solvent

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A computational tool that offers accurate pKa values and atomically detailed knowledge of protonation-coupled conformational dynamics is valuable for elucidating mechanisms of energy transduction processes in biology such as enzyme catalysis, electron transfer, as well as proton and drug transport. Towards this goal we present a new technique of embedding continuous constant pH molecular dynamics within an explicit-solvent representation. In this technique we make use of the efficiency of the Generalized-Born (GB) implicit-solvent model for estimating the free energy of protein solvation, while propagating conformational dynamics using the more accurate explicit-solvent model. Also, we employ a pH-based replica exchange scheme to significantly enhance both protonation and conformational state sampling. Benchmark data of five proteins including HP36, NTL9, BBL, HEWL, and SNase yield an average absolute deviation of 0.53 and a root mean squared deviation of 0.74 from experimental data. This level of accuracy is obtained with 1-ns simulations per replica. Detailed analysis reveals that explicit-solvent sampling provides increased accuracy relative to the previous GB-based method by preserving the native structure, providing a more realistic description of conformational flexibility of the hydrophobic cluster, and correctly modeling solvent mediated ion-pair interactions. Thus, we anticipate that the new technique will emerge as a practical tool to capture ionization equilibria while enabling an intimate view of ionization-coupled conformational dynamics that is difficult to delineate with experimental techniques alone.

A Third Generation Distributed Point Polarizable Water Model

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We introduce here a new generation of distributed point polarizable model (DPP3) for water. The DPP3 model employs six point charge sites, comprised of three atomic sites, two lone-pair sites, and an M-site, with charge penetration incorporated by use of the damping expressions of Freitag et al.. The DPP3 model also employs out-of-plane lone-pair dipole polarizable sites at the same locations as the out-of-plane charges. It is found that the introduction of the lone-pair polarizable sites greatly improves description of the polarization anisotropy of water monomer. The charge-transfer and dispersion terms are kept the same as in DPP2 model, and the exchange-repulsion interaction is fitted to the difference between the sum of electrostatics, polarization, charge-transfer, and dispersion contributions and the CCSD(T) interaction energies for a series of structures for the water dimer.

Development and Validation of Transferable Amide I Frequency Maps for Peptides

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The amide I vibrational mode has widely been used to probe the structure and dynamics of proteins by infrared (IR) spectroscopy. Experimental IR spectra of proteins in the amide I region are usually broad and featureless due to strong overlap of vibrational bands produced by protein backbone and side chains. To understand these IR spectra at the molecular level, we have developed transferable frequency maps for both the backbone and side chain absorptions. The backbone and side chain maps connect the amide I vibrational frequencies with local electric fields, and were developed from experimental spectra of N-methylacetamide (NMA) and acetamide, respectively, in various solvents. To evaluate their performances, we applied the maps, along with proper coupling schemes, to peptides with well-defined α -helical and β -hairpin secondary structures. We further applied them to rat and human islet amyloid polypeptide. The theoretical FTIR line shapes are in good agreement with experiments. The maps are potentially applicable to membrane proteins and thus can further our understanding of protein structure and dynamics in heterogeneous environments.

Application of MR-ccCA to s-block Compounds

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The correlation consistent Composite Approach (ccCA)^{1,2} has proven its utility on hundreds of molecules to date in the prediction of “chemically accurate” (within 1 kcal/mol, on average, of reliable experiment) energetic properties (e.g. enthalpies of formation, binding energies, ionization energies, electronic energies). The ccCA method, like other composite approaches, uses a combination of less quantitative, less computationally demanding calculations to reproduce energies that would be obtained using a much more sophisticated, albeit, more costly method. For ccCA, the targeted method for replication is CCSD(T, full)-DK/aug-cc-pCV ∞ Z-DK.

While ccCA has worked well for species that can be well described with a single-reference wavefunction^{1,2}, in recent work, our group has developed a multi-reference composite approach, MR-ccCA, which is suitable for strongly correlated systems that require a multi-reference wavefunction, such as bond breaking and bond breaking.³ In the current work, we have considered the utility of MR-ccCA on s-block molecules, systems for which a multi-reference wavefunction description can be critical.

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Energy Transfer in Inelastic and Reactive Collisions using Algebraic Methods

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We calculate transition probabilities between discrete states of a diatomic molecule induced by an incoming atom. Our prototype Hamiltonian is constructed treating the translation classically and the internal variables quantum mechanically. The corresponding equations of motion are coupled quasi-classically. We present applications to a canonical ensemble of initial conditions as well as results for the time dependence of transition probabilities for different initial and final states. In the reactive case we are driven to using natural coordinates i.e. the reaction coordinate and the transverse vibrational coordinate.

Density Functional Resonance Theory for Metastable Anions

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Density Functional Resonance Theory (DFRT) is a complex-scaled version of ground-state Density Functional Theory (DFT) that allows one to calculate the resonance energies and lifetimes of metastable anions. The exact energy and lifetime of the lowest-energy resonance is encoded into a complex “density” that can be obtained via complex-coordinate scaling. This complex density is used as the primary variable in a DFRT calculation just as the ground-state density would be used as the primary variable in a DFT calculation. As in DFT, there exists a mapping of the N electron interacting system to a Kohn-Sham system of N non-interacting particles in DFRT. This mapping facilitates self-consistent calculations with an initial guess for the complex density. Model systems are used to test the reliability and practicality of this theory. Since these model systems can be solved exactly and with approximate functionals, one can observe the individual contributions from Hartree, exchange, and correlation to the complex Kohn-Sham potential.

Benchmarking Different Approaches to Address the Charge-Transfer Problem in time-Dependent Density Functional Theory

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The investigation of photoactive compounds still poses a challenge to theoretical chemistry, as currently, there exists no *ab initio* technique that can be readily applied to investigate the photoexcitation dynamics in large molecules. This is particular the case if one also has to account for the chemical environment. The most promising and widely used method in this context is TDDFT, but unfortunately, there remain a number of qualitative deficiencies, which need to be addressed before TDDFT can be used routinely as a tool to model photochemical problems.

In this contribution we address the inability of TDDFT to accurately describe excited states with charge-transfer character. We compare the applicability of long-range corrected hybrid functionals (see e.g. [1]) and an *overlap-dependent shift* (ODS) as proposed by Dreuw *et al.* [2] to describe charge-transfer excitations in a small dipeptide and (phenylacetylene) dendrimers; the latter class of systems is of particular interest as they can be used to build artificial photosynthetic devices.

Unfortunately the ODS depends on the choice of orbitals which are used in the description of a given photoexcitation. Hence, we use a very compact description in terms of natural transition orbitals (NTOs) [3] and recompute the ODS in this orbital basis. Moreover, the NTOs simplify the analysis of the character of a given excited state if there is no dominant configuration in the list of excitation amplitudes. In the NTO description, a maximal correspondence between the excited “particle” and the empty “hole” can be obtained, without changing the physically relevant quantity, the transition density.

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Efficient Energy Transfer in Light-Harvesting Systems, I: Optimal Temperature, Reorganization Energy and Spatial-Temporal Correlations

Jianlan Wu, Fan Liu, Young Shen, Jianshu Cao and Robert J. Silbey

Understanding the mechanisms of efficient and robust energy transfer in light-harvesting systems provides new insights for the optimal design of artificial systems. In this paper, we use the Fenna–Matthews–Olson (FMO) protein complex and phycocyanin 645 (PC 645) to explore the general dependence on physical parameters that help maximize the efficiency and maintain its stability. With the Haken–Strobl model, the maximal energy transfer efficiency (ETE) is achieved under an intermediate optimal value of dephasing rate. To avoid the infinite temperature assumption in the Haken–Strobl model and the failure of the Redfield equation in predicting the Forster rate behavior, we use the generalized Bloch–Redfield (GBR) equation approach to correctly describe dissipative exciton dynamics, and we find that maximal ETE can be achieved under various physical conditions, including temperature, reorganization energy and spatial–temporal correlations in noise. We also identify regimes of reorganization energy where the ETE changes monotonically with temperature or spatial correlation and therefore cannot be optimized with respect to these two variables.

The BMW-MARTINI Force Field: A Coarse-Grained Model for Membrane-Peptide Simulations with Proper Electrostatics

Zhe Wu, Qiang Cui and Arun Yethiraj

We proposed a new coarse-grained (CG) model designed for molecular dynamics simulations with peptides and membrane bilayer. While it largely follows the same topology and parameterization strategy as the MARTINI force field for lipids and amino acids, the new model is based on our recently developed CG water model (Big Multipole Water, BMW, *J. Phys. Chem. B* 2010, 114, 10524-10529). Following a careful parameterization, the BMW-MARTINI force field not only reproduces many fundamental membrane properties, but also yields much improved energetics compared to MARTINI for interactions between charged amino acids with lipid membranes. As a result, stable attachment of cationic peptides (e.g., Arg₈) is observed on the membrane surface as shown in experiments, in contrast to predictions with MARTINI. With a proper description of electrostatics, the BMW-MARTINI model is particularly valuable for the analysis of interactions between highly charged peptides or protein motifs with lipid membrane, which is crucial to the study of antimicrobial peptides, cell penetration peptides and other proteins/peptides involved in the remodeling of biomembranes.

Molecular Insight at the Organic Donor/Acceptor Interface

Shane R. Yost and Troy Van Voorhis

Organic photovoltaics and organic light emitting diodes both rely on an organic-organic interface for their device performance. The difference in the HOMO and LUMO levels of the donor and acceptor molecules creates the driving force for the excited state to break up into a charge transfer state, but this and other processes at the interface are poorly understood on a molecular level. We use a combined quantum mechanical/molecular mechanical technique to model the organic-organic interface. Using this model we are able to study the changes in molecular properties as one approaches the interface, and the effects of thermal/crystalline disorder. We find significant band bending at the interface and a large distribution in binding energy based on relative molecular orientation and thermal fluctuations. These combined effects suggest a reason for the observed barrierless separation of charge transfer states in organic photovoltaics.

SAPT-Based Polarizable Force Field for Modeling Flue Gas Separation in Zeolitic Frameworks

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Zeolitic Imidazolate Frameworks (ZIF) are a family of metal organic frameworks composed of Zn^{2+} and various substituted imidazolate linker groups. These micro-porous materials show excellent promise for gas adsorption and separation applications, especially for CO_2 separation from flue gas, demonstrating good CO_2 absorption capacity and selectivity, tunable and reversible adsorption, and thermal and solvent stability. In this work, we develop a reliable, transferable, and physically motivated force field for ZIFs and gas molecules to conduct both molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations. A cluster model for ZIFs is constructed to reproduce bulk electron density. Subsequent symmetry-adapted perturbation theory (SAPT) calculations are used to calculate total interaction energies between the cluster model and gas molecules, as well as the energy decompositions. Each term from SAPT calculations, including exchange repulsion, dispersion, electrostatic and polarization, is then fitted by physical meaningful functional forms, leading to an accurate ab initio based force field. Associated polarizable gas molecule models (CO_2 , N_2) are also developed in a consistent style. Pure gas properties, especially phase behavior, are benchmarked to ensure the validity of the models and the fitting scheme. This force field is expected to yield robust, transferable results for functionalized ZIFs, and yield physical insights into the ZIF-gas interactions as compared to traditional “generic” models.

Interpretation of the Photoelectron Spectra of Superalkali Species: Li_3O and Li_3O^-

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After several failed attempts to attribute all of the observed peaks in the experimental spectrum to anionic species, neutral species were considered assuming a sequential two-photon absorption mechanism. We find that only two of the six observed peaks can be attributed to photodetachments and that all other observed features can be assigned to ionizations from the ground and excited states of the neutral. Furthermore we have examined the influence of vibrational displacements on the location of the observed peaks. We find that this effect is smaller than 0.05 eV and therefore must be considered as negligible. Nuclear distributions other than three lithium atoms surrounding the oxygen are not likely to be stable. The second electron detachment energy from the anion's triplet C_{2v} state, located close to the D_{3h} minimum, or higher excited states of the neutral species may explain the 1.2 eV peak, but it appears more likely that the triplet state is present in the experimental sample.

Dynamical Mean-Field Theory from a Quantum Chemical Perspective

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We investigate the dynamical mean-field theory (DMFT) from a quantum chemical perspective. Dynamical mean-field theory offers a formalism to extend quantum chemical methods for finite systems to infinite periodic problems within a local correlation approximation. In addition, quantum chemical techniques can be used to construct new *ab-initio* Hamiltonians and impurity solvers for DMFT.

Here, we explore some ways in which these things may be achieved. First, we present an informal overview of dynamical mean-field theory to connect to quantum chemical language. Next, we describe an implementation of dynamical mean-field theory where we start from an *ab-initio* Hartree-Fock Hamiltonian that avoids double counting issues present in many applications of DMFT. We then explore the use of the configuration interaction hierarchy in DMFT as an approximate solver for the impurity problem. We also investigate some numerical issues of convergence within DMFT. Our studies are carried out in the context of the cubic hydrogen model, a simple but challenging test for correlation methods. Finally, we finish with some conclusions for future directions.

Modeling Photoexcited Reactions Of Simple Molecules In Solution

Jing Zhang and D. F. Coker

Photoexcited iodine in rare gas systems offer a paradigm for understanding excited state condensed phase chemistry. Solvent induced nonadiabaticity plays an important role in the dynamics of these systems and modifies electronic structure by introducing off-diagonal coupling elements to our electronic Hamiltonian matrix. A semi-empirical electronic structure method, diatomics-in-molecules (DIM), together with its extension designed for ionic systems, diatomics-in-ionic-systems (DIIS), is applied to dynamical studies of photoexcited iodine in Ar and Xe rare gas systems. Mixed quantum-classical molecular dynamics implemented using a surface hopping algorithm is employed in a trajectory study which successfully describes the nonadiabatic nature of these systems.

We looked into the photoexcited I₂ in its manifold of covalent states in solid Ar, focusing on the cage-bound but otherwise dissociative potential curves. Cage motions disturb the electronic structure and influence the coupling between electronic states to a large extent due to the large-scale intramolecular motion associated with stretching of the I₂ bond resulting from double-photon excitation. Dynamical simulation with a surface hopping algorithm describes the cage-bound state photoexcitation dynamics which has only been simulated by other groups using classical methods that do not allow for nonadiabatic electronic transitions. A characteristic recursion time of the cage-bound state motion is found through our simulation which matches the experimental results, and our simulated pump-probe signals successfully reproduce the experimental spectrum.

Dynamics of Methionine Ligand Rebinding to heme Fe in Cytochrome C

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Geminate recombination of the methionine ligand to heme Fe in ferrous cytochrome c protein following photodissociation displays a rich kinetics that must be interpreted in terms of dynamics on the underlying complex energy landscape. The classical CHARMM force field in the heme pocket has been extended by incorporating *ab initio* potential energy surface calculations, representing the ground singlet state and quintet state, associated with Fe-Methionine bond breaking and rebinding. An algorithm based on Landau-Zener nonadiabatic transition theory has been employed to model the electronic surface hopping between two spin states during the process of ligand dissociation and recombination. Multiple conformational substates of the dissociated methionine ligand are found to be essential to the interpretation of the “fast” and “slow” rebinding time scales observed in experimental studies. The reaction system may be understood in terms of a two-dimensional reaction coordinate distinctly separated from the coupled bath of surrounding protein and solvent degrees of freedom. Reaction rate theory (including transition state theory and Kramers theory) is employed to analyze the properties of the reaction dynamics and provide a detailed understanding of the dependence of the rebinding kinetics on protein sequence, solvation, and temperature. Insights into the reaction dynamics provided by this study lead to suggestions for future experiments to further probe the role of dynamic heterogeneity in the kinetics of ligand-protein binding.

Neck Linker Docking and Interaction with Microtubule Control Kinesin Movement

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Conventional kinesin is a molecular motor that consumes ATP, to transport cellular cargo towards microtubule plus end. Two motor heads of kinesin walk along a microtubule in a hand-over-hand manner, and can take hundreds consecutive steps before detaching from the microtubule. During a single step, the trailing head (TH) detaches from its initial binding site, passes the microtubule-bound leading head, and attaches to the target binding site 16 nm away. It is not clear how the TH selects the target binding site among eight accessible sites. How does the TH recognize and bind to it? These questions are answered using molecular simulations. We show that a conformational change in the leading head named neck linker docking prevents stable binding between the TH and seven other binding sites. The 16 nm step to the target occurs in three distinct stages: the first ~ 5 nm is driven by neck linker docking, the next ~ 7 nm is due to diffusion, and the last ~ 4 nm requires interaction between the TH and the target binding site. Movement of the TH in the first and third stage is directed whereas in the second stage is driven by biased diffusion.

Proton Conduction Across Grain Boundaries Based on (131) Surfaces of Y Doped BaZrO₃

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Fuel cells show great potential as alternative energy sources. Y doped BaZrO₃, among other conductive perovskites, has shown excellent proton conductivity and stability. Since transmission of protons is rate-determining step in fuel cell generation of electricity, it is crucial to study the proton conduction mechanism. Earlier studies in our group have revealed these mechanisms in single perfect crystals of Y doped BaZrO₃ and other perovskites.² However, crystals are usually not perfectly formed and often contain grain boundaries. The lowest energy surfaces of BaZrO₃ are O terminated (311), O terminated (131) and Zr-O terminated (100) surfaces.¹ This poster will consider grain boundaries based on the (131) surface. Possible boundaries will be optimized using DFT with the PBE functional. Proton binding sites and transition states will be found on the most thermodynamically favorable grains. Using the binding sites and transition states as a conduction map of the system, probable conduction pathways through the grain boundary will be found using graph theory methods.^{Error!}

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²M. A. Gomez, M. Chunduru, L. Chigwesh, L Foster, S. J. Fensin, K. M. Fletcher, and L. E. Fernandez, "The effect of yttrium dopant on the proton conduction pathways of BaZrO₃, a cubic perovskite," *J. Chem. Phys* 132 (2010) 214709; M. A. Gomez, M. Chunduru, L. Chigweshe, K. M. Fletcher, "The effect of dopant at the Zr site on the proton conduction pathways of SrZrO₃: An orthorhombic perovskite," *J. Chem. Phys.* 133 (2010) 064701.

³S. Islam, talk at the 2010 Solid State Protonic Conductors 15; H. J. Zhou, Y. B. Mao, and S. S. Wong, "Shape control and spectroscopy of crystalline BaZrO₃ perovskite particles," *J. Mat. Chem.* 17 (2007) 1707-1713.

Flexibility and Preorganization in Binding Between the p53 Tumor Suppressor and the MDM2 Oncoprotein

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It is popularly believed that preorganized ligands bind to their receptors faster than highly flexible ligands, but recent evidence suggests that certain flexible ligands may have an inherent kinetic advantage in binding, particularly intrinsically disordered ligands. We have used atomically-detailed molecular dynamics simulations in conjunction with the weighted ensemble path sampling technique to investigate the binding of one such intrinsically disordered peptide — a 13-residue fragment of the N-terminal activation domain of the p53 tumor suppressor — to the oncoprotein MDM2. We compare the pathways, rates, and thermodynamics of association and dissociation between MDM2 and (1) the native, fully flexible form of the p53 peptide fragment; (2) the native p53 fragment constrained to resemble the bound state; and (3) the P27S mutant of the p53 peptide fragment, which resembles the bound state and has a higher rate of association to MDM2 than the wild type peptide fragment. This allows us to discuss whether preorganization (or lack thereof) confers a kinetic advantage on protein-protein associations.