Princeton University

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November 19, 2006

U.S. Department of Energy
Office of Science
Chicago Office
9800 South Cass Avenue
Argonne, Illinois 60439

RE: Final Report for DOE Grant. No. DE-FG02-05ER15656

Dear Ms. Edwards:

This letter and attachments are meant to serve as a final report for DOE Grant No. DE-FG02-05ER15656, entitled "2005 American Conference on Theoretical Chemistry." The attachments are pdf files containing the conference booklet, poster abstracts, corrections/additions sheet handed out at the conference, and a contacts list of all attendees. A complimentary paper copy of the conference booklet and CD were sent to Dr. Richard Hilderbrandt, my program officer in DOE-BES, in August 2005.

The conference, held 16-21 July 2005 at UCLA, was a great success, according to feedback given to me by participants, many of whom said that it was the best conference they had ever attended. Over 250 people registered for the conference, from all over the country and from many countries abroad as well. The vast majority of the attendees were students and postdocs, who gave 198 poster presentations, in addition to listening to 26 invited talks by outstanding scholars from a diverse set of backgrounds, including chemistry, physics, mathematics, chemical engineering, materials science, and biochemistry.

The DOE contribution of $10,000, which was completely spent, was critical to the success of the conference. Thanks very much again for your support of this triannual event.

Final Certification. I certify that funds provided by the Department of Energy under grant DE-FG02-05ER15656 were expended in accordance with the provisions of the grant and that required scientific reports have been delivered (via this letter and attachments) to the Department of Energy.

Sincerely,

Emily A. Carter
2005 ACTC Conference Chair
Professor of Mechanical and Aerospace Engineering and Applied and Computational Mathematics; Associated Faculty in PICSciE, Chemistry, Chemical Engineering, and PRISM

The following organizations and people who gave generously of their time and money to sponsor the conference and to provide funds for student scholarships are gratefully acknowledged:

Conference Sponsors

- Department of Energy, Basic Energy Sciences (Dr. Richard Hilderbrandt)
- Office of Naval Research (Dr. Peter Schmidt)
- Air Force Office of Scientific Research (Dr. Michael R. Berman)
- Army Research Office (Dr. Peter Reynolds)
- Lawrence Livermore National Laboratory (Drs. Tomas de la Rubia, Laurence Fried, and Christine Wu)
- Los Alamos National Laboratory (Dr. Antonio Redondo)
- National Institute of Standards and Technology (Dr. Anne Chaka)
- Pacific Northwest National Laboratory (Drs. Douglas Ray and Bruce Garrett)

Scholarship Sponsors

- IBM, Life Sciences (Dr. William Swope and Prof. Kenneth Jordan)
- Hewlett-Packard Laboratories (Dr. R. Stanley Williams)
- MOL-CAS 6, Lund University (Prof. Bjorn Roos)
- Institute for Pure and Applied Mathematics (Profs. Mark Green and Stan Osher)
- THEOCHEM - An Elsevier Journal (Dr. Andrew Gent)
- Q-Chem, Inc. (Prof. Martin Head-Gordon)

History of the ACTC

The ACTC has a legacy going back more than half a century. Below we acknowledge the Chairs of the ACTC since its inception:

R. S. Mulliken, 1951	A. Moscowitz, 1970	W. A. Goddard III, 1990
F. A. Matsen, 1955	D. W. Smith, 1972	J. C. Tully, 1993
R. G. Parr, 1959	C. W. Kern, 1975	J. Simons, 1996
H. Shull, 1962	E. R. Davidson, 1978	E. J. Heller, 1999
M. Karplus, 1964	J. C. Light, 1981	K. D. Jordan, 2002
W. T. Simpson, 1966	H. F. Schaefer III, 1984	E. A. Carter, 2005
J. A. Pople, 1968	D. G. Truhlar, 1987	M. A. Ratner, 2008

Welcome to the 2005 American Conference on Theoretical Chemistry! I sincerely hope you leave this conference having enjoyed the vibrant city of Los Angeles, UCLA, and the scientific presentations and discussions you will hear and participate in this week. I am very pleased that the conference has participants from all over the world, from Asia to Europe to Africa to Australia and North and South America, as well as from a variety of disciplines, from the traditional sub-fields of theoretical chemistry (electronic structure, dynamics, and statistical mechanics) to chemical and biological engineering, biochemistry, condensed matter physics, mechanical engineering, materials science, and applied mathematics. Theoretical chemistry impacts and in turn is enriched by all of these disciplines. Our field continues to be vibrant and exciting, in large part because of the cross-fertilization of ideas catalyzed by conferences such as the ACTC.

This conference could not have come to pass without the help of many people. Thanks go first and foremost to my former assistant at UCLA, Marian Olivas, without whom I would have drowned in the details of organizing this conference. Second, thanks go to the staff of the Department of Chemistry and Biochemistry at UCLA (especially Gina King) for their help with the financial side of the conference. Third, thanks go to my scientific advisory committee, who helped me select the speakers: Bill Gelbart, Eric Heller, Mark Ratner, Peter Rossky, and especially Ken Jordan, who also gave me excellent advice from his tour as ACTC Chair. Lastly, thanks go to my assistant at Princeton, Laurie Hebditch, the UCLA Conference Services folks, and Adam Kohm of meetingassistant.com for their copious help in the last months of preparation before the conference.

Before closing, let me call your attention to two reports recently issued by the U. S. National Science Foundation that concern theory. Of particular interest may be this spring's NSF Mathematical and Physical Sciences (MPS) Theory Workshop Report, which can be found at http://www.nsf.gov/attachments/100811/public/MPSTheory_FinalReport-04-02-2005.pdf. It is the outcome of an NSF workshop assessing theoretical research throughout the MPS Directorate. Second, the NSF Chemistry Division's Cyber Workshop Report may also impact theoretical chemists significantly. It can be found at http://bioeng.berkeley.edu/faculty/cyber_workshop/.

Now, onward to the conference! I believe we have ahead of us a very stimulating and diverse set of talks and poster presentations, covering biochemistry, dynamics, electron transfer, electronic structure, materials, multiscale modeling, nano/bio, and statistical mechanics. Note that each of the two poster sessions are organized by the subject areas above, where all first authors with last names starting with A-K present in Poster Session I and those with last names starting with L-Z present in Poster Session II. Lastly, I encourage everyone to participate in the discussions after each talk. We all learn from hearing each other's points of view, so raise your hand, speak up, and enjoy!

> With my best wishes,
> Emily A. Carter, 2005 ACTC Chair

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2005 American Conference on Theoretical Chemistry

Saturday July 16, 2005		
4:00 - 7:00 PM	Registration	De Neve Plaza Room
7:00 - 9:00 PM	Informal Reception	

Sunday, July 17, 2005		
7:30 - 8:30 AM	Breakfast	De Neve Residential Restaurant
8:30 AM	Welcome	Northwest Campus Auditorium
	Chair: Emily A. Carter	
8:45 - 10:15 AM	Session I-A: Dynamics	
	Session Chair: Bruce Garrett	
8:45 AM	Speaker: John Tully	
9:30 AM	Speaker: Todd Martinez	
10:15 AM	Coffee Break	Northwest Campus Auditorium Patio
10:45 AM - 12:15 PM	Session I-B: Biochemistry	Northwest Campus Auditorium
	Session Chair: Doug Tobias	
10:45 AM	Speaker: Bruce Tidor	
11:30 AM	Speaker: Steven Schwartz	
12:15 - 2:00 PM	Lunch	De Neve Residential Restaurant
2:00 - 5:00 PM	*Poster Session ONE*	Bradley International Room
5:00 - 7:30 PM	Free Time/Dinner	(on your own)
7:30 - 9:00 PM	Session II: Multiscale Modeling	Northwest Campus Auditorium
	Session Chair: Nasr Ghoniem	
7:30 PM	Speaker: Karsten Reuter	
8:15 PM	Speaker: Juan de Pablo	

Monday, July 18, 2005		
7:30 - 8:30 AM	Breakfast	De Neve Residential Restaurant
8:30 - 10:00 AM	Session III-A: Statistical Mechanics	Northwest Campus Auditorium
	Session Chair: Chi Mak	
8:30 AM	Speaker: Philip Geissler	
9:15 AM	Speaker: Peter Rossky	
10:00 AM	Coffee Break	Northwest Campus Auditorium Patio
10:30 AM - 12:00 PM	Session III-B: Nano/Bio	Northwest Campus Auditorium
	Session Chair: George Schatz	
10:30 AM	Speaker: Sophia Yaliraki	
11:15 AM	Speaker: Dmitrii Makarov	
12:00 - 1:30 PM	Lunch	De Neve Residential Restaurant
1:30 - 4:30 PM	*Poster Session TWO*	Bradley International Room
5:00 - 6:30 PM	Session IV: Electronic Structure	Northwest Campus Auditorium
	Session Chair: Anna Krylov	
5:00 PM	Speaker: Andrew Rappe	
5:45 PM	Speaker: Martin Head-Gordon	
6:30 PM	Dinner and evening on your own	(Discount tickets for attractions available)

Tuesday, July 19, 2005		
7:30 - 8:30 AM	Breakfast	De Neve Residential Restaurant
8:30 - 10:00 AM	Session V-A: Materials	Northwest Campus Auditorium
	Session Chair: Russel Caflisch	
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10:00 AM	Coffee Break	Northwest Campus Auditorium Patio
10:30 AM - 12:00 PM	Session V-B: Dynamics	Northwest Campus Auditorium
	Session Chair: Craig Martens	
10:30 AM	Speaker: Ronnie Kosloff	
11:15 AM	Speaker: Sharon Hammes-Schiffer	
12:00 - 1:00 PM	Lunch	De Neve Residential Restaurant
1:00 - 5:00 PM	Optional Trip to Getty Museum	
5:00 - 7:30 PM	Dinner	(on your own)
7:30 - 9:00 PM	Session VI: Electronic Structure/Dynamics	Northwest Campus Auditorium
	Session Chair: Antonio Redondo	
7:30 PM	Speaker: Ken Jordan	
8:15 PM	Speaker: Troy van Voorhis	

Wednesday, July 20, 2005		
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8:30 - 10:00 AM	Session VII-A: Multiscale Modeling	Northwest Campus Auditorium
	Session Chair: Stan Osher	
8:30 AM	Speaker: David Srolovitz	
9:15 AM	Speaker: Weinan E	
10:00 AM	Coffee Break	Northwest Campus Auditorium Patio
10:30 AM - 12:00 PM	Session VII-B: Biochemistry	Northwest Campus Auditorium
	Session Chair: Bill Gelbart	
10:30 AM	Speaker: Andrea Liu	
11:15 AM	Speaker: Chris Lee	
12:00-1:00 PM	Lunch	De Neve Residential Restaurant
1:00-2:00 PM	Business Meeting	TBA
	(Sr. Scientists welcome to attend)	
2:00 - 6:00 PM	Free Time	
6:00 - 7:00 PM	Wine Reception	Covel Commons Grand Horizon Room
7:00 - 9:00 PM	Conference Banquet	

Thursday, July 21, 2005		
7:30 - 9:00 AM	Breakfast (check out of rooms)	De Neve Residential Restaurant
9:00 - 10:30 AM	Session VIII-A: Statistical Mechanics	Northwest Campus Auditorium
	Session Chair: Ben Schwartz	
9:00 AM	Speaker: Zhen-Gang Wang	
9:45 AM	Speaker: Katja Lindenberg	
10:30 AM	Coffee Break	Northwest Campus Auditorium Patio
11:00 AM - 12:30 PM	Session VIII-B: Electron Transfer	Northwest Campus Auditorium
	Session Chair: Alexei Stuchebrukhov	
11:00 AM	Speaker: Bob Cave	
11:45 AM	Speaker: Mark Ratner	
12:30 - 2:00 PM	Final Lunch	De Neve Residential Restaurant

SELF-CONSISTENCY AND DETAILED BALANCE IN MIXED QUANTUM-CLASSICAL DYNAMICS

Priya Parandekar and John Tully
Departments of Chemistry, Physics, and Applied Physics
Yale University

Classical molecular dynamics is frequently inadequate for simulating processes such as proton or electron transfer, for which inclusion of quantum mechanical degrees of freedom may be essential. Mixed quantum-classical (MQC) dynamics is the strategy for separating the system into quantum and classical subsystems, and propagating each subject to the influence of the other. This is straightforward when the adiabatic approximation is valid. In situations where non-adiabatic transitions are important, however, proper treatment of the 'quantum back-reaction' - the influence of quantum transitions on the classical forces - has been difficult to achieve. Moreover, most MQC formulations do not satisfy detailed balance, with the consequence that they approach an incorrect final state. This talk will outline these issues and contrast the behavior of the leading MQC approaches: classical path, Ehrenfest and surface hopping.

AB INITIO MOLECULAR DYNAMICS
BEYOND THE BORN-OPPENHEIMER APPROXIMATION

Todd J. Martinez

Department of Chemistry
University of Illinois, Urbana, IL 61801

The ab initio multiple spawning (AIMS) method has been developed for fist principles molecular dynamics including quantum effects such as tunneling and population transfer between electronic states (breakdown of the Born-Oppenheimer approximation). We discuss recent developments and benchmarks in the multiple spawning dynamics method which underlies AIMS. We show that accurate results can be obtained in models with hundreds of dimensions, even when the underlying electronic basis is not the 'natural' adiabatic representation. We provide an overview of recent applications ranging from photoinduced cis-trans isomerization to excited state intramolecular proton transfer (ESIPT) and photodynamics of DNA bases. The role of simultaneous degeneracies of three electronic states in ESIPT is discussed. Extensions of AIMS to condensed phase systems have been pursued using a combination of reparameterized multireference semiempirical (RPMRSE) methods and hybrid quantum mechanical/molecular mechanical (QM/MM) representations of potential energy surfaces. We show that the RPMRSE methods can approach the accuracy of multi-reference perturbation theories such as CASPT2 with limited reparameterization effort. Several representative examples of nonadiabatic dynamics in solution and protein environments using this "nearly" AIMS method are presented and the influence of the solvent/protein environment on excited state reactivity is assessed.

FROM MOLECULAR TO NETWORK ENGINEERING

Bruce Tidor

*MIT Biological Engineering Division and
Department of Electrical Engineering and Computer Science*

Biological outcomes are frequently the result of complex networks of interacting components, often at the level of cells or higher levels of organization. Pharmaceutical intervention generally takes place at the molecular level. The effective integration of systems biology with molecular therapeutics requires bridging molecular understanding and engineering with experiments and theoretical models that capture the behavior of networks and systems. Crossing this bridge in one direction could potentially allow propagating changes at the molecular level to the resultant changes in network outcome; crossing this bridge in the other direction could lead to engineering new molecules that produce desired network behavior. We report studies of cytokine-receptor signaling and trafficking networks. Overall cytokine potency is a combination of lifetime in the body and specific signaling properties. Molecular-level models, calculations, and experiments have been combined with cellular-level studies of network behavior to understand better complexity in these pathways and to engineer rationally altered network function through modification to molecular properties.

DYNAMICS OF CHEMICAL REACTIONS IN ENZYMES:
A REALLY COMPLEX CONDENSED PHASE OR A QUANTUM MACHINE?

Steven D. Schwartz

Seaver Center for Bioinformatics and
Departments of Biophysics and Biochemistry
Albert Einstein College of Medicine, Yeshiva University

This seminar will describe ongoing research on the nature of chemical reactions in enzymes. Classical dogma teaches that enzymes lower the free energy barrier to reaction. We will investigate if this is necessarily the only mechanism used to speed reaction. We study if there are other ways to catalyze chemical reactions employed in biological systems, and how protein dynamics can couple to chemical reaction. The work proceeds through quantum theories of chemical reaction in condensed phase to studies of how the symmetry of coupled vibrational modes differentially affect reaction dynamics. Specific examples will include a variety of condensed phase chemical reactions (liquid and crystalline) and a variety of enzymatically catalyzed reactions including the reactions of alcohol dehydrogenase, lactate dehydrogenase, and purine nucleoside phosphorylase. We will show how classically, optimal types of coupled modes are identified, and how such modes may be selected by evolution. If time permits we will briefly mention new approaches to semiclassical dynamics in such complex systems.
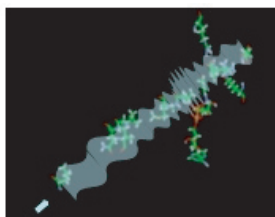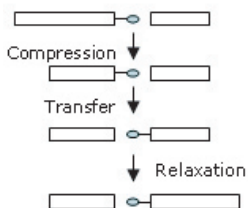
THE STEADY-STATE OF HETEROGENEOUS CATALYSIS, STUDIED WITH FIRST-PRINCIPLES STATISTICAL MECHANICS

Karsten Reuter

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin, Germany

First-principles electronic structure theory calculations have become an increasingly important tool for the predictive modeling of materials properties at the atomistic level. In order to reach technically relevant length and time scales a link with concepts from statistical mechanics and thermodynamics has now to be found. I will sketch corresponding multi-scale modeling attempts for the field of heterogeneous catalysis, concentrating particularly on the relevance of treating the surrounding gas phase, as well as the statistical interplay of the manifold of elementary processes at a catalyst surface.

The effect of a high-pressure gas phase can be especially important in oxidation catalysis over late transition metals, where the O-rich environment may lead to oxide formation at the surface of the catalyst. Using first-principles kinetic Monte-Carlo (kMC) simulations of the CO oxidation reaction over RuO2(110) as an example for such an oxidized surface, strong kinetic effects on the surface configurations actuating catalysis are discerned. High turn-over frequencies in excellent agreement with experimental data are obtained under gas phase conditions where the system is close to a surface phase transition. The resulting phase coexistence at the surface enables specific reaction mechanisms that do not operate at other temperature and pressure conditions including ultra-high vacuum.

MULTISCALE MODELING OF COMPLEX FLUIDS FAR FROM EQUILIBRIUM

Juan J. de Pablo, Orlando Guzman, Juan P. Hernandez,
Michael D. Graham
Department of Chemical and Biological Engineering
University of Wisconsin-Madison

The aim of this talk is to illustrate some of the issues that arise in the modeling of complex fluids, at equilibrium and far from equilibrium, over multiple time and length scales. This is done in the context of two examples. The first considers the structure and dynamics of liquid-crystal based biosensors. Molecular simulations are used to elucidate the nature of defects that arise around nanoparticles suspended in a nematic fluid. The information generated by such simulations is then used in mesoscopic models of defect dynamics to investigate the behavior of many-particle biosensors. The second example considers the relaxation of macromolecules in micro and nanofluidic flows. In this case, the solvent is represented by a fluctuating continuum, but the macromolecule is described at the scale of tens of nanometers, thereby providing insights into how hydrodynamic interactions influence the structure and dynamics of macromolecules in such flows. In both the liquid-crystal and DNA cases, the results of simulations compare favorably with experimental data, serving to validate our proposed multiscale modeling approaches.

COLLECTIVE REORGANIZATION IN NETWORKS OF SEMIFLEXIBLE POLYMERS

Phillip L. Geissler and Sander Pronk
Department of Chemistry
University of California, Berkeley and Physical Biosciences Division
Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Polymer segments much shorter than a persistence length do not respond appreciably to moderate external stresses. Cross-linked networks of such segments, however, oppose shear and compression in unexpected and highly nonlinear ways. We have devised and simulated a reduced computational model for such networks, with the eventual aim of exploring viscoelastic properties of living cells. In our approach thermal undulations of short filaments are integrated out. Concerted motions of multiple filaments are captured through reorganization of the nodes connecting them. This model allows explicit investigation of physical effects neglected in linear, athermal, and mean field theories. I will present results for elastic response, percolation rigidity, and growth of networks out of equilibrium.

PRACTICAL APPROACHES TO CONDENSED PHASE QUANTUM DYNAMICS EXPLOITING QUANTUM DECOHERENCE

Peter J. Rossky
Institute for Theoretical Chemistry
University of Texas at Austin

The computationally convenient description of the quantum mechanical dynamics of electronic systems and of light nuclei in condensed phases is an important goal for the accurate atomistic representation of chemical, biochemical, and materials processes. In electronic systems, the rate of decay of an excited state is influenced by the coherence among the amplitudes for the initial state and the component decay channels. For a species in a condensed phase, the dynamics of the bath can strongly dissipate this coherence and thus modify the rate of electronic evolution. For nuclear dynamics, the coherence between alternative nuclear paths has a parallel significance, and interaction with the surroundings has a similar dissipating effect.

Practical approaches to simulation of these cases will be described which only require evaluation of the classical molecular dynamics of nuclei. The evolution of electronic excited states and the description of the dynamics of light nuclei, including the dissipative role of the environment, will be illustrated in practical cases, including electronic excited state relaxation in solution and in isolated large molecules, and motion in neat liquid para-H_2, He(4), and water.

WHAT CAN GLOBAL OPTIMISATION AND COARSE-GRAINING REVEAL ABOUT SELF-ASSEMBLING SYSTEMS?

Sophia N. Yaliraki
Department of Chemistry
Imperial College, London

The description of biological self-assembling systems often requires a large number of degrees of freedom. Exploring their energy landscape is an important but computationally demanding task. We apply a new methodology that identifies global or local minima of interest without sampling or exhaustive searching. Rather, it relies on a relaxation of the interactions of interest to a sum of squares convex function that can be solved in polynomial time by exploiting computationally efficient semidefinite programming methods. Another advantage of the method is that the level of any approximation is controllable and hence known. We will apply the method to model problems and discuss how it can be used to guide coarse-graining to few but relevant degrees of freedom in protein-protein and lipid-lipid interactions. The role of geometrical anisotropy in the dynamics will be highlighted.

UNFOLDING PROTEINS WITH MECHANICAL FORCES: PUSHING, PULLING AND SQUEEZING MOLECULES USING COMPUTER SIMULATIONS

Dmitrii E. Makarov

Department of Chemistry and Biochemistry
University of Texas at Austin

Proteins that perform "load bearing" functions in living organisms are often unique materials that display a combination of strength and toughness unmatched by any artificial materials. Their unique mechanical properties are believed to be related to the ability of certain protein domains to resist unfolding by mechanical forces. Mechanical pulling has also been implicated as the mechanism by which proteins are denatured and translocated to enable their subsequent degradation by ATP dependent proteases. In this talk, I will report on our group's theoretical and computational studies of protein domains under mechanical tension. I will describe our recent studies of the "topological optimization problem", which have identified protein folds with topology that leads to maximum mechanical resistance. I will further describe the topography of the free energy landscape as probed by mechanical pulling studies and compare the mechanisms of chemical/thermal denaturation, mechanical unfolding, and translocation-induced unfolding. Finally, I will propose a theoretical interpretation of the recent experiments, in which refolding trajectories of proteins were monitored by using single molecule force clamp spectroscopy.

MOLECULAR STRUCTURE, VIBRATIONAL FREQUENCIES, AND ANHARMONICITIES IN ELECTRONIC QUANTUM MONTE CARLO

Myung Won Lee[1], Massimo Mella[2], <u>Andrew M. Rappe</u>[1]
[1]The Makineni Theoretical Laboratories, Department of Chemistry
University of Pennsylvania, Philadelphia, PA 19104-6323, USA
[2]School of Chemistry, Cardiff University
P.O. Box 912, Cardiff CF10 3TB, United Kingdom

The quantum Monte Carlo (QMC) method is an efficient way to solve the time-independent Schrodinger equation for many electron systems. While total system energies have been successfully calculated using this method, less progress has been made for the calculation of other quantities.

Accurate and efficient atomic forces can be achieved by combining three innovations: 1) improved algorithms for minimizing the energy of the variational QMC trial wave function, 2) renormalized estimators that make the evaluation of the Hellmann-Feynman part of the atomic force efficient, and 3) stochastic sampling of Pulay corrections to the force. The results for first-row monohydrides and carbon monoxide will be presented.

The atomic forces agree quantitatively with potential energy surfaces, demonstrating the accuracy of this force procedure. Equilibrium molecular structure, harmonic vibrational frequencies, and anharmonicity constants, derived from the QMC energies and atomic forces, also agree well with experimental values.

AUXILIARY BASIS EXPANSIONS FOR LARGE-SCALE ELECTRONIC STRUCTURE CALCULATIONS

Martin Head-Gordon

Department of Chemistry
University of California, Berkeley and Chemical Sciences Division
Lawrence Berkeley National Laboratory, Berkeley CA 94720

With the development of standardized auxiliary basis sets by Ahlrichs' group, resolution-of-the-identity (RI) methods have become widely used for electronic structure calculations. They offer significant efficiency advantages with negligible loss of accuracy. I shall discuss new developments from my group that extend the scope of RI-based calculations, based on two main themes. The first theme concerns the adaptation of RI methods to novel electronic structure methods. Local second order perturbation theory (MP2) and scaled MP2 methods (that treat only opposite spin correlations) will be briefly summarized. RI methods to treat valence active space methods will then be described, including the problem of second order perturbation corrections to these reference states. Their chemical applicability, as well as the computational performance, will be discussed. The second theme is the problem of treating very large systems by RI methods. One must then address the extent of spatial locality of auxiliary basis expansion coefficients. Numerical experiments show that they can be surprisingly non-local, and that modifications to the standard RI procedure are therefore desirable. We suggest one promising modification. With this in hand, we finally consider the development of reduced scaling RI methods to evaluate Coulomb and mixed spin correlation energies.

TRAPPING OF ELECTRONIC DEFECTS AND DAMAGE PROCESSES IN AMORPHOUS AND CRYSTALLINE SILICA

Hannes Jonsson[1,2], Kiril Tsemekhman[2], Renee M. Van Ginhoven[2,3],
Margaret Gabriel[2], Rene Corrales[3], Eric Bylaska[3]

[1]*Faculty of Science VR-II, University of Iceland, 107 Reykjavik, Iceland*
[2]*Chemistry Department 351700, University of Washington, Seattle WA 98195, USA*
[3]*Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA*

Excitons and electron holes in crystalline and amorphous SiO_2 have been studied using DFT with the PBE0 hybrid functional. The exact exchange term in the functional has been implemented in an efficient way in a plane-wave/pseudo-potential code by using maximally localized Wannier functions. Several self-trapped, triplet state excitons (STE) and doublet state holes (STH) with highly localized spin density were identified and the minimum energy path between these states calculated using the NEB method. Good agreement is found between calculated and observed luminescence of the STEs. The observed reduction in the lifetime of the luminescent STE in quartz with increased temperature can be correlated with thermal activation to a curve-crossing state. The calculated hyperfine constants for the STHs agree well with results of ESR experiments. In some cases, the formation of the STEs and STHs is found to lead to damage in the silica network after the system returns to the singlet state, for example five-fold coordinated Si-atoms and edge sharing tetrahedra which can be associated with relaxed O-interstitital-vacancy pairs. The commonly used GGA functionals fail to predict the localized spin states but favor delocalized states that are inconsistent with experimental findings.

FROM FIRST-PRINCIPLES TO MATERIAL PROPERTIES: TOWARDS PREDICTIVE MODELLING OF IONIC SYSTEMS.

Paul Anthony Madden

Chemistry Department, University of Edinburgh
King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK

Although ions are closed-shell systems, so that their interactions should be governed by the straightforward principles of non-bonding intermolecular forces, simple interaction potentials fail qualitatively to account for the properties of all but the simplest ionic materials. The reason is that the electronic structures of ions in the condensed phase are profoundly affected by their coordination environment. This environment changes from one phase to another and even from one instant to another as ions move about at finite temperature. The resulting many-body contributions to the interactions must be incorporated into any quantitative and transferable model of the interactions. To avoid a direct ab initio approach, and allow simulations on the large time and length scales necessary to recapture many aspects of material behaviour, progress is made by constructing potentials in which the electronic structure of the ions is represented by a small number of additional degrees of freedom, which capture the instantaneous induced multipoles and ionic shape, for example. Such models may be parameterized by using information from condensed-phase ab initio calculations on the interionic forces and the electron density. The accuracy and transferability of such representations may be assessed by comparing the predictions of the model with further ab initio calculations and with experiment. Some examples of the applications of these models to predict the properties of exotic materials under extreme conditions of temperature and pressure, and to examine the microscopic mechanisms underpinning transport and spectroscopic behaviour will be provided.

COMBINING THE ULTRAFAST AND ULTRACOLD: PROSPECTS OF QUANTUM CHEMICAL SYNTHESIS

Ronnie Kosloff

Department of Physical Chemistry and the Fritz Haber Center for Molecular Dynamics
The Hebrew University, Jerusalem, 91904 Israel

The revolution in cooling techniques in the last decade has led to two new chemical regimes which we will term ultracold chemistry. The first is the micro-Kelvin one. In this temperature the de-Broglie wavelength of the atom exceeds the typical van-der-Waals force range. The second colder regime is in the nano-Kelvin regime where the de-Broglie wavelength exceeds the average interatomic separation leading to a degenerate gas. Ultracold chemical synthesis is about overcoming the quantum barrier on the one hand and stabilizing the product on the other. Ultrafast excitation can manipulate the atomic ensemble impulsively creating molecules. Specific examples of such reactions will be described as well as the theoretical and computational methods required to simulate chemical reactions taking place in the extreme quantum regime.

Christiane P. Koch, Jose P. Palao, Ronnie Kosloff and Francoise Masnou-Seeuws
Stabilization of Ultracold Molecules Using Optimal Control Theory
Phys. Rev. A 70, 013402 (2004).

E. Luc-Koenig, R. Kosloff, F. Masnou-Seeuws, M. Vatasescu
Photoassociation of cold atoms with chirped laser pulses: Time-dependent calculations and analysis of the adiabatic transfer within a two-state model
Phys. Rev. A, 70, 033407 (2004).

A. Bertelsen, S. Vogelius, S. Jorgensen, R. Kosloff and M. Drewsen
Photo-dissociation of Cold MgH+ ions Towards rotational temperature measurements and controlled dissociation
Euro. Phys. J. D 31, 403 - 408 (2004).

Christiane P. Koch,, Francoise Masnou-Seeuws and Ronnie Kosloff
Creating ground state molecules with optimal Feshbach resonances in tight traps
Phys. Rev. Lett. 94 (2005).

PROTON-COUPLED ELECTRON TRANSFER: ANALYSIS OF DYNAMICS AND CALCULATION OF COUPLINGS

Sharon Hammes-Schiffer
Department of Chemistry
Pennsylvania State University

A theoretical formulation for proton-coupled electron transfer (PCET) reactions in solution and proteins will be presented. The quantum mechanical effects of the active electrons, transferring proton, and donor-acceptor mode are included in this formulation. Analytical nonadiabatic rate expressions have been derived in various limits. The dynamical effects of the donor-acceptor mode and solvent or protein environment can be included by expressing the rate in terms of a time-dependent probability flux correlation function. The nonadiabatic couplings can be calculated with the recently developed nuclear-electronic orbital (NEO) approach, in which specified nuclei are treated quantum mechanically on the same level as the electrons. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions. Typically the hydrogen nuclei, as well as all electrons, are treated quantum mechanically. The NEO method enables the calculation of nonadiabatic couplings between reactant and product vibronic PCET states. Applications to reactions in solution and enzymes will be discussed. The theoretical calculations are consistent with the experimental data and provide insight into the chemical and physical basis for the observed rates and kinetic isotope effects.

APPLICATIONS OF A ONE-ELECTRON DRUDE MODEL TO ELECTRON ATTACHMENT TO LARGE WATER CLUSTERS

Kenneth D. Jordan[1], Thomas Sommerfeld[1], Feng Wang[2]
[1]Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260
[2]Department of Chemistry, Boston University, Boston MA 02215

In order to accurately describe the binding of an excess electron to a cluster of polar molecules using traditional electronic structure methods, it is necessary to employ large, flexible basis sets and to include electron correlation effects to high order. Recognizing that the electron correlation contribution to the electron binding energy is dominated by dispersion interactions between the excess electron and the electrons of the monomers, we have developed a pseudopotential procedure that captures the key correlation effects. In this approach the electrons of the monomers are modeled by means of quantum Drude oscillators and only the excess electron is treated explicitly. This permits accurate characterization of excess electron-water cluster systems, while using orders of magnitude less computer time than traditional ab initio all-electron methods. The Drude oscillator approach has also been incorporated in a parallel tempering Monte Carlo code, permitting finite-temperature simulations of excess electron-water cluster systems. In this talk, applications of the resulting one-electron model to water clusters as large as $(H_2O)_{30}$ are described.

DENSITY FUNCTIONAL THEORY FOR ELECTRON TRANSFER REACTIONS

Troy Van Voorhis
Department of Chemistry, MIT

We review the well-known shortcomings of approximate density functionals for treating electron transfer (ET) between a donor and an acceptor. Constrained density functional theory (CDFT) provides a practical solution to many of these problems by performing a change of variables so that the charge on the acceptor becomes an independent variable. We have recently developed an efficient implementation of CDFT that makes use of optimized effective potential techniques. We summarize this implementation and present several illustrative applications that demonstrate the strengths of the new formalism: 1) If one treats charge transfer excitations with CDFT, the long range $-1/r$ interaction between the electron and the hole is correctly included, while this effect is lost in linear response calculations using standard functionals 2) Marcus theory parameters can be accurately obtained in a way that is in principle exact (i.e. the results would be exact with the exact density functional) 3) Real time evolution of an initially charge separated state using time-dependent DFT allows one to make a connection to molecular charge transport experiments.

FACETED CRYSTAL GROWTH

David J. Srolovitz[1], Corbett C. Battaile[2], Peter Smereka[3],
Danxu Du[1], Michael Coltrin[2]

[1]*Department of Mechanical and Aerospace Engineering and the Princeton Institute for the Science and Technology of Materials, Princeton University*
[2]*Chemical Processing Sciences Department, Sandia National Laboratories*
[3]*Department of Mathematics, University of Michigan*

The growth of crystals from a vapor necessarily involves events as fast as individual chemical reactions and as slow as the entire deposition process (seconds to hours). I will discuss an integrated description of growth of faceted crystals starting from chemical reactions (first-principles) to the determination of first-principles calculations to the determination of surface orientation-dependent growth rates (kinetic Monte Carlo) to the evoltuion of macroscopic islands and polycrystalline films (level set methods). I will illustrate this through simulations of both CVD of diamond and MOCVD of GaN. I will emphasize the new insights developed for understanding growth morphology.

REACTION PATHWAYS IN COMPLEX SYSTEMS AND THE STRING METHOD

Weinan E[1], Weiqing Ren,[2] and Eric Vanden-Eijnden[3]
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Program in Applied and Computational Mathematics
Princeton University
²Department of Mathematics, Princeton University
³Courant Institute, New York University

How do we understand and quantify reaction in complex systems when the notion of transition states as a few isolated microscopic states becomes irrelevant? In this talk, we will present a theoretical framework as well as a practical numerical method, the finite temperature string method (FTS), that addresses this question. We will show that the notion of intrinsic reaction pathways has to be replaced by that of the transition tubes, which are the tubes of most probable reactive trajectories in configuration space, and we show how to characterize and compute numerically the transition tube. We present several examples to illustrate both the success of this attempt and the difficulties that lie ahead.

ACTIN SELF-ASSEMBLY AND LISTERIA MOTILITY

Andrea J. Liu,[1] Ajay Gopinathan,[2] and Kun-Chun Lee[1,3]

[1]Department of Physics and Astronomy, University of Pennsylvania
[2]University of California, Santa Barbara
[3]Department of Chemistry and Biochemistry, University of California, Los Angeles

The shape and mechanical properties of cells are controlled by the cytoskeleton, which is mainly made of filaments of the protein actin. When cells crawl, the actin cytoskeleton must re-organize and individual actin filaments must polymerize and depolymerize. The growing ends of the filaments are oriented towards the outside of the cell, and their polymerization pushes the cell membrane forwards. The same mechanism comes into play when the bacterium Listeria monocytogenes spreads. On its own, the bacterium can multiply, but in order to spread from one cell to another, it hijacks the actin machinery of the cell to propel itself. I will present a model for the mechanism by which actin polymerization leads to force generation in Listeria propulsion.

EVOLUTION AS KINETICS: MAPPING EVOLUTIONARY PATHWAYS OF HIV-1 DRUG RESISTANCE USING CONDITIONAL SELECTION PRESSURE

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Department of Chemistry and Biochemistry
University of California, Los Angeles, CA 90095

One of the biggest problems in the treatment of AIDS is the rapid evolution of drug resistance, which can occur within weeks of introduction of a new drug. Can the large-scale approaches of genomics provide a new level of strategic intelligence about rapidly evolving pathogens such as HIV? We have sought to combine two very different approaches: evolutionary theory, particularly metrics of selection pressure; and chemical kinetics models. Thus, we model evolution as a kinetic network, a directed graph whose nodes represent individual mutation sites, and whose edges represent the rate of growth of individual mutations in the population through mutation and selection. We have developed a new approach to measure the rates of all possible evolutionary pathways in a genome, as a conditional Ka/Ks network, and have applied this to several datasets, including clinical sequencing of 50,000 HIV-1 samples. These data reveal that specific accessory mutations can greatly accelerate the evolution of multi-drug resistance, while other "kinetic trap" mutations can block it. Our analysis was highly reproducible in four independent datasets, and can decipher a pathogen's evolutionary pathways to multi-drug resistance even while key drug resistance mutations are still rare.

WHAT ARE PHYSICAL GELS?

Zhen-Gang Wang
Division of Chemistry and Chemical Engineering
California Institute of Technology

A solution of associating molecules can transform to a gel state upon changes in temperature and/or other solution conditions (such as pH). While the case of chemical (irreversible) gelation is relatively simple and is well described by percolation theory, there has been a longstanding controversy about the thermodynamic nature of reversible physical gels. In this talk, I will describe a new approach to this problem based on the analogy between gelation and glass transition. I will show that gelation can occur through two principal mechanisms: in the single-phase region, gelation occurs as a result of proliferation of free energy minima each corresponding to a spatially inhomogeneous but nonperiodic distribution of the associating molecules ñ this is the same physics underlying glass transition; in the two-phase region, gelation can be viewed as the continuation of glass transition into the two-phase region, or equivalently as an incomplete phase separation arrested by the onset of glass transition. In both cases the transition is connected with an underlying spinodal of the uniform solution phase.

NOISE INDUCED ORDER IN EXTENDED SYSTEMS AWAY FROM EQUILIBRIUM

<u>Katja Lindenberg</u>[1] and Javier Buceta[2]
[1]Department of Chemistry and Biochemistry
University of California, San Diego
[2]Parc Cientific de Barcelona

The past few years have seen the emergence of dramatically counterintuitive phenomena in even the "simplest" complex systems away from thermodynamic equilibrium. The observations are counterintuitive in that they lead to outcomes that are exactly opposite to those one might expect. Several examples will be discussed as time permits, including:
1) Phase transitions to ordered or limit cycle or patterned states caused entirely by noise in systems that exhibit no order in the absence of noise;
2) Turing instabilities triggered by simple switching between dynamics that by themselves are completely stable and unpatterned. These phenomena are illustrated via numerical simulations and understood in terms of mean field theories that capture these behaviors qualitatively and in some cases even quantitatively.

THEORETICAL STUDIES OF THE ELECTRONIC COUPLING ELEMENT FOR ELECTRON TRANSFER

Robert J. Cave
Department of Chemistry
Harvey Mudd College

The electronic coupling element is the quantity primarily responsible for the distance- and orientation-dependence of the rate of non-adiabatic electron transfer. As a result it has received considerable theoretical attention and a variety of methods have been proposed for its calculation. In this talk several alternatives for the calculation of the coupling element will be reviewed. Results will then be presented for the electronic coupling in a variety of systems of experimental interest obtained using the Generalized Mulliken-Hush method. Future challenges associated with the accurate calculation of the coupling element will also be discussed.

MOLECULAR TRANSPORT STRUCTURES: ELASTIC SCATTERING AND BEYOND

Mark A. Ratner[1], Abe Nitzan[2], and Misha Galperin[1]

[1]Department of Chemistry and Center for Nanotechnology
Northwestern University
[2]School of Chemistry, Tel-Aviv University

Current experimental efforts are clarifying quite beautifully the nature of charge transport in so-called molecular junctions, in which a single molecule provides the channel for current flow between two electrodes. The theoretical modeling of such structures is challenging, because of the uncertainty of geometry, the nonequilibrium nature of the process, and the variety of available mechanisms. The talk will center on the first formulation of the problem in terms of scattering theory, and then on the generalizations needed to make that simple picture relevant to the real experimental situation. These include vibronic coupling, structural disorder and energy transfer.

BIOCHEMISTRY

PI-1 CHIRALLY-SENSITIVE NONLINEAR OPTICAL PROBES OF VIBRATIONAL EXCITONS IN PROTEINS
Darius Abramavicius

PI-2 INTERACTION ENERGIES OF LARGE BIOMOLECULES-COMPUTATIONAL STUDY
Jiri Cerny

PI-3 STRUCTURAL CHARACTERIZATION OF α-HELICES IN POLY-ALANINE
Vernon A. Couch

PI-4 LOW-FREQUENCY MODES OF WILD-TYPE AND D96N BACTERIORHODOPSIN
Henny F. Galan

PI-5 FACTORS AFFECTING THE STABILITY AND PROPENSITY TO AGGREGATE OF AN OFF-LATTICE β-BARREL PROTEIN
Mary A. Griffin

PI-6 THEORETICAL MODELING OF THE CATCH-SLIP TRANSITION IN BIOLOGICAL ADHESION
Kim N Gunnerson

PI-7 COMPUTING THE AMINO ACID SPECIFICITY OF FLUCTUATIONS IN BIOMOLECULAR SYSTEMS
Kay Hamacher

PI-8 ELECTROSTATIC DFT MAP FOR THE COMPLETE VIBRATIONAL AMIDE BAND OF NMA
Tomoyuki Hayashi

PI-9 REPLICA-EXCHANGE METHOD FOR EFFICIENT SAMPLING USING SEMI-FLEXIBLE PROTEIN STRUCTURE SIMULATION
Mengjuei Hsieh

DYNAMICS

PI-10 FROM HIGH-LEVEL MULTIREFERENCE AB INITIO THEORY TO ON-THE-FLY DYNAMICS: THE PHOTOCHEMISTRY OF THE C=C BOND AND BEYOND
Mario Barbatti

PI-11 HOW ENZYME DYNAMICS CATALYZES A CHEMICAL REACTION IN ATOMIC DETAIL: A TRANSITION PATH SAMPLING STUDY
Jodi E Basner

PI-12 UNDERSTANDING THE SPECTROSCOPY AND PHOTOINDUCED RELOCALIZATION OF SOLVATED ELECTRONS IN WEAKLY POLAR FLUIDS: NONADIABATIC MIXED QUANTUM/CLASSICAL SIMULATIONS OF THE EXCITED THF-SOLVATED ELECTRON
Michael J. Bedard-Hearn

PI-13 CONFORMATIONAL TRANSITIONS OF NEUROTOXIN FASCICULIN-2 ASSOCIATED WITH ITS BINDING TO ACETYLCHOLINESTERASE
Jennifer M Bui

PI-14 NUMERICAL PROPAGATION OF THE TIME-DEPENDENT KOHN-SHAM EQUATION IN A GAUSSIAN BASIS USING THE MAGNUS EXPANSION
Chiao-Lun Cheng

PI-15 AB INITIO SIMULATION OF EXCITED STATE PROTON TRANSFER AND THREE-STATE INTERSECTION DYNAMICS IN MALONALDEHYDE
Joshua D. Coe

PI-16 TRAJECTORY SURFACE HOPPING IN THE TIME-DEPENDENT DENSITY FUNCTIONAL THEORY FOR ELECTRON-NUCLEAR DYNAMICS
Colleen F. Craig

PI-17 NON-ADIABATIC EFFECTS IN PROTON COLLISION WITH CO MOLECULES
T. J. Dhilip Kumar

PI-18 ENTANGLED SEMICLASSICAL METHOD IN PHASE SPACE
Jacob Goldsmith

PI-19 ELECTRON RELAXATION DYNAMICS IN CARBON NANOTUBES
Bradley F. Habenicht

PI-20 QUANTIZED HAMILTONIAN DYNAMICS AND STATISTICAL MECHANICS
Eric Heatwole

PI-21 CHARACTERIZATION OF THE TIP4P-EW WATER MODEL: VAPOR PRESSURE AND PROPERTIES IN THE NEAR- AND SUPER-CRITICAL REGION
Hans W. Horn

PI-22 EXCITED STATE DYNAMICS OF THYMINE AND URACIL
Hanneli R. Hudock

PI-23 KINETICS OF THE HYDROGEN ABSTRACTION HCO + ALKANE → HCHO + ALKYL REACTION CLASS: AN APPLICATION OF THE REACTION CLASS TRANSITION STATE THEORY
Lam K. Huynh

PI-24 DYNAMICS OF PROLIFERATING CELL NUCLEAR ANTIGEN LOADED ONTO DSDNA
Ivaylo Ivanov

PI-25 SEMICLASSICAL CORRECTIONS FOR THE HERMAN-KLUK APPROXIMATION
Kenneth G. Kay

PI-26 CARRIER RELAXATION IN PbSe QUANTUM DOTS
Svetlana Kilina

PI-27 QUANTUM/CLASSICAL MOLECULAR DYNAMICS FOR A DOUBLE WELL COUPLED TO A DISSIPATIVE BATH
Soo Young Kim

PI-28 FREE ENERGY PROFILE ALONG A DISCRETIZED REACTION PATH VIA THE HYPERPLANE CONSTRAINT FORCE AND TORQUE
Konstantin N Kudin

ELECTRON TRANSFER

PI-29 INTERFACIAL CHARGE-SEPARATION DYNAMICS IN TYPE II ORGANIC POLYMER PHOTOVOLTAIC SYSTEMS
Eric R Bittner

PI-30 *AB INITIO* CHARACTERIZATION OF ELECTRON TRANSFER COUPLING IN PHOTO-INDUCED SYSTEMS
Hung-Cheng Chen

PI-31 DNA CHARGE TRANSFER: AN ATOMISTIC MODEL
Tobias Cramer

PI-32 *AB INITIO* NONADIABATIC MOLECULAR DYNAMICS OF THE ULTRAFAST ELECTRON INJECTION ACROSS THE ALIZARIN-TIO$_2$ INTERFACE
Walter R Duncan

PI-33 FULL CI MIXED QUANTUM-CLASSICAL MD SIMULATIONS OF SOLVATED SODIDE
William J Glover

PI-34 ANALYSIS OF DYNAMICAL ASPECTS OF PROTON-COUPLED ELECTRON TRANSFER REACTIONS
Elizabeth Hatcher

PI-35 RELATIVE CONTRIBUTION OF INCOHERENT HOPPING AND COHERENT SUPEREXCHANGE CHARGE TRANSFER MECHANISM WITHIN SHORT DNA SEQUENCES IN THE PRESENCE OF AT BASE PAIR BRIDGES
Heeyoung Kim

PI-36 EXCITATION ENERGY TRANSFER RATE CONSTANTS IN MESO-MESO LINKED Zn(II) PORPHYRIN ARRAYS WITH ENERGY ACCEPTING 5,15-BISPHYENYLETHYNYLATED Zn(II) PORPHYRIN
Heeyoung Kim

PI-37 DAMAGE TO DNA BY VERY LOW ENERGY ELECTRONS
Iwona Anusiewicz

PI-38 INTERACTION OF WATER MOLECULES WITH THE Pt(111) SURFACE
Líney Árnadóttir

PI-39 QUANTUM COMPUTING FOR QUANTUM CHEMISTRY
Alan Aspuru-Guzik

PI-40 A SPARSE ALGORITHM FOR THE EVALUATION OF THE LOCAL ENERGY IN QUANTUM MONTE CARLO
Alan Aspuru-Guzik

PI-41 ZORI 0: A PARALLEL QUANTUM MONTE CARLO ELECTRONIC STRUCTURE PACKAGE
Alan Aspuru-Guzik

PI-42 DFT STUDY ON A LIGHT-HARVESTING MOLECULAR DEVICE
Tunna Baruah

PI-43 ANALYTICAL GRADIENTS OF THE TIME DEPENDENT DENSITY FUNCTIONAL (TDDFT) EXCITATION ENERGIES FOR CONTINUUM SOLVATION MODELS: THEORY AND APPLICATIONS TO GEOMETRIES AND PROPERTIES OF EXCITED STATES
Roberto Cammi

PI-44 EXCITED ELECTRONIC STATES OF SMALL WATER CLUSTERS
Daniel M. Chipman

PI-45 SIXTEEN VALENCE-ELECTRON SPECIES CONTAINING BORON: $[B, N, S, H_2]$.
Carol A. Deakyne

PI-46 ELECTROSTATIC COMPARISON OF SEVERAL WATER MODELS
Albert A. DeFusco

PI-47 VIBRATIONAL ANHARMONICITY IN THE $(H_2O)_N$, N = 2-6, WATER CLUSTERS
Kadir Diri

PI-48 A RESOLUTION-OF-THE-IDENTITY IMPLEMENTATION OF THE LOCAL TRIATOMICS-IN-MOLECULES MODEL FOR SECOND-ORDER MØLLER-PLESSET THEORY WITH APPLICATION TO ALANINE TETRAPEPTIDE CONFORMATIONAL ENERGIES
Robert A. DiStasio Jr.

PI-49 DIFFUSION MONTE CARLO FOR ENERGIES OF HYDROCARBONS
Dominik Domin

PI-50 AN IMPROVED HYBRID EXCHANGE KERNEL FOR CHARGE-TRANSFER STATES IN TD-DFT
Anthony D. Dutoi

PI-51 A THEORETICAL STUDY OF THE EFFECT OF COORDINATING SOLVENT ON ION PAIR SUBSTITUTION REACTIONS
Jayasree G Elambalassery

PI-52 ELECTRON HOLES IN AMORPHOUS SILICA CAN INDUCE DAMAGE
Margaret A. Gabriel

PI-53 DFT STUDY ON HYDROGEN BOND PROMOTED DIELS-ALDER CYCLOADDITIONS. REACTION MECHANISM AND ORIGINS OF ENANTIOSELECTIVITY
Ruth Gordillo

PI-54 MULTIGRID ORBITAL-FREE DENSITY FUNCTIONAL THEORY
Gregory S Ho

PI-55 A PARALLEL ELECTROMAGNETIC MOLECULAR LOGIC GATE
Oded Hod

PI-56 EFFECTIVE LINEAR SCALING SCHEME FOR THE KOHN-SHAM COULOMB PROBLEM
Gongyi Hong

PI-57 LOCALIZED ELECTRONIC STATES AROUND A SINGLE KONDO IMPURITY
Patrick Huang

PI-58 THE RESOLUTION OF IDENTITY ATOMIC ORBITAL LAPLACE-TRANSFORMED SECOND-ORDER MOLLER-PLESSET THEORY FOR PERIODIC SYSTEMS
Artur F. Izmaylov

PI-59 PROBING THE RESPONSE OF ATOMIC CLUSTERS TO ELECTRIC FIELDS VIA DENSITY FUNCTIONAL THEORY-BASED POLARIZABILITY CALCULATIONS
Koblar A. Jackson

PI-60 FUNCTIONAL-GROUP-BASED ELECTRONIC STRUCTURE METHODS
Benjamin G. Janesko

PI-61 RESONANCE RAMAN SCATTERING OF MOLECULES FROM RESONANCE POLARIZABILITY DERIVATIVES
Lasse Jensen

PI-62 THE NIST COMPUTATIONAL CHEMISTRY COMPARISON AND BENCHMARK DATABASE
Russell D Johnson

PI-63 FAST CORRELATION METHOD USING LOCAL AUXILIARY BASIS EXPANSIONS
Yousung Jung

PI-64 THE ART OF BOND BREAKING. AN ODYSSEY THROUGH THE COMPUTATIONAL AND INTERPRETATIONAL PROBLEMS OF MC, M=SC, TI, V, AND MN.
Apostolos Kalemos

PI-65 EFFICIENT SCF METHOD FOR LARGE SYSTEMS OF WEAKLY INTERACTING COMPONENTS
Rustam Z. Khaliullin

PI-66 ATOMISTIC SIMULATION OF CITRIC ACID COORDINATION TO 111 AND 100 AG SURFACE
Dmitri S. Kilin

PI-67 DISSOCIATION POTENTIAL CURVES OF LOW-LYING STATES IN TRANSITION METAL HYDRIDES. III. ECP CURVES FOR HYDRIDES OF GROUPS 6 AND 7
Shiro Koseki

PI-68 EQUILIBRIUM GEOMETRIES AND PROPERTIES OF THE GROUND AND ELECTRONICALLY EXCITED STATES OF VINYL, PROPEN-1-YL, PROPEN-2-YL, TRANS-1-BUTEN-2-YL, AND TRANS-2-BUTEN-2-YL DOUBLET RADICALS
Lucas P Koziol

PI-69 MOLECULAR STRUCTURE, VIBRATIONAL FREQUENCIES, AND ANHARMONICITIES IN ELECTRONIC QUANTUM MONTE CARLO
Myung Won Lee

MATERIALS

PI-70 DETERMINATION OF GAS ADSORPTION SITES IN POROUS MATERIALS USING AB-INITIO METHODS
Corneliu Buda

PI-71 ADSORPTION AND DISSOCIATION OF CO ON CLEAN AND S-PRECOVERED $Fe(100)$: A DFT STUDY
Daniel Curulla Ferre

PI-72 COMPOSITIONAL DEPENDENCE OF THE FIRST SHARP DIFFRACTION PEAK IN SILICATE GLASSES
Jincheng Du

PI-73 STRUCTURE AND REACTIVITY OF STANNIC OXIDE SURFACES IN THE PRESENCE OF OXYGEN
Emily A. A. Jarvis

PI-74 MAGNETIC STRUCTURE AND ADHESION OF THE $Fe(100)/Cr(100)$ AND $Fe(110)/Cr(110)$ INTERFACES
Donald Johnson

PI-75 CHEMISORPTION ON STRAINED METAL SURFACES: PREDICTIVE INSIGHT FROM ORBITAL-SPECIFIC ASPECTS OF SUBSTRATE ELECTRONIC STRUCTURE
Sara E. Mason

Multiscale Modeling

PI-76 CALCULATING THE ELASTIC BENDING MODULUS OF LIPID BILAYER EDGE
Frank Yong Jiang

PI-77 INFLUENCE OF SUBUNIT STRUCTURE ON THE OLIGOMERIZATION STATE OF LIGHT HARVESTING COMPLEXES
Harindar Keer

Nano/Bio

PI-78 SUM OF SQUARES OPTIMISATION – APPLICATIONS IN THEORETICAL CHEMISTRY
Martin G. Burke

PI-79 CLASSICAL DYNAMICS SIMULATIONS FOR A LIGHT-DRIVEN MOLECULAR MOTOR
Kelly D. Burtt

PI-80 MODELING VIRAL CAPSID ASSEMBLY DYNAMICS
Michael F. Hagan

PI-81 COMPUTER SIMULATIONS OF THE TRANSLOCATION AND UNFOLDING OF A PROTEIN PULLED MECHANICALLY THROUGH A PORE
Lei Huang

PI-82 IONIC CONDUCTANCE CALCULATION IN A PEPTIDE NANOTUBE
Hyonseok Hwang

PI-83 PHOTOCHEMISTRY OF THE PHOTOACTIVE YELLOW PROTEIN
Chaehyuk Ko

Statistical Mechanics

PI-84 FINDING THE MECHANISM AND RATE OF TRANSITIONS IN QUANTUM MECHANICAL SYSTEMS WITHIN THE HARMONIC APPROXIMATION
Andri Arnaldsson

PI-85 THERMODYNAMICS FROM 'BASIN-SAMPLING': APPLICATION TO ATOMIC CLUSTERS
Tetyana V. Bogdangar

PI-86 DECAY OF METASTABLE PHASES IN A MODEL FOR THE CATALYTIC OXIDATION OF CO ON A SURFACE
Gloria M. Buendia

PI-87 NEW ALGORITHMS FOR MONTE CARLO SIMULATION OF LARGE SYSTEMS OF CHARGED PARTICLES
Brian G. Cheney

PI-88 SEQUENCE-DEPENDENT CYCLIZATION OF SHORT DNA SEQUENCES
Luke F. Czapla

PI-89 POLYMER BASED MOLECULAR MOTORS: CHARACTERISATION AND EFFICIENCY
  Matthew Downton

PI-90 VARIATIONAL GAUSSIAN WAVEPACKET SIMULATIONS OF EQUILIBRIUM PROPERTIES OF QUANTUM MANY-BODY SYSTEMS
  Pavel A. Frantsuzov

PI-91 MONTE CARLO SIMULATION OF PHASE EQUILIBRIA USING DFT POTENTIALS
  Lev David Gelb

PI-92 PATH INTEGRAL THERMOCHEMISTRY
  Kurt R. Glaesemann

PI-93 SIMULATIONS OF WATER IN GIANT PLANETS: DISCOVERY OF SYMMETRIC H-BONDING IN THE SUPERIONIC PHASE
  Nir Goldman

PI-94 NONEQUILIBRIUM SUPEROPERATOR GREENS FUNCTION THEORY OF DENSITY CORRELATION FUNCTIONS; BEYOND THE GW-APPROXIMATION
  Upendra Harbola

PI-95 TIP-SHAPE EFFECT ON THE PULL-OFF FORCE IN ATOMIC FORCE MICROSCOPY
  Joonkyung Jang

PI-96 DYNAMICAL EXCHANGES IN FACILITATED MODELS OF SUPERCOOLED LIQUIDS
  YounJoon Jung

PI-97 VIBRATIONAL ENERGY RELAXATION RATES IN LIQUID SOLUTIONS FROM SEMICLASSICAL MOLECULAR DYNAMICS SIMULATIONS
  Being J. Ka

PI-98 THROUGH THE CHANNEL AND AROUND THE CHANNEL: VALIDATING AND COMPARING MICROSCOPIC APPROACHES FOR EVALUATION OF FREE ENERGY PROFILES FOR ION PENETRATION THROUGH ION CHANNELS
  Mitsunori Kato

PI-99 TOPOGRAPHY OF THE FREE ENERGY LANDSCAPE PROBED VIA MECHANICAL UNFOLDING OF PROTEINS
  Serdal Kirmizialtin

BIOCHEMISTRY

PII-1 CATALYTICALLY RELEVANT MOTIONS IN ENZYMES
Sara Nunez

PII-2 HYDRATION AND TAUTOMERIZATION OF NUCLEIC ACID BASES: AB INITIO AND MOLECULAR DYNAMICS STUDY IN THE GAS PHASE, IN A MICROHYDRATED ENVIRONMENT AND IN AQUEOUS SOLUTION
Jaroslav Rejnek

PII-3 AB INITIO FREE ENERGY PROFILES FOR ENZYMATIC REACTIONS USING MODEL POTENTIALS
Edina Rosta

PII-4 HOW WELL DOES PB CONTINUUM SOLVENT COMPARE WITH EXPLICIT SOLVENT?
Chunhu Tan

PII-5 ESTIMATING EFFECTS OF MUTATIONS ON P53 STABILITY WITH POISSON-BOLTZMANN THEORY
Yu-Hong Tan

PII-6 COMPUTED ENERGETICS OF PROTEINS AT THE DIFFERENT LEVELS OF THE PROTEIN STRUCTURE
Ivan Y Torshin

PII-7 THE CONCEPT OF MOLECULAR ENERGETIC PROFILES IN APPLICATION TO TRNA STRUCTURES
Ivan Y Torshin

PII-8 FINDING REARRANGEMENT PATHWAYS
Semen A. Trygubenko

PII-9 CATECHOL TO SEMIQUINONE TO QUINONE: A THEORETICAL STUDY OF THE FEATURES RESPONSIBLE FOR RADICAL INITIATION, PROPAGATION, ANTI/PRO-OXIDANT CHARACTER AND CELL TOXICITY
James S. Wright

PII-10 A COMPUTATIONAL PLATFORM FOR STUDYING THE MULTIDIMENSIONAL COHERENT VIBRATIONAL SPECTROSCOPY OF PROTEIN DYNAMICS
Wei Zhuang

PII-21 SEMICLASSICAL SIMULATION OF THE VIBRATIONAL DEPHASING OF IODINE IN A CRYOGENIC KRYPTON MATRIX
Jeanne M. Riga

PII-22 SEMICLASSICAL LIOUVILLE METHOD FOR THE SIMULATION OF ELECTRONIC TRANSITIONS WITH A SINGLE ENSEMBLE OF CLASSICAL TRAJECTORIES
Eduardo J Roman

PII-23 PRONOUNCED NON-CONDON EFFECTS IN THE ULTRAFAST INFRARED SPECTROSCOPY OF WATER
Jordan R. Schmidt

PII-24 A SEMI-CLASSICAL TREATMENT OF NONADIABATIC DYNAMICS
XiaoGeng Song

PII-25 ENERGY TRANSFER AT A GAS-LIQUID INTERFACE
Tamas Szabo

PII-26 AB INITIO PHOTODYNAMICS OF BENZENE: MODELING PHOTOELECTRON SPECTRA
Alexis L. Thompson

PII-27 ADSORPTION OF GLYPHOSATE ON MONTMORILLONITE INTERLAYER SURFACES
Lorena Tribe

PII-28 QUANTUM INSTANTON EVALUATION OF THE KINETIC ISOTOPE EFFECTS
Jiri Vanicek

PII-29 CALCULATION OF TIME CORRELATION FUNCTIONS USING THE SEMICLASSICAL INITIAL VALUE REPRESENTATION
Charulatha Venkataraman

PII-30 INTERNAL ROTATIONAL MOTIONS OF METHYL, TRIFLUOROMETHYL AND *TERT*-BUTYL GROUPS IN CRYSTALLINE SOLIDS
Xianlong Wang

PII-31 THE DECOMPOSITION OF PETN AT EXTREME CONDITIONS
Christine J. Wu

ELECTRON TRANSFER

ELECTRONIC STRUCTURE

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PII-78 INTERACTION OF Au CLUSTERS AND DEFECTIVE TiO$_2$ SURFACE
Piti Treesukol

PII-79 THREE-BODY EFFECTS ON PHASE EQUILIBRIUM PROPERTIES OF NOBLE GASES
Liping Wang

PII-80 FUTURE POLYNITRAMINE EXPLOSIVES
Amir Weitz

PII-81 THE ORIGIN OF THE HALOGEN EFFECT IN DIELS-ALDER REACTIONS INVOLVING FURAN
Susan N. Pieniazek

PII-82 SMALL Pd CLUSTERS, UP TO THE TETRAMER AT LEAST, ARE HIGHLY MOBILE ON THE MgO(100)SURFACE
Lijun Xu

NANO/BIO

PII-83 MOLECULAR DYNAMICS SIMULATIONS OF THE MECHANICAL UNFOLDING OF PROTEINS
Pai-Chi Li

PII-84 CHEMICAL REACTION OF SMALL GAS MOLECULES WITH THE 5-1DB DEFECT ON THE SIDEWALL OF THE SINGLE-WALLED CARBON NANOTUBES
Lei Vincent Liu

PII-85 MONTE CARLO SIMULATION OF ACTIN SELF-ASSEMBLY
Xinjiang Lü

PII-86 SIMULATION OF VIBRATIONAL RESONANCES IN INELASTIC ELECTRON TUNNELING
Jeremy B Maddox

PII-87 PRINCIPLES OF INTERACTIONS AND MOLECULAR BIOMECHANICS OF PACKING OF MALACHITE GREEN BY THE RNA APTAMER
Dat H. Nguyen

PII-88 ON COARSE-GRAINING ANISOTROPIC SYSTEMS: NEW ELLIPTIC POTENTIALS
Leonid Paramonov

PII-89 HEAT RECTIFICATION IN MOLECULAR JUNCTIONS
Dvira Segal

PII-90 COMPUTATIONAL STUDY OF FOLDING PATHWAYS OF COLD SHOCK PROTEINS
Sergio Urahata

PII-91 SCATTERING FROM AN IMPURITY IN A QUANTUM WIRE: THE HALL OF MIRRORS WAVEFUNCTION
J. Y. Vaishnav

PII-92 DYNAMIC SPIN MODEL FOR DNA PULLING EXPERIMENT
Stephen Whitelam

PII-93 BEYOND LINEAR RESPONSE THEORY OF HELIUM TO ROTATION
Heather D. Whitley

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POSTER SESSION I

POSTER I-1
CHIRALLY-SENSITIVE NONLINEAR OPTICAL PROBES OF VIBRATIONAL EXCITONS IN PROTEINS

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The third order optical response is usually described using the response functions which are fourth rank tensors. The symmetry of isotropic solutions imposes restrictions on its different components: only the elements with two repeating indexes survive isotropic rotational averaging in the dipole approximation.

To first order in the optical wavevector we predict additional chirally - sensitive components of the response in time and frequency domain for isotropic ensembles. The third order optical response of excitons is calculated using a Green's function solution of the Nonlinear Exciton Equations which establish a quasiparticle scattering mechanism. The nonlocal nonlinear response function is calculated in momentum space, where the problem size reduces to the exciton interaction radius, thus the obtained expressions can be applied as to globular proteins as to periodic infinite structures. Applications are made to coupled anharmonic vibrations in the amide I infrared band of peptides. Chirally-sensitive and non sensitive signals are compared for α helical and β sheet ideal structures and for several globular proteins.

We find that frequency domain chirally-sensitive signals reveal additional peaks in 2D plots of third order susceptibility. Peak pattern also dramatically changes in time domain signals. In both cases the peaks, associated with spatially separated modes, are amplified.
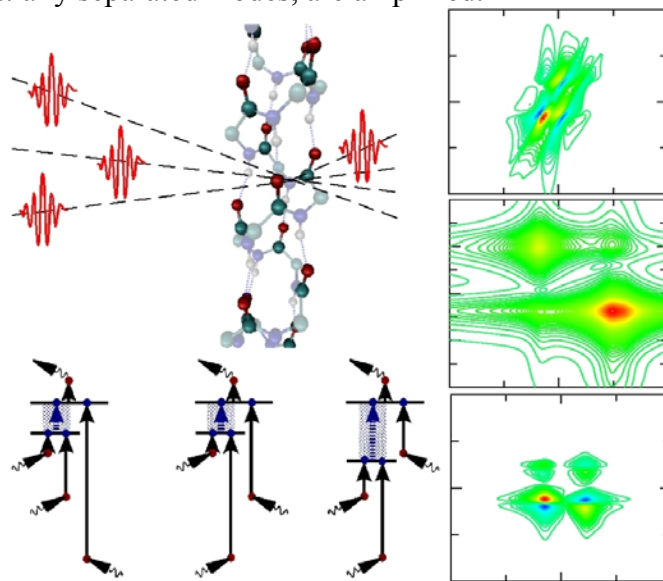
POSTER I-2
INTERACTION ENERGIES OF LARGE BIOMOLECULES -COMPUTATIONAL STUDY

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Interaction energies of the hydrophobic core of protein Rubredoxine were studied by means of semi-empirical SCC-DFTB-D, DFT, RI-DFT and correlated methods. The results showed clearly that it is crucial to include the dispersion energy during the calculation. We successfully introduced empirical dispersion term into the DFT calculations. Our recently derived RI-DFT-D method was used for calculations of interaction energies for different protein and nucleic acid molecules.

POSTER I-3
STRUCTURAL CHARACTERIZATION OF α -HELICES IN POLY-ALANINE
<u>Vernon A. Couch</u>, Neal N. Cheng, William H. Fink
Department of Chemistry, University of California Davis

The structural characteristics of α-helices in poly-alanine based peptides have been investigated via molecular dynamics simulation with the goal of understanding the basic features of peptide simulations within the context of a model system, and to shed insight into the formation and stabilization of α-helices in short peptides. The effect of peptide length, terminal charges, proline substitution, and temperature on the α-helical secondary structure have been studied. The simulations have shown that distinct secondary structure begins to develop in peptides with lengths approaching 10 residues while ambiguous structures occur in shorter peptides. The helical content of peptides with length ≥10 amino acids is observed to be nearly constant up to $(Ala)_{40}$. Interestingly, terminal charges and proline in the 2nd position from the N-terminus alter the secondary structure locally with little effect on the overall α-helical content of the peptide. The free energy profile of helix formation was also investigated. A barrier to the formation of helices with more than 2 consecutive hydrogen bonds in the (i,i+4) pattern was observed, while the free energy increases linearly with additional hydrogen bonds. Values for the change in enthalpy and entropy per hydrogen bond are reported.

LOW-FREQUENCY MODES OF WILD-TYPE AND D96N BACTERIORHODOPSIN

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Low-frequency collective motions of proteins are important to their biological function. The low-frequency modes of wild-type (WT) and D96N bacteriorhodopsin were calculated using normal mode analysis. The THz spectra were generated by calculating the dipole derivative associated with each mode. The spectra generated show general trends which correlate well with published time-domain THz spectra, but in many cases, the calculated resonances do not agree with experiment. The effect of the presence of a water shell around the protein on the THz spectra has also been studied. An increase in the intensity of the THz absorption is observed which is consistent with hydration experiments. A shift in the spectrum is observed as well. The water layer can act as a damping shell, decreasing the extent of motion of the protein atoms, thereby affecting the normal modes. Normal modes not predicted by the calculations but observed experimentally are to be expected due to protein-protein or protein-membrane interactions, as well as phonon vibrations. Analysis of Cα atomic fluctuations associated with the low frequency modes show the global collective motions. We hope ultimately to use THz spectroscopy as a probe of structure-function relationships in retinal proteins.

POSTER I-5
FACTORS AFFECTING THE STABILITY AND PROPENSITY TO AGGREGATE OF AN OFF-LATTICE β -BARREL PROTEIN

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[1]University of California Santa Barbara, Department of Chemistry and Biochemistry,
[2]University of California Santa Barbara, Department of Physics

We study the effects of confinement, sequence frustration and surface interactions on the thermodynamics of dimerization of an off-lattice minimalist β-barrel protein, using replica exchange molecular dynamics. We vary the degree of frustration of the protein by tuning the specificity of the hydrophobic interactions and investigate dimerization in confining spheres of different radii. We also investigate surface effects by tethering the first residue of one of the proteins to a uniformly repulsive surface. We find that increasing confinement and frustration stabilizes the dimer, while adding a repulsive surface decreases its stability. Different ensembles of structures, including properly dimerized and various partially dimerized states, are observed at the association transition temperature T_a, depending on the amount of frustration and whether a surface is present. The ensemble of states at T_a is not affected by the size of the confining sphere. Configurations with a high propensity to form aggregates are only observed in the absence of a repulsive surface and are more populated for the more frustrated protein model.

POSTER I-6
THEORETICAL MODELING OF THE CATCH-SLIP TRANSITION IN
BIOLOGICAL ADHESION

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[1]University of Washington,
[2]University of Washington,
[3]University of Washington

Leukocytes that are carried in the blood stream are responsible for removing agents that cause inflammation in tissues. The mechanism by which leukocytes leave the blood stream and enter the inflamed tissue is called extravasation. This process is facilitated by the ability of selectin proteins, produced by the endothelial cells of blood vessels, to form transient bonds with the leukocytes. In the case of P-selectin, the protein bonds with P-selectin glycoprotein ligands (PSGL-1) produced by the leukocyte. Recent atomic force microscopy and flow chamber analyses of the binding of P-selectin to PSGL-1 provide evidence for an unusual biphasic catch-bond/slip-bond behavior in response to the strength of hydrodynamic flow. This biphasic process is not well-understood. There are several theoretical models for describing this phenomenon. These models use different profiles for potential energy landscapes and how they change under force. We will present a simple theoretical model for describing this phenomenon.

POSTER I-7
COMPUTING THE AMINO ACID SPECIFICITY OF FLUCTUATIONS IN BIOMOLECULAR SYSTEMS

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[2]Department of Physics, University of California, San Diego,
[3]Departments of Chemistry & Biochemisty and Department of Pharmacology, University of California, San Diego

We developed a new amino acid specific method for the computation of spatial fluctuations of proteins. To show the consistency with regards to experiments we applied the method to a set of test proteins. As a first application we present successful results for the problem of drug resistance of HIV-1 protease in its wild-type-form compared to the V82F-I84V-mutant.

ELECTROSTATIC DFT MAP FOR THE COMPLETE VIBRATIONAL AMIDE BAND OF NMA

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An anharmonic vibrational Hamiltonian for the amide I, II, III and A modes of N-methyl acetamide (NMA), parametrized by the 19 components of an external electric field and its 1st and 2nd derivative tensors, is calculated at the DFT(BPW91/6-31G(d,p))level. The infrared spectrum of NMA in TIP3 water is calculated using this Hamiltonian together with the fluctuating solvent electric field obtained from the MD simulations. Sampling the global electric field structure in the region of the transition charge densities (TCDs) is crucial for realistic lineshape simulations. Normal mode analysis of an NMA-$3H_2O$ cluster shows that the 660 cm^{-1} to 1100 cm^{-1} oscillation found in the frequency autocorrelation functions for amide modes can be ascribed to the two bending vibrations of intermolecular hydrogen bonds to the amide oxygen of NMA.
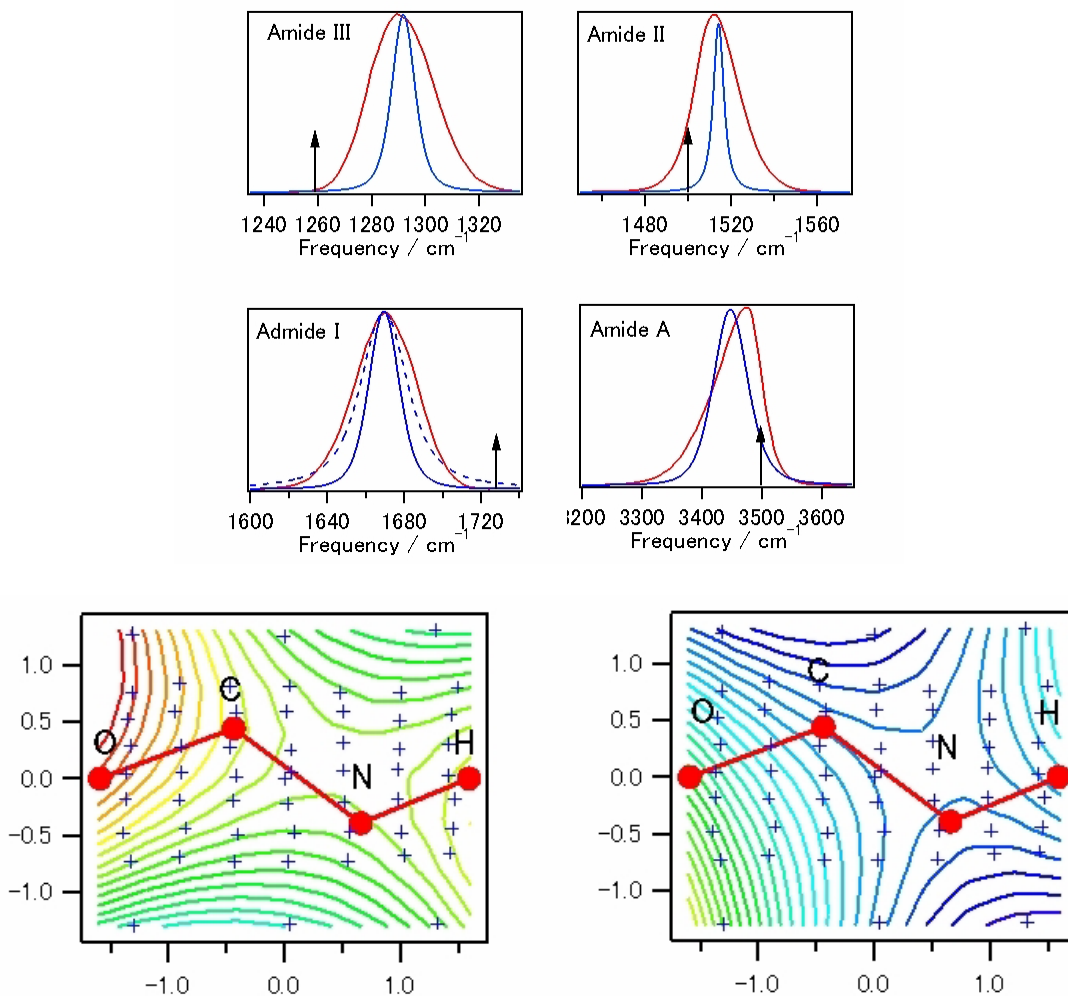
POSTER I-9
REPLICA-EXCHANGE METHOD FOR EFFICIENT SAMPLING USING SEMI-FLEXIBLE PROTEIN STRUCTURE SIMULATION

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Predicting protein structure from its amino acid sequence has been a grand challenge in structure biology and theoretical chemistry. This challenge involves building theoretical energy model for protein structures and efficient sampling over the energy landscape. Here, energy models describing intra-molecular interactions and solvation interactions are important and crucial for accurate simulations. In this study, we use all-atom force-field with some solvation interactions as the energy model for computer simulation. In order to simplify the energy landscape, the degree of freedom of the system is reduced with semi-flexible molecular dynamics. Also replica-exchange sampling method is used for searching the energy minima or stable configurations of the protein structures.

Different force-fields with different solvation models on different protein structures are used to obtain the simulation data. It is shown that applying shake algorithm on different group of the atoms plays an important role reaching stable configurations in the simulation. The analysis of the simulation can provide important clues for further study on protein folding.

POSTER I-10
FROM HIGH-LEVEL MULTIREFERENCE AB INITIO THEORY TO ON-THE-FLY
DYNAMICS: THE PHOTOCHEMISTRY OF THE C=C BOND AND BEYOND

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The photochemical properties of pi systems are of fundamental chemical importance. A comprehensive, theoretical description encompasses several computational steps starting from the calculation of electronically excited states up to dynamics calculations. The computation of excited-state surfaces is particularly difficult since the required wave functions have a complicated multireference structure and conical intersections will occur. In the present contribution the analytic MR-CI gradient and nonadiabatic coupling features developed for the COLUMBUS program system are used to discuss the characteristics of the energy surfaces of ethylene and of a selected set of molecules containing polar C=C bonds (silaethylene, fluorethylene and formiminium cation). The latter is of interest since it is the smallest member of protonated Schiff bases. Nonadiabatic surface-hopping dynamics calculations based on the semiempirical AM1 method, CASSCF and MRCI will be presented.

An outlook will be given on strategies to calculate larger systems including lower-level methods. This discussion will concentrate in particular on the treatment of protonated Schiff bases as model for retinal, which is the basic chromophore in the primary process of vision

POSTER I-11
HOW ENZYME DYNAMICS CATALYZES A CHEMICAL REACTION IN ATOMIC DETAIL: A TRANSITION PATH SAMPLING STUDY

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Albert Einstein College of Medicine

We have applied the Transition Path Sampling algorithm (TPS) to the reaction catalyzed by the enzyme Lactate Dehydrogenase (LDH). This study demonstrates the ease of scaling TPS for applications on many degree of freedom systems, whose energy surface is a complex terrain. A Monte Carlo, importance sampling method, TPS is capable of surmounting barriers in path space, and focuses simulations on rare events such as enzyme catalyzed atom transfers. Generation of the transition path ensemble resolves a paradox in the literature where some studies exposed the catalytic mechanism of hydride and proton transfer by LDH to be concerted and others stepwise. TPS has confirmed both mechanisms are paths from reactants to products. This is a direct result of the algorithm's ability to move through path space and not localize sampling to one sub-area of the energy surface. To identify a reduced reaction coordinate, time series of both donor-acceptor distances and residue distances from the active site have been examined. During the transition from pyruvate to lactate, residues behind the transferring hydride compress toward the active site causing residues behind the hydride acceptor to relax away. A perturbation which disrupts the compression/relaxation transition compromises the reaction.

POSTER I-12
UNDERSTANDING THE SPECTROSCOPY AND PHOTOINDUCED RELOCALIZATION OF SOLVATED ELECTRONS IN WEAKLY POLAR FLUIDS: NONADIABATIC MIXED QUANTUM/CLASSICAL SIMULATIONS OF THE EXCITED THF-SOLVATED ELECTRON

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In weakly polar solvents such as tetrahydrofuran (THF), the solvated electron's absorption spectrum peaks in the mid-infrared, but no definitive assignment has been offered for its origin or underlying structure. We present the results of mixed quantum/classical molecular dynamics simulations and make a detailed assignment of the absorption spectrum. Like water, the THF-solvated electron has strong optical transitions between an *s*-like ground state and a few *p*-like excited states. Unlike water, we find that there are only two (rather than three) nearly-degenerate *p*-like states and there exist several transitions to bound excited states in disjoint cavities. We find that the disjoint cavities act as electron traps and are an inherent property of liquid THF. Our nonadiabatic simulations show that after excitation, the THF-solvated electron can relax to the ground state in a cavity far from where it started, which is consistent with the results of pump-probe experiments from our group, which found that photoexcitation can induce a relocalization of the electron. Finally, to investigate which solvent motions induce electronic relaxation, we introduce a new formalism that projects quantum operators onto classical degrees of freedom. This method calculates exactly how molecular motions cause quantum observables to change with time.

POSTER I-13
CONFORMATIONAL TRANSITIONS OF NEUROTOXIN FASCICULIN-2 ASSOCIATED
WITH ITS BINDING TO ACETYLCHOLINESTERASE

Jennifer M Bui[1,2,3], J. Andrew McCammon[1,2,3]
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[3]Department of Pharmacology

The neurotoxin fasciculin2, FAS2, is a pico-molar protein inhibitor of synaptic acetylcholinesterase, AChE. The dynamics of the encounter between FAS2 and AChE is influenced by conformational variations both before and after protein binding. Sub-microsecond molecular dynamics trajectories of apo-forms of fasciculin, corresponding to different conformational substates, are reported here with reference to the conformational changes of the loop I of this three-finger toxin. This highly flexible loop exhibits an ensemble of conformations within each substate. The high energy barrier found between the two major substates lead to transitions that are slow on the time scale of the diffusional encounter of FAS2 and AChE. The more stable of the two apo substates may not be the one observed in the complex with AChE. It seems likely that the more stable apo form binds rapidly to acetylcholinesterase; and conformational re-adjustments then occur in the resulting encounter complex.

POSTER I-14
NUMERICAL PROPAGATION OF THE TIME-DEPENDENT KOHN-SHAM EQUATION IN A GAUSSIAN BASIS USING THE MAGNUS EXPANSION

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Massachusetts Institute of Technology

We derive and implement an efficient method for numerically propagating the Time-Dependent Kohn-Sham equation. We use the Magnus expansion to obtain 4th, 6th and 8th order approximations to the propagator that treat time-ordering in a unitary manner, and we use a polynomial extrapolation to treat the implicit time-dependence of the Kohn-Sham Hamiltonian. This approach allows one to use quite large time steps (e.g. 1-2 au), and run longer simulations. Application of our methodology to the study of molecular resistance and resonant energy transfer is demonstrated.

AB INITIO SIMULATION OF EXCITED STATE PROTON TRANSFER AND THREE-STATE INTERSECTION DYNAMICS IN MALONALDEHYDE

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[2]Beckman Institute,
[3]Frederick Seitz Materials Research Laboratory

The role of excited state proton transfer has been explored in a variety of contexts such as polymer stabilization, data storage, optical switching, and as a mechanism for bioluminescence. Recent studies have included ultrafast photoionization and transient absorption experiments. We present results using the *ab initio* multiple spawning (AIMS) method for electronic relaxation and excited state intramolecular proton transfer (ESIPT) in malonaldehyde. Our methodology makes use of a state-averaged CASSCF wavefunction combined with an adaptive basis set method for performing molecular dynamics with coupled Gaussians. Proton transfer proceeds freely on S_2, and is strongly coupled to electronic relaxation. The process is complete upon passage to S_1 due to the presence of a substantial energetic barrier. ESIPT competes with an alternative pathway involving rotamerization about the C=C bond, leading to an intersection of the *three* lowest singlet states. The dynamical relevance of this (thus far) rarely observed topological feature is briefly explored.

TRAJECTORY SURFACE HOPPING IN THE TIME-DEPENDENT DENSITY FUNCTIONAL THEORY FOR ELECTRON-NUCLEAR DYNAMICS

Colleen F. Craig, Walter R. Duncan, Oleg V. Prezhdo
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The mean-field treatment of quantum back-reaction of the electronic degrees of freedom on the nuclear trajectory is the source of many qualitative breakdowns of time-dependent density functional theory (TDDFT) for electron-nuclear dynamics. These breakdowns occur when attempting to describe phenomena such as current-induced heating and power dissipation in nanoscale electronics, electron and hole dynamics in quantum dots and carbon nanotubes, and non-radiative relaxation of biological chromophores. The problem is resolved by the development of the trajectory surface hopping approach for TDDFT. This method is applied to the photoinduced electron injection from a molecular chromophore into TiO_2 surface, where traditional TDDFT correctly predicts the timescale, but not the mechanism of the injection; and to the excited state relaxation of the green fluorescent protein chromophore, where traditional TDDFT dramatically underestimates the relaxation rate.

NON-ADIABATIC EFFECTS IN PROTON COLLISION WITH CO MOLECULES

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We investigate the non-adiabatic effects exhibited by proton collisions with CO molecules. Proton and H-atom time-of-fight spectra of CO molecules shows charge transfer (CT) process is an order of magnitude less probable than inelastic scattering[1]. The ab initio potential energy curves have been computed for the low-lying electronic states using MRCI method employing cc-pVTZ basis set. Three different molecular configurations has been considered, i.e., H^+ approaching in collinear geometries towards (i) the C end, (ii) the O end, and (iii) the center of mass of CO in perpendicular direction. In all the three cases, the ground-state ($1^1\Sigma^+$) and the first excited-state ($2^1\Sigma^+$) show avoided crossing exhibiting Demkov coupling[2] (Fig.1a). The non-adiabatic coupling elements have been computed using MRCI wavefunctions by finite-difference method (Fig.1b). The adiabatic basis is transformed to diabatic basis to eliminate the non-adiabatic coupling terms. Time dependent wavepacket dynamics on the diabatic potentials is carried out using Chebyshev propagator scheme. Probability of CT is found to be on an average of 10% transferred to the CT channel confirming the experimental observation.
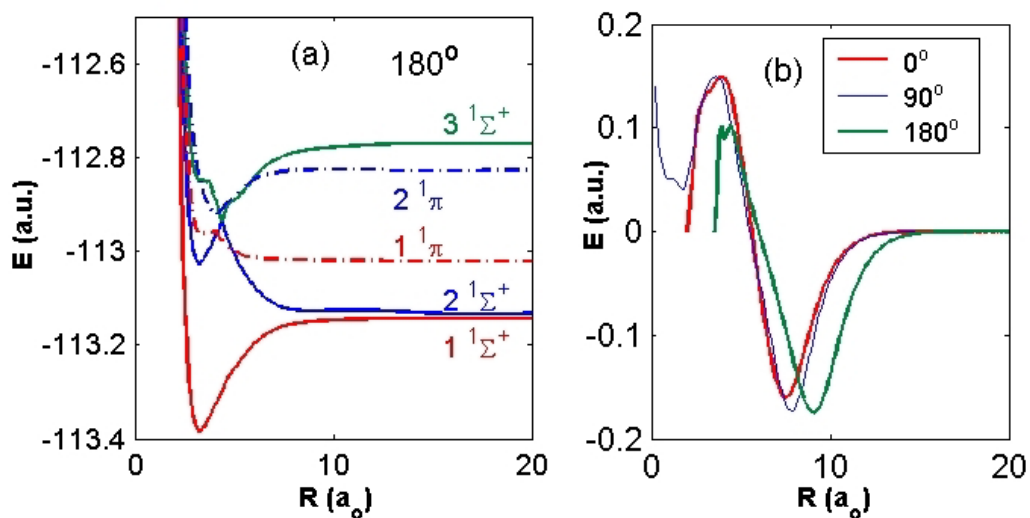
References:

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[2]M. Kimura and N. F. Lane, Adv. At., Mol., Opt. Phys. **26**, 79 (1989).

POSTER I-18
ENTANGLED SEMICLASSICAL METHOD IN PHASE SPACE

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UC Irvine

In previous work, we have described a novel approach to solving quantum phase space Liouville equations and classical Fokker Planck equations using entangled ensembles of classical trajectories [1-3]. In this poster, we extend the methodology for determining the forces acting on quantum phase space trajectories, and apply the approach to a treatment of both quantum and thermal effects. We investigate the thermally activated escape of a particle from a metastable well and examine the role of quantum mechanics in modifying the classical limit dynamics of this process.

ELECTRON RELAXATION DYNAMICS IN CARBON NANOTUBES

<u>Bradley F. Habenicht</u>, Colleen F. Craig, Oleg V. Prezhdo
University of Washington, Department of Chemistry, Seattle, Wa

We have investigated the electron relaxation dynamics of the zig-zag (7,0) carbon nanotube. The nanotube was modeled using density functional theory, while the interband transitions were described using a fewest switches surface hopping algorithm. The electrons were excited to states corresponding to the second Van Hove singularity in the density of states. Our simulations show a timescale of several femtoseconds for electron relaxation to the band edge, and a complex, multiple time-scale relaxation for holes. Analysis of the autocorrelation functions show that the relaxation is dependent upon both low and high energy Raman modes, depending on the state within the singularity to which the electron is excited. Our timescales are in good agreement with ultrafast spectroscopy experiments.

QUANTIZED HAMILTONIAN DYNAMICS AND STATISTICAL MECHANICS

Eric Heatwole, Oleg V. Prezhdo

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Quantized Hamiltonian Dynamics (QHD) is a simple and elegant approximation to quantum mechanics. Using this formalism it is possible to approximate quantum mechanics by propagating classical equations of motion within an extended phase space. This makes QHD a natural extension of classical molecular dynamics which retains lower order quantum effects such as zero point energy and lower order tunneling. However, it is unclear how to correctly approach statistical mechanics within the QHD framework, since the addition of the extra dimensions leads to an over-counting of states. Several ideas are put forth to deal with this problem: the addition of a weight function, rescaling β (the inverse temperature), and using several versions of the quantum Langevin equation to drive the system to equilibrium by coupling the QHD system to a heat bath.

Calculation of the Quantum Mechanical Thermal Rate Constant for the OH + H$_2$ → H$_2$O + H Reaction Using Flux Autocorrelation Function

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The thermal rate constant of the three-dimensional OH + H$_2$ → H$_2$O + H reaction was computed using flux autocorrelation functions. We have used a time-independent L^2 basis set for a converged calculation for total angular momentum zero and the separable rotation approximation for higher total angular momentum. The basis functions used for the calculations were formed using a product of distributed Gaussian functions and harmonic oscillator functions. Two modes that actively participated in the bond-making process were treated using two-dimensional distributed Gaussian functions, and the remaining modes were treated using harmonic oscillator functions. The eigenvalues and eigenvectors of the Hamiltonian were obtained by solving the resulting generalized eigenvalue equation. The flux autocorrelation function was represented in the basis formed by the eigenvectors of the Hamiltonian and the rate constant was obtained by integrating the flux autocorrelation function for a variationally determined dividing surface. The choice of the final time to which the integration is carried is determined by identifying a plateau region. The potential energy surface is from Wu, Schatz, Lendvay, Fang, and Harding (WSLFH). The calculated thermal rate constant results were compared with values computed by wave packet methods.

POSTER I-22
EXCITED STATE DYNAMICS OF THYMINE AND URACIL
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Department of Chemistry, University of Illinois at Urbana-Champaign

The excited states of DNA bases are of interest because of their role in the formation of UV-induced mutagenic dimers. Although the chemical structures of thymine and uracil differ by only a methyl group, dimers occur mainly in thymine. Ultrafast spectroscopic experiments have shown that there is a significant difference in the excited state lifetimes of these two molecules, which may play a role in explaining the propensity for dimer formation in thymine. We have used theoretical and simulation methods to compare the excited state dynamics of thymine and uracil in an effort to provide a mechanistic explanation for the observed differences in lifetimes. Our simulations are based on ab initio multiple spawning (AIMS) dynamics, where the electronic and nuclear Schrodinger equations are solved simultaneously. The results are further verified by comparison to high-level ab initio electronic structure methods, including dynamic electron correlation effects through multireference perturbation theory, at important points along the dynamical pathways. Our results provide an explanation of the photochemical mechanism leading to nonradiative decay of the electronic excited state in uracil and thymine and some suggestions as to the origin of the different lifetimes.

POSTER I-23
KINETICS OF THE HYDROGEN ABSTRACTION HCO + ALKANE → HCHO + ALKYL REACTION CLASS: AN APPLICATION OF THE REACTION CLASS TRANSITION STATE THEORY

Lam K. Huynh, Thanh N. Truong.
Chemistry Department, University of Utah

This paper presents an application of the Reaction Class Transition State Theory (RC-TST) to predict thermal rate constants for hydrogen abstraction reactions of the type CHO + Alkane → HCHO + Alkyl. We have derived all parameters for the RC-TST method, coupling with a Linear Energy Relationship (LER), so that rate constants for any reaction in this class can be predicted from its reaction energy calculated either at the AM1 semi-empirical or BH&HLYP/cc-pVDZ level of theory. The RC-TST/LER thermal rate constants compare quantitatively well to those available in the literature. Detailed analyses of the results show that the RC-TST/LER method is an efficient method for accurately predicting rate constants for a large number of reactions in this class to within a factor of two compared to those calculated directly from the Transition State Theory with Eckart tunneling corrections.

POSTER I-24
DYNAMICS OF PROLIFERATING CELL NUCLEAR ANTIGEN LOADED ONTO DSDNA

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We have carried out simulations aimed at understanding at the molecular level the protein-protein interactions responsible for binding of structurally diverse repair enzymes to Proliferating Cell Nuclear Antigen (PCNA). PCNA serves as a processivity factor (sliding clamp), encircling DNA at sites of replication and repair. We have studied the interactions of both human and archaeal PCNA (hPCNA and Archaeoglobus fulgidus PCNA) with double stranded DNA and a peptide derived from the C terminal region of the repair enzyme flap endonuclease-1. Multi-nanosecond classical molecular dynamics revealed a rather unusual pattern of correlated motions within and between the three equivalent domains of PCNA evident from the computed covariance matrices. This may suggest that binding to one of the conserved PIM (PCNA interaction motif) regions may influence subsequent binding to the other PIM sites.

Cα cross-correlation matrix for aPCNA
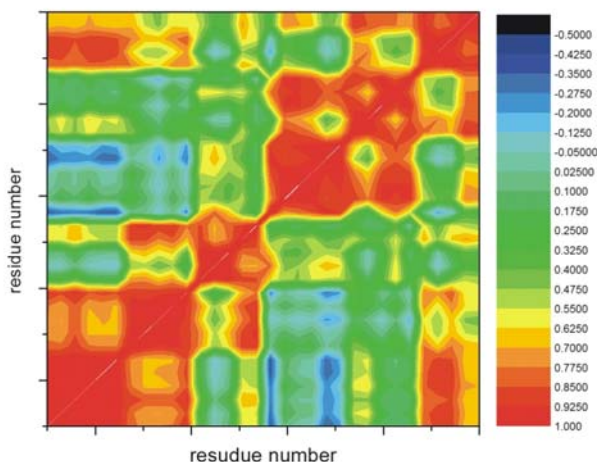
SEMICLASSICAL CORRECTIONS FOR THE HERMAN-KLUK APPROXIMATION

Kenneth G. Kay, Gili Gleisner

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The Herman-Kluk (HK) approximation for the propagator is derived semiclassically for a multidimensional system as an asymptotic solution of the Schrodinger equation. The propagator is obtained in the form of an expansion in Planck's constant, in which the lowest-order term is the HK formula. Thus, the result extends the HK approximation to higher orders in Planck's constant. Examination of the various terms shows that the expansion is a uniform asymptotic series and establishes the HK formula as a uniform semiclassical approximation. Successive terms in the series should allow one to improve the accuracy of the HK approximation near the semiclassical limit in a systematic and purely semiclassical manner, analogous to a higher-order WKB treatment of time-independent wave functions. Numerical calculations of the correction terms are found to support these expectations. Additional approximations that improve the efficiency of such calculations are examined.

POSTER I-26
TITLE: HOT CARRIER RELAXATION IN PbSe QUANTUM DOTS.
Svetlana Kilina
University of Washington

The hot carrier relaxation in PbSe quantum dots has been analyzed with nonadiabatic molecular dynamics simulation. An ab-initio molecular dynamics trajectory is launched for 3ps with initial velocities rescaled to match the room temperature. Nonadiabatic couplings between adiabatic states of electrons and holes are calculated at each time step and used to construct time-dependent Hamiltonian that drives the electron-hole relaxation. The initial excitation on the frequency three times larger than gap was prepared to match the experiment of Klimov et al. [Phys.Rev. Lett. 92, 186601 (2004)], displaying photoinduced charge multiplication effect. The calculated photoexcited electron relaxation time of 2ps is of the same order of magnitude as the one found in experiment. The simulation provides a detailed atomistic picture of the relaxation process.

POSTER I-27
QUANTUM/CLASSICAL MOLECULAR DYNAMICS FOR A DOUBLE WELL COUPLED TO A DISSIPATIVE BATH

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A hybrid quantum/classical molecular dynamics approach is applied to a proton transfer reaction represented by a symmetric double well system coupled to a dissipative bath. In this approach, the proton is treated quantum mechanically, and the bath modes are treated classically. The transition state theory rate constant is obtained from the potential of mean force, which is generated along a collective reaction coordinate with umbrella sampling techniques. The transmission coefficient, which accounts for dynamical recrossings of the dividing surface, is calculated with a reactive flux approach combined with the molecular dynamics with quantum transitions surface hopping method. The calculated rates are consistent with the fully quantum dynamical calculations of Topaler and Makri for this model system. The fundamental effects of dissipation in quantum/classical molecular dynamics simulations are analyzed. These results have important implications for applications to hydrogen transfer reactions in solution and proteins.

ACTC 2 0 0 5

FREE ENERGY PROFILE ALONG A DISCRETIZED REACTION PATH VIA THE HYPERPLANE CONSTRAINT FORCE AND TORQUE

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We derive a convenient computational approach for evaluation of the free energy profile (FEP) along some discretized path defined as a sequence of hyperplanes. A hyperplane is fully specified by any of its point and a tangent vector. The FEP is obtained as an integral of two components. The translational component of the free energy is computed by integrating the hyperplane constraint force. The rotational component is evaluated via the hyperplane torque. Both ingredients—the constraint force and the hyperplane torque—are evaluated on each hyperplane independently. The integration procedure utilizes a set of reference points defining a point of rotation on each hyperplane, and these points can be chosen before or after the sampling takes place. A shift in the reference points redistributes the FEP contributions between the translational and rotational components. For systems where the FEP is dominated by the potential energy differences, reference points residing on the minimum energy path present a natural choice. We demonstrate the validity of our approach on several examples. In each case, the rotational component of the FEP represents a sizable contribution to the total FEP, so ignoring it would yield clearly incorrect results.

INTERFACIAL CHARGE-SE PARATION DYNAMICS IN TYPE II ORGANIC POLYMER PHOTOVOLTAIC SYSTEMS

Eric R Bittner

University of Houston

In this paper we consider the essential electronic excited states in parallel chains of semiconducting polymers that are currently being explored for photovoltaic and light-emitting diode applications. In particular, we focus upon various type II donor-acceptor heterojunctions and explore the relation between the exciton binding energy to the band off-set in determining the device characteristic of a particular type II heterojunction material. As a general rule, when the exciton binding energy is greater than the band off-set at the heterojunction, the exciton will remain the lowest energy excited state and the junction will make an efficient light-emitting diode. On the other hand, if the off-set is greater than the exciton binding energy, either the electron or hole can be transferred from one chain to the other. Here we use a two-band exciton to predict the vibronic absorption and emission spectra of model polymer heterojunctions. Our results underscore the role of vibrational relaxation and suggest that intersystem crossings may play some part in the formation of charge-transfer states following photoexcitation in certain cases.
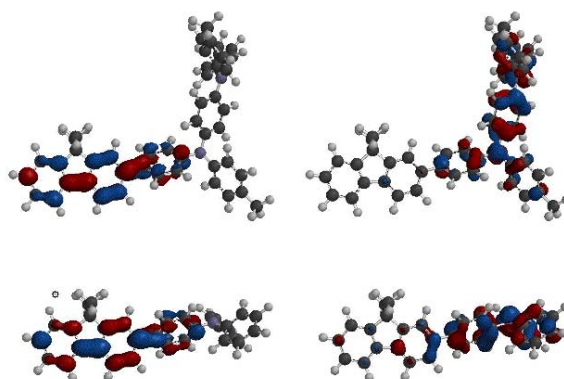
FIG. 6: (color onlne) Semiempirical (PM3) LUMO (left) and HOMO (right) wave functions for PFB (top) and TFB (bottom) monomer

POSTER I-30
***AB INITIO* CHARACTERIZATION OF ELECTRON TRANSFER COUPLING IN PHOTO-INDUCED SYSTEMS**

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To investigate electron transfer (ET) couplings for photo-induced electron transfer reactions, we proposed and tested the use of *ab initio* quantum chemistry calculation for excited states with generalized Mulliken-Hush (GMH) method. Configuration-interaction Singles (CIS) calculation was performed to model the locally excited (LE) and charge-transfer (CT) states. When calculated in vacuum, the CT state energy may be too high, which allows unrealistic mixing with other high-lying locally-excited states, leading to overestimation in ET coupling. We show that the image charge approximation (ICA), as a simple solvent model, can be used to lower the energy of the CT state. Consequently the ET couplings are close to experimentally inferred values. We found that the coupling strength is weakly dependent on the details of the solvent model, indicating the validity of the Condon approximation. Therefore, a trustable coupling can be obtained via this CIS-GMH scheme, with ICA as a tool to improve the result as well as a quality check. We have tested our method to systems that were studied experimentally before. Our results, both the coupling magnitudes and the exponential-decay slopes, are in good agreement with experimental values.

POSTER I-31
DNA CHARGE TRANSFER: AN ATOMISTIC MODEL
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In this work, we address the phenomenon of charge transport in DNA using a simple, but chemically specific approach intimately related to the Su-Schrieffer-Heeger model. The emerging potential energy surface for hole transport exhibits basins of attraction which correspond to small polaronic structures mainly localized on individual bases. Thermally activated hopping between this states is analyzed using Marcus' theory of charge transfer. Our results are fully compatible with the conjecture of long-range charge transfer in DNA via two competing mechanisms, and the computations provide the corresponding charge-transfer rates both in the short-range superexchange and in the long-range hopping regime as the output of a single atomistic theory.[1] Finally, the model allows the computation of the transport properties of systems containing modified bases and of more complex arrangements of base pairs as an additional element of verification.[2, 3]
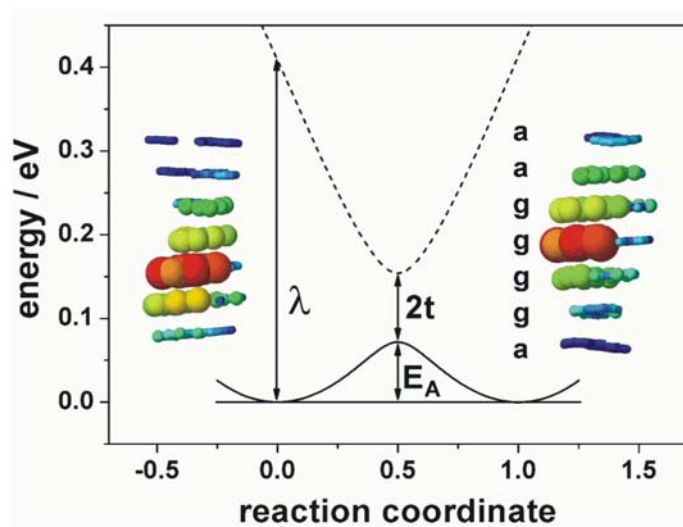
[1] T. Cramer, S. Krapf, T. Koslowski, J. Phys. Chem. B 2004, 108, 11812.
[2] T. Cramer, S. Krapf, T. Koslowski, Phys. Chem. Chem. Phys. 2004, 6, 3160.
[3] T. Cramer, A. Volta, A. Blumen, T. Koslowski, J. Phys. Chem. B 2004, 108, 16586.

**AB INITIO NONADIABATIC MOLECULAR DYNAMICS OF THE ULTRAFAST
ELECTRON INJECTION ACROSS THE ALIZARIN-TIO$_2$ INTERFACE**

Walter R Duncan, William M Stier, Oleg V Prezhdo
University of Washington Chemistry Department

The observed 6 fs photoinduced electron transfer (ET) from the alizarin chromophore into the TiO$_2$ surface is investigated by *ab initio* nonadiabatic molecular dynamics in real-time and at the atomistic level of detail. The system derives from the dye-sensitized semiconductor Graetzel cell. In contrast to the typical Graetzel cell systems, where molecular donors are in resonance with a high density of semiconductor acceptor states, TiO$_2$ sensitized with alizarin presents a novel case in which the molecular photoexcited state is at the edge of the conduction band (CB). Thermal fluctuations of atomic coordinates are particularly important both in generating a nonuniform distribution of photoexcited states and in driving the ET process. The nonadiabatic simulation resolves the controversy regarding the origin of the ultrafast ET by showing that while ultrafast transfer is possible with the nonadiabatic mechanism, it proceeds mostly adiabatically in the alizarin-TiO$_2$ system. The simulation indicates that the electron is injected into a localized surface state within 8 fs and spreads into the bulk on a 100 fs or longer timescale. The molecular architecture seen in the alizarin-TiO$_2$ system permits efficient electron injection into the edge of the CB without the energy loss associated with injection high into the CB.

POSTER I-33
FULL CI MIXED QUANTUM-CLASSICAL MD SIMULATIONS OF SOLVATED SODIDE

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Department of Chemistry & Biochemistry, UCLA

We explore the equilibrium properties of solvated sodide (Na-) at 300K in SPC-Flex water using mixed quantum-classical adiabatic molecular dynamics (MD) in order to characterize its charge transfer to solvent (CTTS) band. In order to extend previous simulations on this system in which only one of the valence electrons of sodide was treated quantum mechanically, we use an efficient real-space full configuration interaction (FCI) method to generate two-electron wavefunctions at each MD timestep. The proper treatment of both valence electrons introduces more bound excited states and modifies the ground state properties. MD simulations on a solvated sodium "atom" system were also performed which displays marked differences to the sodide in that it dissociates to a solvated sodium cation and a solvated electron under ambient conditions. The potential of mean force for the sodium atom system is mapped out and the role of thermal fluctuations involved in dissociation is discussed.

POSTER I-34
ANALYSIS OF DYNAMICAL ASPECTS OF PROTON-COUPLED ELECTRON TRANSFER REACTIONS

Elizabeth Hatcher, Alexander Soudackov, Sharon Hammes-Schiffer
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We present a general theoretical formulation for proton-coupled electron transfer (PCET) reactions in the framework of a molecular representation of the environment. This formulation describes the proton donor-acceptor vibrational mode and the solvent dynamically. The transferring hydrogen, the active electrons and, in some cases, the donor-acceptor mode are treated quantum mechanically. The nonadiabatic rate constant is expressed in terms of a time-dependent probability flux correlation function and accounts for correlations between the fluctuations of the proton donor-acceptor distance and the nonadiabatic PCET coupling. The time correlation functions in the rate expression can be calculated from classical molecular dynamics simulations on the reactant vibronic surface. The results for model PCET systems immersed in water are presented. We analyze the impact of varying the proton donor-acceptor vibrational frequency, the solvent reorganization energy, and the distance dependence of the nonadiabatic coupling. These studies elucidate the fundamental dynamical aspects of PCET reactions.

POSTER I-35
RELATIVE CONTRIBUTION OF INCOHERENT HOPPING AND COHERENT SUPEREXCHANGE CHARGE TRANSFER MECHANISM WITHIN SHORT DNA SEQUENCES IN THE PRESENCE OF AT BASE PAIR BRIDGES

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Path integral scheme is employed to short DNA sequences to determine the type of governing charge transfer mechanism. The system is modeled based on the tight-binding system-bath Hamiltonian with three electronic states, i.e., a GC single pair as a donor, AT base pairs as bridges, and a GC triple pair as an acceptor, coupled with a dissipative bath that represents the DNA backbone and solvents. Relative contribution of incoherent hopping, coherent superexchange and partially coherent hopping pathways to the whole charge transfer process is evaluated using the recently developed on-the-fly filtered propagator path integral method. Role of potential parameters and solvents are discussed.

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POSTER I-36
EXCITATION ENERGY TRANSFER RATE CONSTANTS IN MESO-MESO LINKED Zn(II) PORPHYRIN ARRAYS WITH ENERGY ACCEPTING 5,15-BISPHYENYLETHYNYLATED Zn(II) PORPHYRIN

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The excitation energy transfer process occurring in energy donor-acceptor linked porphyrin array system is theoretically modeled and simulated using the on-the-fly filtered propagator path integral method. The compound consists of an energy donating meso-meso linked Zn(II) porphyrin array and an energy accepting 5,15-bisphenylethynylated Zn(II) porphyrin, in which the donor array and the acceptor are linked via a 1,4-phenylene spacer. Systems with one to twenty four porphyrin units in the donor array are modeled with the two-state tight-binding model that is coupled to dissipative baths. Real-time path integral simulations provide the time-evolution of the site population and, the excitation energy transfer rate constants are determined. Simulations and experiments show an excellent agreement indicating that the path integration is a useful tool to investigate the energy transfer dynamics in molecular assemblies.

DAMAGE TO DNA BY VERY LOW ENERGY ELECTRONS

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We examined the possibility that very low-energy electrons could induce strand breakes in DNA. Specifically, we suggested that electrons in the 1 eV range can attach to a low-lying antibonding orbital of one of DNA's bases and that intramolecular electron transfer can occur allowing the attached electron to migrate through the neighboring ribose group and onto a terminal phosphate unit as a C-O bond is broken and a strand break occurs.

We probed the mechanism of processes like this using various fragments of DNA (a cytosine nucleotide, a CCC codon containing three such nucleotides π-stacked, a fragment with thymine (T) replacing cytosine). On the basis of our work we suggest the following:

1. electrons with energies even below 1 eV could cause SSBs,

2. the barrier on the anion surface is caused by an avoided crossing between the base $\pi *$ and C-O $\sigma*$ anion states,

3. these barriers differ when thymine replaces cytosine or when π-stacking is included,

4. attachment to the phosphate P=O $\pi *$ orbital is more endothermic than attachment to a base $\sigma *$ orbital,

5. solvation stabilizes the $\sigma *$ anion and renders it not susceptible to detachment,

6. the barriers typical of our findings yield SSB formation rates as high as 105 s^{-1}.

INTERACTION OF WATER MOLECULES WITH THE Pt(111) SURFACE

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The interaction of water molecules with the Pt(111) surface has been studied using DFT and the PW91 functional. Early stages of ice crystal nucleation and the possibility of dissociation have in particular been addressed. A water molecule sits on top of a Pt atom with binding energy of 0.30 eV. Diffusion is predicted to become active on the time scale of seconds at 43 K which is in reasonable agreement with recent experimental results of Kay and coworkers [JCP 2004]. The binding at steps and kinks on the Pt(111) surface is substantially stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively. The lowest energy configuration has the water molecule sitting on top of edge or kink atoms. At low coverage, clusters of water molecules would, therefore, be expected to line the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. [PRL 1996]. While the dissociation of water molecules is uphill by 0.72 eV on the flat terrace, it is almost neutral energetically at the step but has an activation energy barrier of 0.94 eV (see figure below). The dissociation will, however, not occur thermally because desorption will occur more readily.

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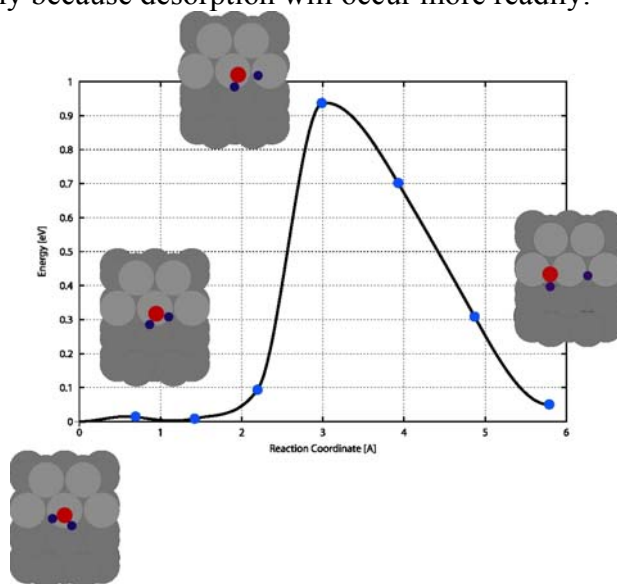
POSTER I-39
QUANTUM COMPUTING FOR QUANTUM CHEMISTRY

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The calculation time for the energy of atoms and molecules scales exponentially with system size on a classical computer, but polynomially using quantum algorithms. Calculations of the H_2O and LiH molecular ground-state energies have been carried out on a quantum computer simulator using a recursive phase estimation algorithm. Only four quantum bits are required for the read-out register, in addition to those required to store the wavefunction. The number of quantum bits required is linear with the size of the molecule studied. The algorithm and its applications, as well as prospects for its physical implementation will be presented.
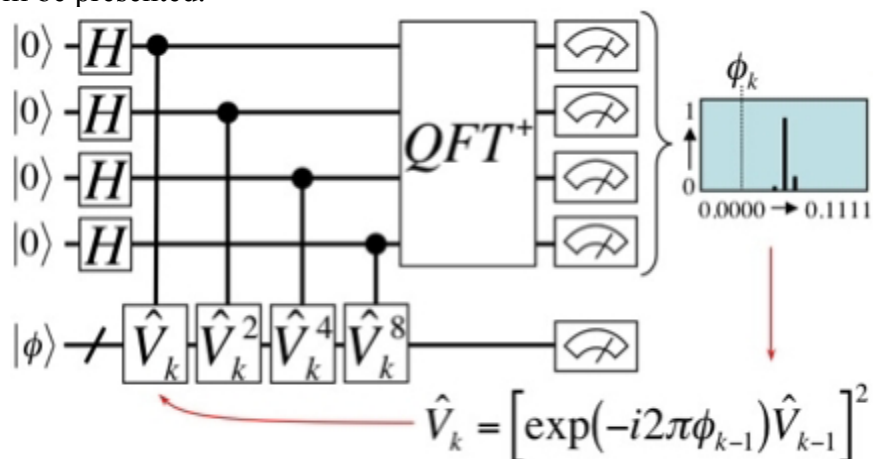
$$\hat{V}_k = \left[\exp(-i2\pi\phi_{k-1})\hat{V}_{k-1} \right]^2$$

ACTC 2 0 0 5

A SPARSE ALGORIT HM FOR THE EVALUATION OF THE LOCAL ENERGY IN QUANTUM MONTE CARLO

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A new algorithm is presented for the sparse representation and evaluation of Slater determinants in the quantum Monte Carlo (QMC) method. The approach, combined with the use of localized orbitals in a Slater-type orbital basis set, significantly extends the size molecule that can be treated with the QMC method. Application of the algorithm to systems containing up to 390 electrons confirms that the cost of evaluating the Slater determinant scales linearly with system size.

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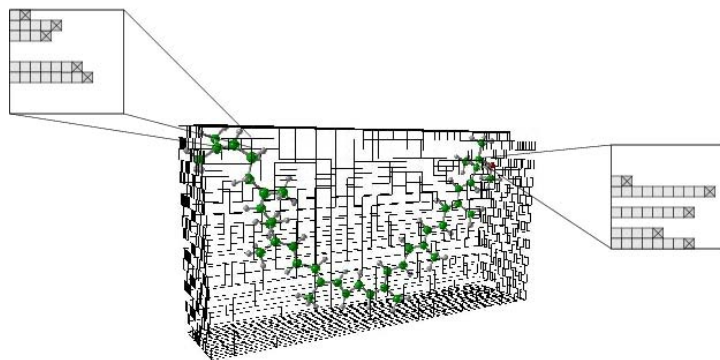
ZORI 1.0: A PARALLEL QUANTUM MONTE CARLO ELECTRONIC STRUCTURE PACKAGE

Alan Aspuru-Guzik[1], Romelia Salomon-Ferrer[1,2], Brian Austin[1,2], Raul Perusquia-Flores[1], Mary A. Griffin[3], Ricardo A. Oliva[4], David Skinner[5], Dominik Domin[1], William A. Lester, Jr.[1,2]

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The Zori 1.0 software package has been written for quantum Monte Carlo simulations of the electronic structure of molecules. Zori performs variational an diffusion Monte Carlo calculations as well as correlated wave function optimization. The memory requirements for Zori are very low and CPU demands for evaluating the local energy scales linearly with system size for Slater determinants and quadratically for correlation functions, allowing simulation of molecules with several hundred electrons. The parallel strategy for Zori scales to the 1000 processor regime.

DFT STUDY ON A LIGHT-HARVESTING MOLECULAR DEVICE

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We investigate the photo-induced charge separation process in a molecular triad containing a porphyrin, carotenoid and C60 molecule which act as chromophore, electron donor and acceptor, respectively [P.A. Liddell et al., J. Am. Chem. Soc. 119, 1400 (1997)]. The photo-induced charge separation process results in a large dipole moment for the charge-separated excited state. Our calculations were done using density-functional theory as implemented in the NRLMOL code to optimize the triad geometry and to determine the electronic structure of the ground state and metastable charge-separated states. We find that the molecular states are more or less localized on a given component of the triad and that excitations between the molecular levels can result in a huge dipole moment of about 180 Debye. The transition probabilities between various states were obtained from Einstein's A and B coefficients which were used in a classical Monte-Carlo simulation to estimate the time constants. Our calculations show the importance of local electric
fields and the results show that this molecule can be useful for solar-cell technologies.

POSTER I-43
ANALYTICAL GRADIENTS OF THE TIME DEPENDENT DENSITY FUNCTIONAL (TDDFT) EXCITATION ENERGIES FOR CONTINUUM SOLVATION MODELS: THEORY AND APPLICATIONS TO GEOMETRIES AND PROPERTIES OF EXCITED STATES.

Roberto Cammi[1], Bendetta Mennucci[2], Jacopo Tomasi[2], Giovanni Scalmani[3], Mike Frisch[3]
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[2] University of Pisa, ITALY,
[3]Gaussian Inc.

The analytical gradients theory of the TDDFT excitation energies is extended to molecules in solution described within the Polarizable Continuum Model (PCM) framework. The relevant aspects of this extension are discussed and numerical applications to the study of geometries and one-electron properties of the lowest excited states of 4-dimethylamino benzonitrile (DMABN) and of para-nitro aniline (PNA) in various solvents are presented.

EXCITED ELECTRONIC STATES OF SMALL WATER CLUSTERS

Daniel M. Chipman

Radiation Laboratory, University of Notre Dame

For an isolated gas phase water monomer, it is well known that the lowest excited state is strongly dissociative upon OH stretching. However, we establish with electronic structure studies on small water clusters that when the OH moiety is hydrogen bonded to a neighboring water molecule the lowest excited singlet and triplet state each becomes nondissociative for stretching of an OH bond. This may serve as a basis to interpret recent experimental evidence that suggests a significant lifetime for excited water in irradiated thin ice films. It also raises the intriguing possibility of energy transport over substantial distances in both liquid water and ice by migration of a neutral exciton.

POSTER I-45
SIXTEEN VALENCE-ELECTRON SPECIES CONTAINING BORON: [B, N, S, H$_2$].

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In order to gain new insight into the structure and bonding of boron-containing molecules, we have recently been investigating fundamental sixteen valence-electron species with the general formulas [B, X, Y, H$_2$] and [B, X, Y, H$_3$]$^+$. In our most recent work, the investigation has been extended to the [B, N, S, H$_2$] system. Intuition suggests that [B, N, S, H$_2$] has the structure H$_2$NBS, a boron analog of the well-known cumulenes H$_2$CCCH$_2$ and H$_2$CCO. However, high level quantum chemical calculations disclose multiple minima on the singlet potential energy surface of [B, N, S, H$_2$]. The calculations yield a variety of possible structures for this species, including the expected acyclic, cyclic and hydrogen-bonded. Barriers to the rearrangements between isomers have also been evaluated. AIM and NBO analyses have been carried out to gain an understanding of the bonding in the various isomeric forms of [B, N, S, H$_2$].

ELECTROSTATIC COMPARISON OF SEVERAL WATER MODELS
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Department of Chemistry University of Pittsburgh

An accurate description of the electrostatic potential of the water monomer is required to properly describe the interactions between water monomers in a water cluster. In this work the electrostatic potentials from several water models have been compared to those from MP2 and QCISD calculations with basis sets as large as aug-cc-PVQZ basis set. The implications for one electron models for describing the binding of an excess electron to water clusters is discussed.

VIBRATIONAL ANH ARMONICITY IN THE $(H_2O)_N$, N = 2-6, WATER CLUSTERS

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The contribution of vibrational anharmonicity to the vibrational frequencies of small water clusters $[(H_2O)_n$, n=2-6] is investigated by means of the second-order vibrational perturbation theory approach (VPT2) in conjunction with the Becke3LYP and MP2 electronic structure methods. The anharmonicity corrections are combined with corrections to the harmonic frequencies due to high-order electron correlation effects calculated using the QCISD method, to obtain theoretical estimates of the OH stretch frequencies. The resulting frequencies are found to be in excellent agreement with experiment. Our results also allow us to examine the contribution of vibrational anharmonicity to the binding energies of the clusters.

A RESOLUTION-OF-THE-IDENTITY IMPLEMENTATION OF THE LOCAL TRIATOMICS-IN-MOLECULES MODEL FOR SECOND-ORDER MØLLER-PLESSET THEORY WITH APPLICATION TO ALANINE TETRAPEPTIDE CONFORMATIONAL ENERGIES

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In this work, we incorporate the resolution-of-the-identity (RI) approximation into the theoretical framework of the local triatomics-in-molecules (TRIM) MP2 model. The resultant model, RI-TRIM MP2, emerges as a robust fourth-order methodology that extends the regime of practical MP2 calculations. With RI-TRIM MP2, correlation energy corrections can easily be obtained for systems that contain more than 125 heavy atoms with a computational timing cost less than that of the prerequisite SCF procedure and popular DFT alternatives. In this work, the chemical performance of RI-TRIM MP2 is numerically assessed against untruncated RI-MP2 and DFT (B3LYP) in determining the relative energies of 27 different alanine tetrapeptide conformations at the cc-pVXZ (X = D, T, and Q) levels and the results are extrapolated to the complete basis set limit. As the quality of the basis set employed increases, we report a significant reduction in the error introduced by the RI-TRIM approximation—at the cc-pVDZ level the RMS relative error was found as 0.192 kcal/mol and is decreased to an almost negligible 0.040 kcal/mol at the complete basis set limit. The findings reported herein also provide the first computational evidence demonstrating that the TRIM model approaches exactness as the one-particle basis approaches completeness.

POSTER I-49
DIFFUSIO N MONTE CARLO FOR ENERGIES OF HYDROCARBONS

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Chemical modeling of fuel and flame combustion requires highly accurate thermodynamic values for the involved hydrocarbon molecules and radicals. To understand the accuracy of the diffusion Monte Carlo (DMC) method for combustion related systems a systematic DMC study of the atomization energies, heats of formation and bond dissociation energies for 22 small hydrocarbons was performed using simple correlated single determinant guiding functions. The systems studied include hydrocarbons ranging from one to four carbons and include radicals with diverse bonding arrangements. Diffusion Monte Carlo's mean absolute deviations from experiment (ε_{MAD}[**]) are 1.9 kcal/mol for atomization energies, 2.2 kcal/mol for heats of formation at 298K, and 2.5 kcal/mol for bond dissociation energies. DMC is superior to the density functional method B3LYP ($\varepsilon_{MAD} = 4.2$kcal/mol) for calculation of bond dissociation energies and of similar quality to that of CBS-Q ($\varepsilon_{MAD}= 2.0$kcal/mol). Although significantly more computational expensive than other ab initio methods for small molecules, DMC's favorable N^3 scaling and intrinsic parallelism enables its use for large systems not practical with other high accuracy ab initio methods. Furthermore, improvements in DMC energies are anticipated by using multi-determinant guiding functions.

[**] $\varepsilon_{MAD} = \Sigma \mid \text{Energy}_{experimental} - \text{Energy}_{calculated} \mid$

AN IMPROVED HYBRID EXCHANGE KERNEL FOR CHARGE-TRANSFER STATES IN TD-DFT

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Recently, the poor behavior of TD-DFT as regards charge-transfer (CT) excited states has been discussed in the literature. Dreuw et al [*J. Chem. Phys.* **119** 2943 (2003)] pointed out that, in TD-HF, the response of the exchange operator accounts for the Coulombic rise of CT state energies as a function of the distance over which an electron is transfered. In TD-DFT there is no replacement for this effect and the correct CT behavior is lost.

Tawada et al [*J. Chem. Phys.* **120** 8425 (2004)] proposed using an HF-like exchange operator in DFT and TD-DFT, but with a modified integral kernel: $\mathrm{erf}(\omega r)/r$. In our work, we improve on this general idea by modifying the kernel further: $(1/2)[\mathrm{erf}(\omega(r+r_0))+\mathrm{erf}(\omega(r-r_0))]/r$. For a given r_0, an ω can be chosen such that the kernel is extremely flat near the origin, out to approximately r_0. This approach does not modify the energy of any excitations which take place inside a radius of r_0, but qualitatively corrects the energy of CT states.

Other additions to the kernel are being pursued to improve quantitative accuracy. This method relies on non-trivial evaluation of modified two-electron integrals. These integrals with an explicit cut-off radius may find other uses.

A THEORETICAL STUDY OF THE EFFECT OF COORDINATING SOLVENT ON ION PAIR SUBSTITUTION REACTIONS.

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Solvent effects on ionic S_N2 reactions have been extensively studied. Even though ion pairing has been observed and affect the S_N2 reactivity, studies of ion pair reactions are rare and such reactions in solution have not been explored computationally. Solvent effects on ion pair reactions have been theoretically studied by analyzing reactions of alkyl halides, RX and LiX (X=F,Cl,Br) with coordinated solvent, dimethyl ether.

The computations led to two transition structures (C2v-TS and Cs-TS) for the methyl systems (Figure1A).The path of lower energy barrier is through the Cs-TS for fluoride. The difference between the two TSs is reduced for chloride and the C2v-TS becomes more favored for bromide. A comparison of X-C-X bond angle in C2v-TSs shows an order of Br>Cl>F (103.258, 98.527, 83.317). It implies more relaxed TS for bromide with longer bond distances and large X-C-X bond angle. For a deeper understanding of the mechanism, IRC calculations have been carried out. Such calculation on higher alkyls generated an eclipsed system on one end and staggered conformation in the other, which is contrary to the principle of microscopic reversibility (Figure1B). All these results will be presented in detail.
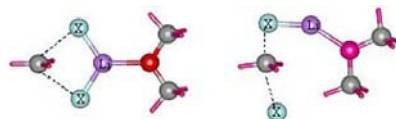
Figure 1A
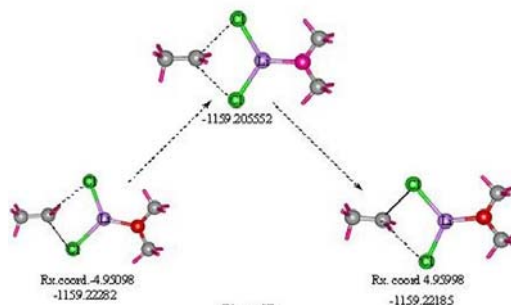
Figure 1B

ELE CTRON HOLES IN AMORPHOUS SILICA CAN INDUCE DAMAGE

Margaret A. Gabriel[1], Kiril Tsemekhman[1], Renée M. Van Ginhoven[1,2], L. René Corrales[2], Eric J. Bylaska[2], Hannes Jónsson[1,3]

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Electron holes in amorphous SiO_2 have been studied using DFT with the PBE0 hybrid functional. The system consists of 72 atoms and has periodic boundary conditions. The PBE0 functional, which includes exact exchange, was implemented using maximally localized Wannier functions to make the calculations efficient. Several self-trapped holes (STH) with localized spin density were identified. The most localized ones have the hole mostly trapped in a non-bonding p-orbital on a single O-atom with stretched bonds. In the least localized states, the spin density is shared between two O-atoms with a common Si-neighbor. The O-Si-O bond angle is then reduced by as much as 16 degrees. States intermediate between these two have also been found. The calculated hyperfine splitting is in good agreement with ESR measurements of Griscom. Further displacement of one of the O-atoms can lead to a broken Si-O bond configuration with lower energy. In one sample out of ten, the relaxation of such a configuration after recapture of an electron resulted in a damaged silica framework and formation of coordination defects which represent a relaxed O-interstitital-vacancy pair. We note that GGA functionals fail to reproduce the localized hole states.
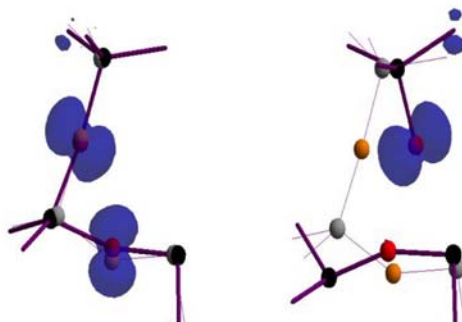
Left: Self-trapped hole (red spheres O-atoms, black Si-atoms, blue lobes spin density) superimposed on the original glass structure (orange spheres O-atoms, grey Si-atoms). The spin density is shared between two oxygen atoms with a common Si-neighbor. The O-Si-O angle decreases by 16 deg.

Right: A broken bond structure that is 0.25 eV lower in energy. Now the spin density is localized mainly in one O-atom. Relaxation of this structure in the singlet state results in damaged Si-O network.

DFT STUDY ON HYDROGEN BOND PROMOTED DIELS-ALDER CYCLOADDITIONS. REACTION MECHANISM AND ORIGINS OF ENANTIOSELECTIVITY

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Rawal and coworkers reported the synthesis of diene 3-(tertbutyldimethylsiloxy)-1-dimethylamino-1,3-butadiene. This diene is 25 times more reactive than Danishefsky's diene with methacrolein.[1,2] The second-order rate constants of the reaction with methacrolein in chloroform-d, acetonitrile-d_3, and benzene-d_6 (1.2×10^{-2}, 2.9×10^{-3} and 2.0×10^{-3}, respectively) indicate that the reaction is slightly accelerated by polar solvents.[3] The increased reaction rate in chloroform was attributed to a C-H·;·;·O hydrogen bond.[3]

B3LYP/6-31G(d) calculations show that the nature of the mechanism of the cycloaddition with acrolein depend on the number of hydrogen bonds involved in the catalytic process. The uncatalyzed reaction and the reaction catalyzed by one MeOH both proceed by asynchronous but concerted pathways. Introduction of a second alcohol molecule produces a change in the reaction mechanism to a stepwise mechanism pathway, involving a zwitterionic intermediate.[4]

Acceleration by chiral diols has been exploited for asymmetric catalysis. TADDOLs and BAMOLs catalyze Diels-Alder cycloadditions of Rawal's diene with aldehydes and ketones with high ee.[5,6,7] Transition state geometries for the reaction involving TADDOL catalysis were optimized with Morokuma's IMOMO method with a combination of B3LYP/6-31G(d) and AM1 levels of theory.[8]

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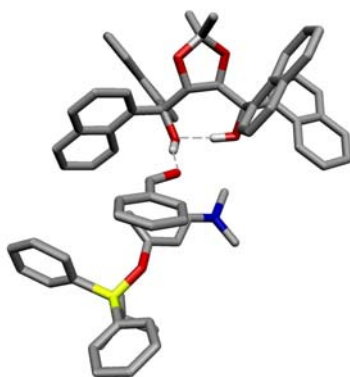
MULTIGRID ORBITAL-FREE DENSITY FUNCTIONAL THEORY

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The advantage of Orbital-Free Density Functional Theory (OFDFT) over traditional Density Functional Theory methods is that the computational effort can be made easily to scale linearly with system size. OFDFT with periodic boundary conditions has been shown to work well for metallic, nearly-free electron-like systems. Certain systems, such as single isolated nanowires or screw dislocations in bulk crystals, are not conveniently represented in reciprocal space without significantly added computational cost. To study these systems, a method to perform OFDFT in real space is desirable. Other benefits of real-space OFDFT, such as ease of parallelization, utility in embedding methods and the possibility of local refinement, also exist.

Here, we present our efforts toward an implementation of OFDFT in real space. We have chosen to use the fast linear iterative solver known as the multigrid method, which is based on a multiscale paradigm, to minimize the electronic energy. It uses multiple grids, each with different mesh sizes, to solve for different components of a problem. We will present preliminary results, comparing to our earlier Fourier-based conjugate gradient OFDFT code.

A PARALLEL ELECTROMAGNETIC MOLECULAR LOGIC GATE

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A theoretical study of transport through a three-terminal molecular ring in the presence of a magnetic field is presented. The physical principles necessary to achieve logic operations based on the Aharonov-Bohm effect are discussed. We show that a proper combination of a gate potential and a realistic magnetic field can be used to obtain parallel logic operations such as AND and AND+NOT.
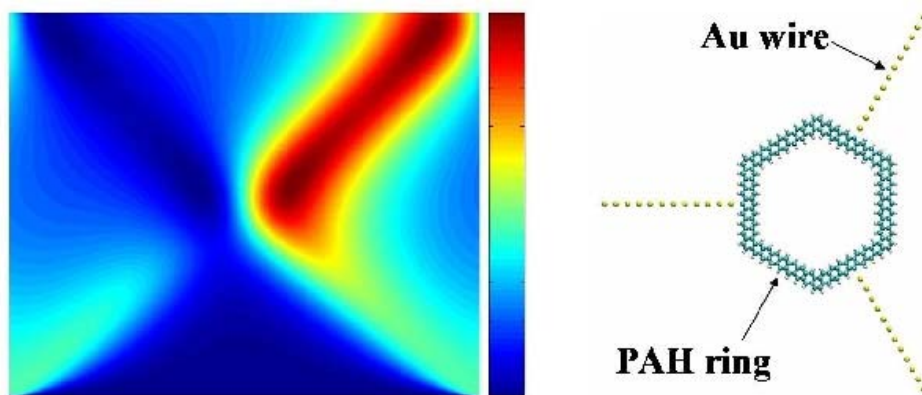
EFFECTIVE LINEAR SCALING SCHEME FOR THE KOHN-SHAM COULOMB PROBLEM

<u>Gongyi Hong</u>, Thorsten Ritz

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Calculation of Coulomb repulsion energy for a charge distribution dominates the cost in the Kohn-Sham density functional theory (DFT) calculation. Linear scaling of computational cost with system size is an essential prerequisite for DFT-based calculation of processes involving systems of hundreds of atoms as frequently encountered in descriptions of protein co-factors. Here we present a linear scaling scheme of calculating Coulomb energy with high performance. Furthermore, the major time-consuming steps in this approach can be merged into the numerical integration of the exchange-correlation energy, and consequently the bottle-neck of calculating Coulomb energy is substantially reduced.

LOCALIZED ELECTRONIC STATES AROUND A SINGLE KONDO IMPURITY

Patrick Huang[1], Emily A. Carter[1,2]

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Scanning tunneling microscopy (STM) experiments of a single, magnetic adatom on non-magnetic metal surfaces reveal intriguing features in the electronic structure around the magnetic adatom [e.g. Manoharan et al., Nature 403, 512 (2000)]. This has been interpreted as the formation of a "Kondo cloud", in which the localized d-electrons on the magnetic adatom hybridize with the metal band states, to form an extended open-shell singlet near the Fermi level.

We present a first-principles study of the electronic structure of a single Co adatom on Cu(111). Our approach is based on an embedding strategy [Kluner et al., PRL 86, 5954 (2001)] in which the Co adatom and nearest neighbor Cu atoms are regarded as a metal cluster embedded in a periodic slab background. The total Co/Cu(111) system is treated using density functional theory (DFT), which allows for a mean-field treatment of an extended periodic system. Using the DFT density from the total system, the effect of the background is cast into an effective embedding potential acting on the cluster. Hartree-Fock and explicitly-correlated theories (i.e. configuration interaction) are subsequently applied to the embedded cluster in the presence of the embedding potential.

POSTER I-58
THE RESOLUTION OF IDENTITY ATOMIC ORBITAL LAPLACE-TRANSFORMED
SECOND-ORDER MOLLER-PLESSET THEORY FOR PERIODIC SYSTEMS

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A new algorithm for second-order Moller-Plesset perturbation theory (MP2) is presented. We introduce the resolution of identity in previously developed atomic orbital Laplace-transformed method to reduce two electron integrals generation and transformation steps scalings. The splitting of the correlation energy on the exchange and Coulomb parts allows us to compute them more efficiently. The exchange contribution due to its short-range nature can be done by regular contraction of integrals with efficient screening. The inherent spatial decay properties of the density matrices and the atomic orbital basis allows us to make scaling of exchange contribution calculation near-linear with respect to the system size. For the Coulomb contribution we exploit the Gaussian fast multipole method which scales linearly asymptotically. As benchmark periodic MP2 calculations we present energy of unit cell and band gap results on trans-polyacetylene, bulk neon, and boron nitride.

PROBING THE RESPONSE OF ATOMIC CLUSTERS TO ELECTRIC FIELDS VIA DENSITY FUNCTIONAL THEORY-BASED POLARIZABILITY CALCULATIONS

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Our group is carrying out density functional theory (DFT) based studies of the electric polarizability of atomic clusters, using a finite-field method. We have applied the method to silicon clusters, where we have explored the dependence of the polarizability on cluster shape. We find that the polarizability is systematically larger for prolate vs compact shapes. By examining this difference as a function of size, we find that both classes of structures exhibit metallic behavior in response to external fields. We have also studied Cu clusters, to better understand a recent experiment (Knickelbein, J. Chem. Phys. 120, 10450 (2004)) where an unusually strong response for small Cu clusters was observed. Our results establish theoretical ";error bars"; for the calculated polarizabilities and show that the observed response must include effective contributions, for example from permanent cluster dipole moments. Finally, we are developing a scheme for decomposing the total cluster polarizability into contributions from individual atoms. The scheme naturally produces a charge transfer (metallic) and atomic dipole (non-metallic) component for each atom. We use the method to compare size-related trends in the response from Na, Si and Ar clusters.

POSTER I-60
FUNCTIONAL-GROUP-BASED ELECTRONIC STRUCTURE METHODS

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The electronic properties of molecular functional groups (methyl, benzyl, etc.) are generally conserved across different molecules. However, atomic basis sets for ab initio calculations use the same electronic variational space on an element regardless of the functional group it is in. Semiempirical methods (AM1, PM3) also generally do not incorporate functional group information. We explore methods for performing accurate, inexpensive calculations on molecules by parameterizing functional-group-specific basis sets and semiempirical Hamiltonians. Functional group (FG) basis sets are designed to include only those electronic degrees of freedom that are important in a "training set" of representative molecules. The basis functions are contractions over a large atomic basis on all atoms in the group. Contraction coefficients are obtained from principle component analysis of the group's calculated electron densities in the training set. When the functional group's chemical identity is maintained (e.g. no bonds in the group are broken), FG basis sets provide accuracies similar to a large atomic basis while using a smaller number of basis functions. FG semiempirical Hamiltonians are also parameterized to reproduce the results of ab initio calculations on representative molecules.

RESONANCE RAMAN SCATTERING OF MOLECULES FROM RESONANCE POLARIZABILITY DERIVATIVES

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In Raman Scattering measurements where the wavelength of the excitation laser is close to an electronic excitation of the molecule the intensity of the signal is enhanced by a factor of up to 10^4-10^6. [1] This Resonance Raman Scattering (RRS) is an important tool in analytic chemistry due to a higher selectivity than Normal Raman Scattering (NRS). In this work we will present a method to calculate the RRS of molecules from resonance polarizability derivatives within time-dependent density functional theory. It is an extension of a method to calculate the (non-) resonance polarizabilities by including a finite lifetime of the electronic excited states.[2] The method is a short-time approximation and will in the non-resonance case (NRS) be identical to the standard theory of Placzek. We will present some initial results for small molecules and compare with results obtained from excited-state gradients and experiments.
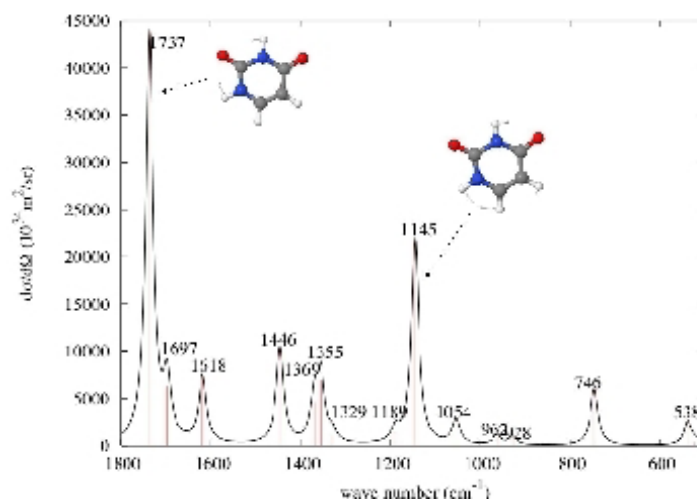
Figure 1 : Calculated Resonance Raman Scattering of uracil at $\lambda = 266$ nm

References:
(1) A. B. Meyers.
Chem. Rev. **96**, 911, 1996
(2) L. Jensen, J. Autschbach, G. C. Schatz.
J. Chem. Phys., **accepted**, 2005

POSTER I-62
THE NIST COMPUTATIONAL CHEMISTRY COMPARISON AND BENCHMARK
DATABASE
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The NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB) is a website and database which allows users to compare ideal-gas thermochemical properties determined by experiment or by quantum chemical calculations. The database contains experimental data for 670 molecules, and over 100000 calculations on those species. Types of data include enthalpies of formation, entropies, geometries, vibrational frequencies, and dipole moments. The primary goal of the CCCBDB is to allow comparisons of thermochemistry. As part of this goal geometric and vibrational data are included. The CCCBDB contains experimental geometric and vibrational data for 400 molecules. The CCCBDB tries to answer the question "How good is that ab initio calculation?" This poster will describe the data present in the CCCBDB, the tools available through the website for comparisons, and the future plans of the CCCBDB. The CCCBDB is accessible at http://srdata.nist.gov/cccbdb.

FAST CORRELATION METHOD USING LOCAL AUXILIARY BASIS EXPANSIONS

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Correct treatment of dispersion interactions that are critical in describing ubiquitous stacking phenomena must involve correlated electronic structure methods beyond Hartree-Fock. Even the most popular density functional theories under the present-day implementations completely neglect the long-range correlation effects, thereby making them inappropriate for such systems. The simplest correlation method, namely Mollet-Plesset theory, however, still has an unfavorable scaling behavior, where the computational complexity increases as the fifth power of system size. Here we report a quadratic scaling scaled-opposite-spin MP2 (SOS-MP2) algorithm within the resolution-of-identity and Laplace transform framework that can be routinely applied to very large molecules, such as systems with more than 100 heavy atoms or 2000 basis functions. Quadratic algorithm (in terms of CPU, I/O, and memory/disk requirement) is achieved by exploiting the physical locality and hence sparsity of the auxiliary basis expansion coefficients that results from the local density fitting with the attenuated Coulomb operator. Errors associated with using attenuated Coulomb metric instead of a full Coulomb one are also assessed to be very small, i.e., 0.01 kcal/mol in the root mean squared error of atomization energies for 148 neutral molecules of G2 set. Some large-scale applications are also presented using the new quadratic algorithm.

POSTER I-64
THE DECOMPOSITION OF PETN AT EXTREME CONDITIONS
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We have carried out tight binding molecular dynamics simulations of solid PETN to study its decomposition process at the Chapman-Jouguet (CJ) condition (density = 2.39g/cc, and T=4200K) of detonation. The Inter-atomic interaction are determined by the self-consistent charge density-functional tight binding (SCC-DFTB) method. We analyzed the time histories of formations of intermediates and products, which provided us insight into the chemical kinetics of PETN decomposition.

POSTER I-65
EFFICIENT SCF METHOD FOR LARGE SYSTEMS OF WEAKLY INTERACTING COMPONENTS

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An efficient method for removing the SCF diagonalization bottleneck is proposed for systems of weakly interacting components. The method is based on the locally projected SCF for molecular interactions equations (LP SCF MI) of Gianinetti et.al. [E. Gianinetti, I. Vandoni, A. Famulari, M. Raimondi, *Adv. Quantum Chem.* 31, 1998, 251]. A generalization of the DIIS method for non-orthogonal molecular orbitals is formulated to increase the rate of convergence of the LP SCF MI. A fast scalable second-order single-excitation perturbative correction is developed to improve the LP SCF MI energies. The resulting energies closely reproduce the conventional counterpoise corrected SCF energy. Extensive test calculations are performed on large water clusters up to several hundred molecules. Compared to conventional SCF, speed-ups of the order of $(N/O)^2$ have been achieved for the diagonalization step, where N is the size of the AO basis, and O is number of occupied molecular orbitals.

ACTC 2 0 0 5

POSTER I-66
ATOMISTIC SIMULATION OF CITRIC ACID COORDINATION TO 111 AND 100 AG SURFACE

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The control of Ag quantum dot growth in solution of citric acid is modeled with density functional numeric simulation. The sum of ground-state energy of an isolated citric acid and ground state energy of 100 / 111 silver surfaces is compared to the optimized ground state energy of citric acid attached to the these surfaces. The difference of these energies provides the binding energy of the citric acid to Ag surface which is.16eV /.60 eV, per ligand molecule, according to the numeric results. The inter atomic distances of citric acid match the inter atomic distance of 111 surface, and mismatch the inter-atomic distance of 100 surface. According to the analysis of the silver-to-oxygen distances the citric acid on the 100 surface forms two coordination bonds while citric acid on the 111 surface forms four bonds. The atomistic numeric simulation supports the experimental fact that citric acid ligand blocks the 111 surfaces of a quantum dot and allow for a growth of the 100 surfaces leading to the control of the shape of the quantum dot.

DISSOCIATION POTENTIAL CURVES OF LOW-LYING STATES IN TRANSITION METAL HYDRIDES. III. ECP CURVES FOR HYDRIDES OF GROUPS 6 AND 7

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[3]Department of Chemistry, Iowa State University

The dissociation energy curves of low-lying spin-mixed states in mono-hydrides of Groups 6 and 7 were calculated using effective core potential (ECP) approach. This approach is based on the multi-configuration self-consistent field (MCSCF) method, followed by first-order configuration interaction (FOCI) calculations, in which the method employs an ECP basis set proposed by Stevens and co-workers (SBKJC) augmented by a set of polarization functions, and spin-orbit coupling effects are estimated within one-electron approximation using effective nuclear charges. The present paper reports a comprehensive set of theoretical results including the dissociation energies, equilibrium distances, electronic transition energies, harmonic frequencies, anharmonicities, and rotational constants for several low-lying spin-mixed states in the hydrides. Transition dipole moments are also computed among the spin-mixed states and large peak positions of electronic transitions are predicted for these hydrides. The periodic trends of physical properties are investigated on the basis of the results reported in the present series of our researches.

ACTC 2 0 0 5

EQUILIBRIUM GEOMETRIES AND PROPERTIES OF THE GROUND AND ELECTRONICALLY EXCITED STATES OF VINYL, PROPEN-1-YL, PROPEN-2-YL, TRANS-1-BUTEN-2-YL, AND TRANS-2-BUTEN-2-YL DOUBLET RADICALS

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In this work, optimized geometries and vertical transition energies have been calculated for the vinyl, propen-1-yl, propen-2-yl, trans-1-buten-2-yl, and trans-2-buten-2-yl doublet radicals using the ROHF-EOM-CCSD method with the 6-311(2+,2+)G** basis set. The permanent dipole and oscillator strengths were also calculated. Moreover, optimized geometries for the first excited state, $\pi \rightarrow n$, were found for each molecule and the adiabatic transitions were calculated. For the vertical energies, excitations to both Rydberg and valence orbitals were calculated. The states' orderings in different systems were compared to elucidate the effects of neighboring alkyl groups on low lying states. An important consequence of adding alkyl groups is a decrease in binding energy of the unpaired electron, due to inductive effects.

MOLECULAR STRUCTURE, VIBRATIONAL FREQUENCIES, AND ANHARMONICITIES IN ELECTRONIC QUANTUM MONTE CARLO

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The quantum Monte Carlo (QMC) method is an efficient way to solve the time-independent Schroedinger equation for many electron systems. While total system energies have been successfully calculated using this method, less progress has been made in the case of other quantities.

We present here that the atomic forces can be accurately and efficiently calculated by combining three innovations: 1) new improved algorithms for minimizing the energy of the variational QMC trial wave function, 2) new renormalized estimators that make Hellmann-Feynman part of the atomic force efficient, and 3) stochastic sampling of Pulay corrections to the force. The results for some diatomic molecules are presented.

The atomic forces agree well with potential energy surfaces, demonstrating the accuracy of this force procedure. Equilibrium molecular structure, harmonic vibrational frequencies, and anharmonicity constants, derived from the QMC energies and atomic forces show good agreeement with the experimental data.

ACTC 2 0 0 5

POSTER I-70
DETERMINATION OF GAS ADSORPTION SITES IN POROUS MATERIALS USING AB-INITIO METHODS.

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University of Michigan

The difficulties encountered by experimental methods to determine the adsorption sites in porous materials (Metal Organic Frameworks – MOFs) emphasize the importance of computational studies in this area. Besides, theoretical methods can be use to develop new materials with high selectivity and superior storage capabilities. In this work the adsorption energy barriers for H2, as well as N2 and Ar, are investigated using DFT functionals associated with customized basis sets for several prospective adsorption sites in MOFs. An adsorption sequence has been proposed based on relative energy associated to each individual site. Some experimentally determined sites (for N2 and Ar) have been confirmed by theoretical calculations, while some new (for H2) are proposed.

ADSORPTION AND DISSOCIATION OF CO ON CLEAN AND S-PRECOVERED Fe(100): A DFT STUDY

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The Fischer-Tropsch Synthesis is an attractive route for the production of chemicals and fuels from coal, natural gas, and potentially even biomass sources. Depending on the feedstock, the formation of various sulfur and nitrogen-containing compounds is concomitant with the production of syngas. These compounds are widely regarded as catalyst poisons in the FTS. Sulfur is reported to cause a decline in catalyst activity, as well as an increased propensity towards methane formation. Fe(100) surface has been mainly used to model iron catalysts in fundamental studies. Experiments show that the addition of small amounts of sulfur does not modify significantly the TPD spectrum of CO on Fe(100). As the sulfur coverage is increased, new TPD features develop at 356 and 288 K, whereas the desorption features characteristic of the free-sulfur Fe(100) decrease in intensity. At the saturation coverage of sulfur, only one desorption feature is observed in the TPD spectrum at 183 K. TPD experiments show the poisoning effect of sulfur on the CO dissociation; the desorption feature at 820 K that corresponds to the recombination and desorption of C and O from the surface decreases in intensity as the sulfur coverage is increased and eventually vanishes at sulfur coverages above 1/4 ML.

$$CO(\alpha 3)' \qquad 1.29eV \qquad TS \qquad 0.97eV \qquad CO(\beta 1)$$

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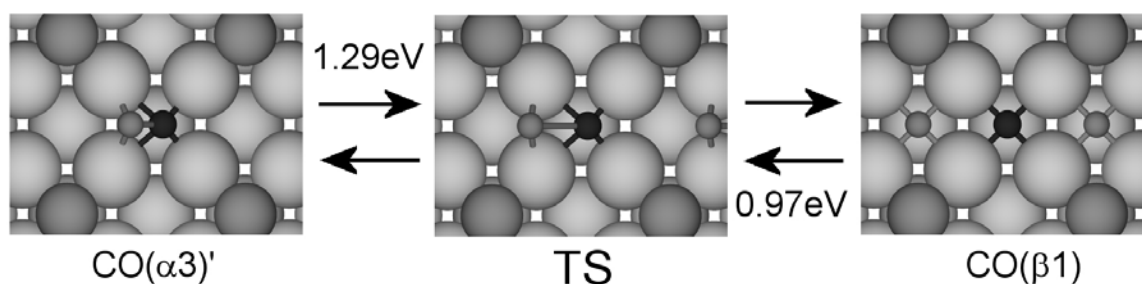
POSTER I-72
COMPOSITIONAL DEPENDENCE OF THE FIRST SHARP DIFFRACTION PEAK IN SILICATE GLASSES

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The first sharp diffraction peak (FSDP) has been considered to be the signature of the medium range order of covalent glasses and its origin is still highly controversial. The intensity and position of the FSDP is found to change with temperature, pressure and glass composition. These changes can be used to understand the structural origins of the FSDP. In this work, we have studied the compositional dependence of the FSDP in lithium, sodium and potassium silicate glasses using classical molecular dynamics computer simulations. The simulated neutron structure factors are compared with available experimental results. The calculated partial structure factors and Faber-Ziman factors are used to determine the detailed contributions to the FSDPs. Characteristic repeat distance and correlation length were obtained by fitting the FSDPs to Lorentzian functions. Our simulation results support that the negative scattering length of lithium ion is the cause of the anomaly of the FSDP in lithium silicate and increasing alkali oxide concentration leads to a decrease of the characteristic repeat distance, where the decrease is greater for larger alkali cations.

Fig. 1 Dependence of the characteristic repeat distance with alkali oxide concentration.
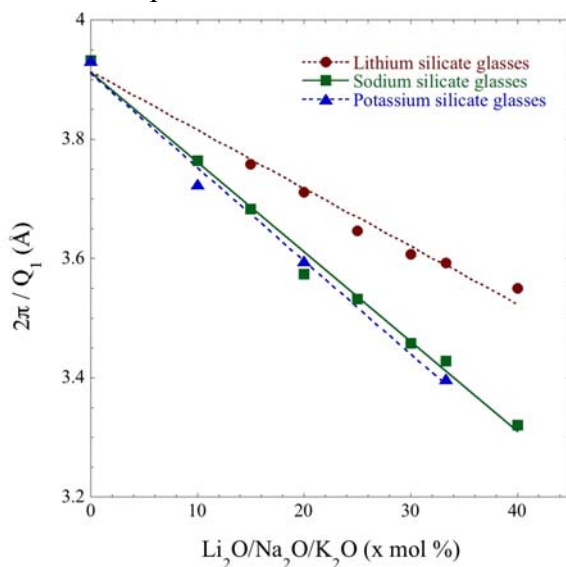
POSTER I-73
STRUCTURE AND REACTIVITY OF STANNIC OXIDE SURFACES IN THE PRESENCE OF OXYGEN

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Stannic Oxide (SnO_2) is a technologically important material for catalysis and gas sensing applications. In such uses, a detailed understanding of the surface structure is critical for an atomic-level description of the operationally relevant phenomena. We investigate the (110), (101), and (100) low index surfaces via density functional calculations. The free energy of the surface structures is calculated as a function of oxygen chemical potential and compared with low energy He^+ ion scattering spectroscopy, low energy electron diffraction, and scanning tunneling microscopy results. Additionally, we investigate the reaction barriers to oxygen dissociation on the reduced low index surfaces. An appreciation for the kinetic influence on the surface structures is crucial since many experimental preparation conditions may be far from permitting global surface equilibration. Armed with density functional results encompassing both thermodynamic and kinetic predictions of these low index surfaces, we discuss the local structures of these ideal surfaces and extrapolate our findings to polycrystalline films used in practical applications.

MAGNETIC STRUCTURE AND ADHESION OF THE Fe(100)/Cr(100) AND Fe(110)/Cr(110) INTERFACES

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Chromium is widely used as a protective coating for steel surfaces. We report the results of spin-polarized density functional theory calculations on the bcc Fe(100)/Cr(100) and bcc Fe(110)/Cr(110) interfaces using the all-electron projector augmented wave method. We predict the magnetic structure and the ideal adhesion energies (E_{AD}) for the two interfaces, which exhibit very low lattice mismatch (~0.6%). Fe and Cr bulk properties agree well with experiment. Both the (100) and (110) interfaces are predicted to exhibit ferromagnetism in Fe and anti-ferromagnetism for Cr. The magnetic moments are typical of the bulk materials with smaller magnetic moments near interfaces and greater magnetic moments near surfaces. The calculated values of E_{AD} is 5.7 J/m^2 for the (100) interface and 5.3 J/m^2 for the (110) interface. The interface strength is greater than the intrinsic adhesion of iron, which is due largely in part to the strong magnetic interactions at the interface.

POSTER I-75
CHEMISORPTION ON STRAINED METAL SURFACES:
PREDICTIVE INSIGHT FROM
ORBITAL-SPECIFIC ASPECTS OF SUBSTRATE ELECTRONIC STRUCTURE

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We present a study of CO chemisorption spanning a variety of facets, strain states, and ad-atom geometries for various transition metals. We use DFT to track chemisorption energies, electronic structure, charge transfer, and orbital overlap in these systems. Through decomposing the solid-state band structure into orbital-specific components, we are able to understand and predict how strain and other geometric modifications to the substrate influence chemisorption. Additionally, we explain periodic trends in the susceptibility of chemisorption to geometric substrate perturbations.

POSTER I-76
CALCULATING THE ELASTIC BENDING MODULUS OF LIPID BILAYER EDGE

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Certain mixed-lipid systems (e.g. "bicelles") are known to form disk, ribbons, and pore structures in which the bilayer edge is stabilized by one of the components. To develop a theory for how the morphologies of these systems depend on composition, it is important to know how flexible the edges are. We use coarse-grained molecular dynamics (MD) simulations to study the in-plane fluctuations the edges of pure and mixed bilayer ribbons. Through fitting to a theoretical model and a simple Monte Carlo (MC) model, the in-plane bending modulus and line tension of the edge can be calculated from the fluctuations. From this study, the in-plane bending modulus of various bilayer edges are of the order of 10-28 J-m (i.e., ~30 kBT-nm).

INFLUENCE OF SUBUNIT STRUCTURE ON THE OLIGOMERIZATION STATE OF LIGHT HARVESTING COMPLEXES

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Light harvesting complexes 2 (LH2) from *Rhodospirillum (Rs.) molischianum* and *Rhodopseudomonas (Rps.) acidophila* form ring complexes out of eight or nine identical subunits, respectively. We investigate computationally what factors govern the different ring sizes. Starting from the crystal structure geometries, we embed two subunits of each species into their native lipid-bilayer/water environment. Using molecular dynamics simulations with umbrella sampling and steered molecular dynamics, we probe the free energy profiles along two reaction coordinates, the angle and the distance between two subunits. We find that two subunits prefer to arrange at distinctly different angles, depending on the species, at about 42.5° for Rs. molis- chianum and at about 38.5° for Rps. acidophila, which is likely to be an important factor contributing to the assembly into different ring sizes. Our calculations suggest a key role of surface contacts within the transmembrane domain in constraining these angles, whereas the strongest interactions stabilizing the subunit dimers are found in the C-, and to a lesser extent, N-terminal domains. The computational approach developed by us provides a promising starting point to investigate the factors contributing to the assembly of protein complexes.

SUM OF SQUARES OPTIMISATION – APPLICATIONS IN THEORETICAL CHEMISTRY

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A key research challenge is the efficient identification of the global minimum potential energy and associated coordinates of complex systems since such problems possess NP-hard complexity. Current approaches have two clear drawbacks: i) extensive sampling of configurational space is required before the lowest point is identified. ii) the algorithm doesn't produce proof that the global minimum has been found.

A new & highly significant development in optimisation theory provides a hierarchy of provable and successively closer lower bound approximations to the global minimum for the class of NP-hard problems which can be expressed as polynomial optimisation problems. The lower bound approximation is produced by lifting the polynomial to a higher dimensional sum of squares (convex) polynomial. Optimisation of a sum of squares polynomial may be expressed as a semidefinite programme (for which provably polynomial time algorithms exist).

We apply this approach to bounding classical potential energy surfaces. Work is also underway on application to elliptic potentials for coarse grained molecular dynamics. Our studies demonstrate the effectiveness of the approach for small systems and particularly for potentials where multiple low lying minima prove pathologically difficult for conventional algorithms.

CLASSICAL DYNAMICS SIMULATIONS FOR A LIGHT-DRIVEN MOLECULAR MOTOR

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The operation of a molecular motor is studied theoretically. The motor consists of a dibenzofulvene rotor sterically geared into a chiral, linked trityl stator. The rotor is actuated by light absorption with subsequent isomerization about the exocyclic double bond of dibenzofulvene (angle θ). Because this torsional motion is geared into a chiral potential, there exists the possibility for preferential clockwise or counter-clockwise rotation (angle φ).

The electronic structure of the ground and excited states of the dibenzofulvene rotor is studied by ab initio calculations. These are used with molecular mechanics potentials for the rotor-stator gearing to obtain a qualitatively reasonable potential surface for the full motor. These calculations show that the motor is locked at ambient temperatures in the absence of light absorption. The Photoisomerization is studied by classical trajectories on the excited electronic state following photon absorption. Nosé-Hoover dynamics is used to create thermal initial conditions for the Franck-Condon region on the ground state.

The results of these calculations are interpreted in terms of the preference for the unidirectional bias in rotary motion that would be required for a useful nanoscale motor. The structure features and experimental conditions required to optimize motor performance are discussed.
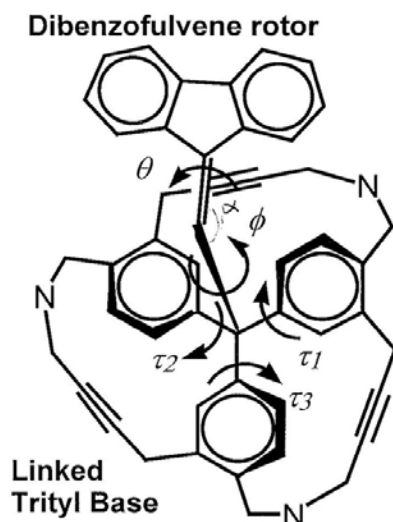
MODELING VIRAL CAPSID ASSEMBLY DYNAMICS

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The assembly of protein subunits into a virus capsid is remarkable. In many different organisms and environments, capsids avoid kinetic and thermodynamic traps to assemble rapidly and with high fidelity. Identifying the properties of capsid components that enable such robust assembly could play a critical role in the development of anti-viral strategies and drug delivery vehicles. In this work we develop a class of models with which we study the assembly of capsid-like objects without pre-assumed paths or nucleation steps. Using Brownian dynamics, we generate an ensemble of paths with which we characterize features essential for successful assembly and we also identify two forms of kinetic traps. By comparing these results to the dynamics of a Master-equation description of assembly, we shed light on some approximations that are commonly used to develop coarse-grained models of capsid assembly.

POSTER I-81
COMPUTER SIMULATIONS OF THE TRANSLOCATION AND UNFOLDING OF A PROTEIN PULLED MECHANICALLY THROUGH A PORE

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Protein degradation by ATP-depended proteases and protein import into the mitochondrial matrix involve unfolding of proteins upon their passing through narrow constrictions. It has been hypothesized that the cellular machinery accomplishes protein unfolding by pulling mechanically at one and of the polypeptide chain. We have used Langevin dynamics simulations of a minimalist off-lattice model of the ubiquitin domain to explore this hypothesis and to study the unfolding of a protein pulled mechanically through a narrow pore. We find that the unfolding mechanism involves a number of intermediates, depends on the magnitude of the pulling force and on whether the force is applied at the N- or the C-terminus of the chain. It is also different from the unfolding mechanism observed when the two termini are pulled apart, as in single molecule mechanical unfolding experiments. Our simulations indicate that, in the course of translocation, proteins unfold sequentially from the end containing the targeting sequence.

IONIC CONDUCTANCE CALCULATION IN A PEPTIDE NANOTUBE

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Northwestern University

Ionic conductance calculations in a peptide nanotube are performed. The peptide nanotube is composed of 8 flat ring-shaped cyclic D,L octapeptide subunits which are stacked on top of each other and is embedded in lipid bilayers. The calculations are carried out by using Poisson-Nernst-Planck (PNP) equation and hybrid grid-based dynamic grand canonical Monte Carlo simulation (grid-based DGMC) / mean field (MF) method, respectively. In PNP equation, some parameters such as diffusion constants of ions are optimized by fitting computational results to experimental data. The calculation shows the linear relationship in voltage-current curves. Hybrid grid-based DGMC/MF method is also fulfilled to take into account ion size and ion correlation effects in a nonequilibrium and inhomogeneous system since these effects are not realized properly in PNP equation. In the method, DGMC simulation is employed to deal with ionic motions while MF equation is used to describe dielectric boundaries.

PHOTOCHEMISTRY OF THE PHOTOACTIVE YELLOW PROTEIN

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Photoinduced trans-cis isomerization is an example of how nature converts light to mechanical energy. In Photoactive Yellow Protein (PYP), photoinduced isomerization of the chromophore eventually leads to protein-wide structural change and biological signal transduction. The chromophore of PYP is anionic trans-p-coumaric acid (pCA). In this work, we report on radiationless non-isomerizing reaction pathways of neutral pCA. The phenyl ring distorted conical intersection between S_0/S_1 as well as nonadiabatic recrossing of the isomerization barrier on S_1 are shown to be responsible for the wavelength dependent photochemistry of neutral pCA. In addition, photochemistry of the anionic phenolate form of pCA is compared to the results on neutral pCA. To fully understand the photochemistry of PYP, we investigate reparameterized multireference semiempirical quantum mechanical/molecular mechanical (QM/MM) methods. We also present new pseudospectral implementations of configuration interaction singles (PS-CIS) and time-dependent density functional theory (PS-TDDFT) which can be applied in this context. The accuracy of QM/MM and pseudospectral approaches are tested by computing vertical excitation energies of the neutral pCA in an aqueous microsolvated environment. The observed computational savings from the pseudospectral approximation suggest that fully ab initio calculations of the excited states in the full protein environment are possible.

FINDING THE MECHANISM AND RATE OF TRANSITIONS IN QUANTUM MECHANICAL SYSTEMS WITHIN THE HARMONIC APPROXIMATION

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In harmonic quantum transition state theory based on Feynman Path integrals (FPI), the identification of transition mechanism and estimation of rate constants involves finding a first order saddle point on the temperature dependent, NP-dimensional, effective potential energy surface, where N is the number of classical degrees of freedom and P is the number of system replicas in the FPIs. The saddle point corresponds to the so-called 'instanton'. Once the relevant saddle points have been found, the rate can be estimated by using harmonic approximation to the partition functions at the initial and transition states. We have implemented a method to locate instantons in complex, high dimensional systems using atomic forces from either empirical potential functions or directly from ab initio estimates, without the need for second derivatives of the energy. The method is a quantum mechanical extension of the minimum mode following method of Henkelman and Jonsson [JCP., **111**, 7010 (1999)]. Application to various surface reactions will be presented, in particular the associative desorption of H_2 from a Cu(110) surface, and the reaction of N-adatoms with hydrogen to form ammonia on the Ru(0001) surface.

Calculated rate of H2 desorption from Cu(110)
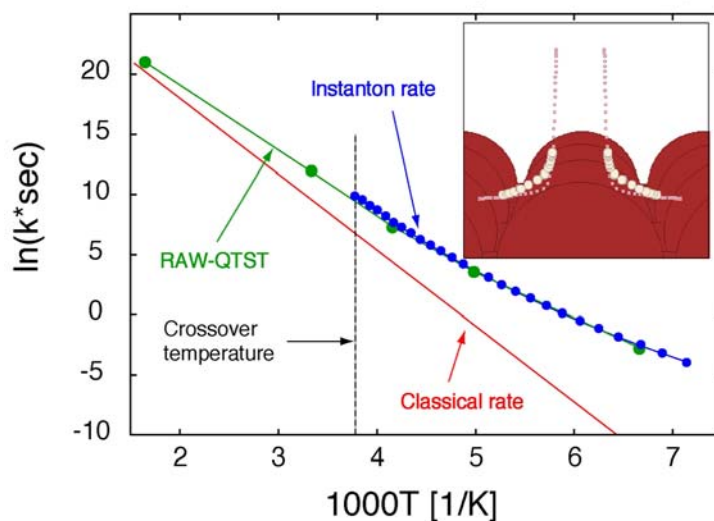
ACTC 2 0 0 5

THERMODYNAMICS FROM 'BASIN-SAMPLING': APPLICATION TO ATOMIC CLUSTERS

Tetyana V. Bogdan, David J. Wales

Department of Chemistry, University of Cambridge, UK

We present a 'basin-sampling' approach for calculation of the potential energy density of states for classical statistical models. It aims to combine an efficient method for a direct calculation of the density of states with a successful algorithm for taking transitions between different regions of configuration space. It is based on a Wang-Landau type uniform sampling of local minima and basin-hopping global optimisation method with a novel approach for approximating the relative contributions from local minima in terms of volumes of basins of attraction. We have employed 'basin-sampling' to study phase changes in atomic clusters modelled by the Lennard-Jones potential, and for ionic clusters and bulk glass formers, most of which have multi-funnel energy landscapes. The approach proved to be efficient for systems involving broken ergodicity and has allowed us to calculate converged heat capacity curves for systems that could previously only be treated using the harmonic superposition approximation. Benchmarks are also provided by comparison with parallel tempering and Wang-Landau simulations, where these proved feasible.

POSTER I-86
DECAY OF METASTABLE PHASES IN A MODEL FOR THE CATALYTIC OXIDATION OF CO ON A SURFACE

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We present a kinetic Monte Carlo study of the dynamical behavior of a Ziff-Gulari-Barshad model with CO desorption for the catalytic oxidation of CO on a surface. Finite size scaling analysis and the fourth-order order-parameter cumulant show that below a critical CO desorption rate, the model exhibits a nonequilibrium first-order phase transition between low and high CO coverage phases. We measure the metastable lifetimes associated with the transition from the low CO coverage to the high CO coverage, and viceversa. Our results indicate that the transition process follows a mechanism very similar to the decay of metastable phases associated with equilibrium phase transitions and can be described by the classic Kolmorogov-Johnson-Mehl-Avrami theory of phase transformation by nucleation and growth. The desorption parameter plays the role of temperature and the distance to the coexistence curve plays the role of an external field or supersaturation. We identify two distinct regimes, depending on whether the system is far from or close to the coexistence curve, in which the statistical properties and the system size dependence of the lifetimes are different corresponding to multidroplet or single-droplet decay, respectively.

POSTER I-87
NEW ALGORITHMS FOR MONTE CARLO SIMULATION OF LARGE SYSTEMS OF CHARGED PARTICLES

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Systems of biopolymers in solution are often modeled as a set of point charges in a periodically replicated box. The rate determining step of Monte Carlo simulations for such systems is the evaluation of the energy of intermolecular electrostatic interactions, typically done by means of a technique called the Ewald sum. The computational cost of Monte Carlo simulations using the Ewald sum in its simplest implementation is proportional to the square of the number of charged particles in the system, making large-scale simulations intractable. We are investigating new methods, based on ideas from Monte Carlo cluster algorithms and fast multipole methods, to dramatically lower this cost. We discuss preliminary calculations on a prototypical large system: 10,000 water molecules in the extended simple point charge (SPC/E) model of water.

SEQUENCE-DEPENDENT CYCLIZATION OF SHORT DNA SEQUENCES

Luke F Czapla, Wilma K Olson

Rutgers University - Department of Chemistry and Chemical Biology

A new non-canonical Monte Carlo sampling methodology is applied to approximate the conformational properties of DNA in a discrete elastic base-pair step model. This technique can be used to investigate arbitrary-length DNA with greatly enhanced sampling sizes ($N=10^{16}$) and elucidate sequence-dependent features which are expected to contribute greatly to the dynamics of DNA at short lengths. Electrostatic repulsion between base-pair steps is also considered.

DNA is modeled as either intrinsically straight or with local sequence-dependent bending, twisting, and shearing, both with or without anisotropic bending and more deformable base-pair steps. These models are intended to fit data from cyclization experiments of short DNA sequences by Cloutier and Widom, which suggest possible faults in current theories of DNA elasticity, and to address the need for further modeling and sampling techniques.

POLYMER BASED MOLECULAR MOTORS: CHARACTERISATION AND EFFICIENCY

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We present studies of a polymer based molecular motor that uses the `flashing ratchet' principle at the Brownian dynamics level. The external biasing field is formed either by an asymmetric sawtooth potential or an array of infinite line electrodes that mimics a more experimentally realistic external potential. In contrast with motors based on single particles, increasing the size of the ratcheting object leads to improvements in performance: the particle may perform work against larger external fields and the coherency of transport improves. We consider the balance between fluctuations in monomer velocity and the input of energy from the external potential and calculate the rectification efficiency of the motor on this basis. Finally, we make an attempt to scale the simulation results to show the feasibility of constructing a motor that uses long segments of DNA.

POSTER I-90
VARIATIONAL GAUSSIAN WAVEPACKET SIMULATIONS OF EQUILIBRIUM PROPERTIES OF QUANTUM MANY-BODY SYSTEMS.

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The Variational Gaussian Wavepacket (VGW) method for computation of equilibrium density matrices of quantum many-body systems recently suggested by the authors is presented. Within this method the density matrix is expressed in terms of a Gaussian resolution, in which each Gaussian is propagated independently in imaginary time. The Gaussian is represented by its center, the width matrix and the scale, treated as dynamical variables. The expectation values of observables are evaluated by Monte Carlo sampling of the initial Gaussian positions. The method demonstrated surprisingly good accuracy in applications to model systems and to Neon Lennard-Jones (LJ) clusters. For the latter case the results obtained by the VGW method are in good quantitative agreement with the available results using the Path Integral Monte Carlo (PIMC) calculations.

We report converged VGW heat capacity curves for a range of Ne_n clusters and compare them with those for the classical LJ clusters. Our results indicate that quantum effects lead to qualitative differences in equilibrium properties of such systems. In particular, the liquid-solid phase transitions that are observed in the LJ clusters are not observed in Ne clusters.

POSTER I-91
MONTE CARLO SIMULATION OF PHASE EQUILIBRIA USING DFT POTENTIALS
Lev David Gelb, Ted Carnahan
Washington University in St. Louis

We have directly simulated liquid-vapor phase equilibria in alkali metals via simulation framework in which a combination of modern Monte Carlo sampling methods (Hyper-Parallel Tempering, Gibbs Ensemble Monte Carlo, and pre-sampling with an approximate potential) are used in concert with standard electronic structure codes such as **Gaussian** and **NWChem** to perform phase-equilibria calculations with *ab initio* potentials. Accuracy, computational efficiency, code integration, parallelization, and on-the-fly optimization of the presampling potential are discussed and evaluated. Other promising applications of the approach include gas adsorption equilibria, solvation free energies, and chemical reactions in solution. The method can be easily extended to inclusion of nuclear quantum effects via path-integral methods.

POSTER I-92
PATH INTEGRAL THERMOCHEMISTRY

Kurt R. Glaesemann, Laurence E. Fried
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The calculation of thermochemical data relies upon accurate molecular energies. The rotational and vibrational effects must be accounted for, in order to obtain the needed accuracy. These effects are generally calculated using a normal mode analysis. Such an analysis assumes perfect harmonicity. We present a path integral Monte Carlo method for going beyond the traditional harmonic analysis. This method includes all thermal, vibrational, and rotational effects a priori. The underlying classical potential is calculated using ab initio methods, such as CCSD(T) and MBPT2. This approach explicitly includes electronic-vibrational coupling. Results for several chemical systems are presented and anharmonic effects are found to be significant. Analytical methods for estimating the optimal path discretization have been developed. A novel potential energy caching scheme, which greatly improves computational efficiency, is also presented. A new path integral energy estimator is presented that improves upon the thermodynamic energy estimator via a free particle projection, thus reducing computational demand.

POSTER I-93
SIMULATIONS OF WATER IN GIANT PLANETS: DISCOVERY OF SYMMETRIC H-BONDING IN THE SUPERIONIC PHASE

Nir Goldman, Laurence E. Fried, I-Feng W. Kuo, Christopher J. Mundy
Lawrence Livermore National Laboratory

We detail herein results of ab initio Molecular Dynamics simulations of water at conditions close to the isentropes of Neptune and Uranus (temperatures of 1000 - 2000K, and densities of 2.0.-3.0 g/cc). We have calculated the lifetimes and concentrations of molecular and non-molecular species, and ionic conductivity and vibrational spectra. Comparison is made to experiment where possible. At these conditions, we observe the onset of a "superionic phase" in which oxygen anions exhibit glassy behavior, and protons diffuse rapidly (10^{-5} - 10^{-4} cm^2/s) by jumping between oxygen lattice points. We observe two distinct transitions along the superionic phase line. The first consists of a "dynamically ionized" phase, wherein H_2O is the dominant species, but all species lifetimes are exceedingly short-lived such that they are better described as ensembles of transitions states, rather than molecules. At higher densities, we observe a transition to a polymeric phase, in which water has formed partially covalent, symmetric hydrogen bond networks. These results profoundly improve our knowledge of the phase diagram of water. Furthermore they have important implications for the modeling of the interiors of Neptune and Uranus and their corresponding magnetic fields.

POSTER I-94
NONEQUILIBRIUM SUPEROPERATOR GREENS FUNCTION THEORY OF DENSITY CORRELATION FUNCTIONS; BEYOND THE GW-APPROXIMATION.

Upendra Harbola, Shaul Mukamel
Department of Chemistry, University of California-Irvine, CA 92697

Nonequilibrium many-body Greens functions theory is formulated in terms of Liouville space operators. Unlike the Hilbert space, the generalized (nonequilibrium) Hedin's equations are obtained directly in real time. Liouville space generating functional technique is used to derive a closed Dyson-like equation for the density-correlation function. Connection with TDDFT and Bethe-Salpeter formulation is discussed. Applications to intermolecular forces and STM current will be discussed.

POSTER I-95
TIP-SHAPE EFFECT ON THE PULL-OFF FORCE IN ATOMIC FORCE MICROSCOPY

Joonkyung Jang

School of Nano Science & Technology, Pusan National University, Busan, South Korea 609-735

We study the capillary force in atomic force microscopy by using Monte Carlo simulations. Adopting a lattice gas model for water [1], we simulated water menisci that form between a rough silicon-nitride tip and a mica surface. Unlike its macroscopic counterpart, the water meniscus at the nanoscale gives rise to a capillary force that responds sensitively to the tip roughness. We have considered several rough tips in our simulations (see Figure 1). Compared to the smooth tip, each rough tip contacts with the mica surface through a smaller area. This reduced tip-mica contact area yields a decrease in pull-off force. With only a slight change in tip shape, the pull-off force significantly changes its qualitative variation with humidity.

References
1. J. Jang, G. C. Schatz, and M. A. Ratner, Phys. Rev. Lett. 92, 085504 (2004); J. Chem. Phys. 120, 1157 (2004); Phys. Rev. Lett. 90, 156104 (2003); J. Chem. Phys. 116, 3875 (2002).
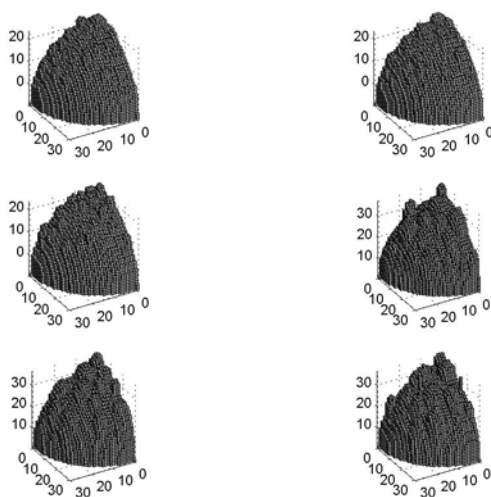
POSTER I-96
DYNAMICAL EXCHANGES IN FACILITATED MODELS OF SUPERCOOLED LIQUIDS
YounJoon Jung[1], Juan P. Garrahan[2], David Chandler[1]
[1]Department of Chemistry, University of California, Berkeley, CA,
[2]School of Physics and Astronomy, University of Nottingham, Nottingham, UK

We investigate statistics of dynamical exchange events in coarse-grained models of supercooled liquids in spatial dimensions d=1, 2, and 3. The models, based upon the concept of dynamical facilitation, capture generic features of statistics of exchange times and persistence times. Here, distributions for both times are related, and calculated for cases of strong and fragile glass formers over a range of temperatures. Exchange time distributions are shown to be particularly sensitive to the model parameters and dimensions, and exhibit more structured and richer behavior than persistence time distributions. Mean exchange times are shown to be Arrhenius, regardless of models and spatial dimensions. Specifically, $<t_x> \sim c^{-2}$, with c being the excitation concentration. Different dynamical exchange processes are identified and characterized from the underlying trajectories. We discuss experimental possibilities to test some of our theoretical findings.

Refs: Phys. Rev. E 69, 061205 (2004); cond-mat/0504535 (submitted to J. Chem. Phys.)
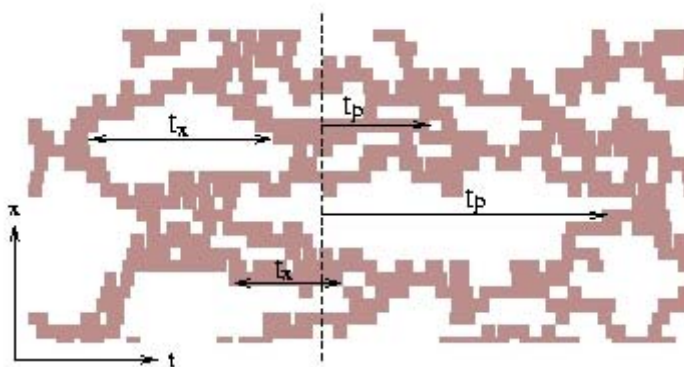
FIG. 1: Exchange and persistence times are shown in the trajectory of $d = 1$ FA model at $T = 0.8$. Shaded regions represents parts of space-time with excitations, while white regions represent parts with no excitations.

POSTER I-97
VIBRATIONAL ENERGY RELAXATION RATES IN LIQUID SOLUTIONS FROM
SEMICLASSICAL MOLECULAR DYNAMICS SIMULATIONS

Being J Ka, Eitan Geva
Department of Chemistry, University of Michigan

One of the most fundamental ways in which the environment affects molecular dynamics is via vibrational energy relaxation (VER). The calculation of VER rates is challenging since the frequency of most molecular vibrations is relatively high in comparison to kT. This implies that both the relaxing mode and solvent accepting modes should be treated quantum mechanically. The standard approach to this problem employs ad-hoc Quantum Correction Factors (QCFs). The development of a more rigorous approach for calculating VER rates is therefore highly desirable. The Local-Harmonic-Approximation Linearized-Semiclassical (LHA-LSC) method, developed in our group, provides such a rigorous methodology, which is flexible, feasible and accurate. In this poster, we will provide an overview of the method, and present applications to: (1) Neat diatomic liquids (Oxygen and Nitrogen); (2) Atom/diatom liquid mixtures (Oxygen/Argon); and (3) A polyatomic solute in a liquid (CO2 in argon). Comparison to experimental results, when available, demonstrates the accuracy of the method, and its ability to capture the enhancement of the quantum VER rate by orders of magnitude relative to the classical prediction. We also show that, in the case of a polyatomic solute, quantum mechanics and classical mechanics can predict different VER pathways.

THROUGH THE CHANNEL AND AROUND THE CHANNEL:
VALIDATING AND COMPARING MICROSCOPIC APPROACHES FOR EVALUATION OF
FREE ENERGY PROFILES FOR ION PENETRATION THROUGH ION CHANNELS

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Microscopic calculations of free energy profiles for ion transport through biological ion channels presents a very serious challenge mainly due to the major convergence problems associated with the heterogeneous landscape of the electrostatic environment in ion channels. The present study is aimed at reducing the above problems by defining benchmarks that are directly relevant to ion channels and can also give converging results. It is done by constructing a series of models of a truncated gramicidin channel with different numbers of water molecules. These models are then used to validate and compare the adiabatic charging free energy perturbation (FEP) approach combined with an umbrella sampling approach and the potential of mean force (PMF) approach. It is found that both approaches work quite well until we move to the fully solvated channel case. The FEP approach may be more useful in evaluating the overall barrier for moving ions from water to ion channels and in some cases it might be beneficial to use the FEP approach for selective points along the channel and then to connect these points by PMF calculations.

**TOPOGRAPHY OF THE FREE ENERGY LANDSCAPE PROBED VIA MECHANICAL
UNFOLDING OF PROTEINS.**

Serdal Kirmizialtin, Lei Huang, Dmitrii E. Makarov
Department of Chemistry and Biochemistry, University of Texas at Austin

In single molecule pulling experiments, proteins are unfolded mechanically by pulling their ends apart. Application of mechanical forces generally alters the unfolding pathway. To understand what slice of the multidimensional free energy landscape is accessible via mechanical pulling experiments and to compare the mechanical and the chemical/thermal unfolding pathways, we have studied the mechanical unfolding and refolding of a minimalist off-lattice model of the protein ubiquitin. We find that while the free energy profile along typical ";chemical"; reaction coordinates may exhibit two minima, corresponding to the native and denatured states, the free energy $G(z)$ is typically a monotonic function of the mechanical coordinate z equal to the protein extension. Application of a stretching force along z tilts the free energy landscape resulting in a multistable free energy $G(z)-fz$ being probed in mechanical unfolding experiments. We further study the refolding trajectories after the protein has been pre-stretched by a large force and demonstrate that the stretching forces required to destabilize the native state thermodynamically are larger than those expected on the basis of previous experimental estimates of $G(z)$. Finally, we propose an explanation of the slow folding phase that was recently observed in the refolding of proteins under mechanical tension.

POSTER I-100
SEMICLASSICAL SIMULATION OF THE VIBRATIONAL DEPHASING OF IODINE IN A CRYOGENIC KRYPTON MATRIX

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[2]Computer Science Department, The Jerusalem College of Technology, Jerusalem, Israel

We describe simulations of the decay of quantum vibrational coherence in Iodine embedded in a cryogenic Kr matrix. We employ a numerical method based on the semiclassical limit of the quantum Liouville equation [1]. Our approach allows the simulation of the dynamics of off-diagonal density matrix elements using classical trajectories and ensemble averaging. The state-dependent interaction of the iodine chromophore with the rare gas environment is modeled using a recently developed method for constructing state-dependent many-body potentials for quantum vibrations in many-body classical environments [2]. The approach is based on an adiabatic separation between high frequency quantum vibrational modes of the solute and the lower frequency classical motion of the solvent, and on a first order perturbation theory description of the dependence of the quantum energies on bath configuration. The vibrational dephasing rates for coherences prepared between the ground vibrational state |0> and excited state |n> are calculated as a function of n and lattice temperature T. Excellent agreement is obtained with recent experiments performed by Apkarian and coworkers [3].

POSTER SESSION II

POSTER II-1
CATALYTICALLY RELEVANT MOTIONS IN ENZYMES
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Recently it has become increasingly acceptable that in some enzymes dynamics may play a role, in particular when a local vibration is strongly coupled to a transferred hydrogen or hydride. We present evidence that such "dynamic" effects may be present in other circumstances as well, thus representing a more general mechanism that influences catalysis.

Crystallographic studies of human PNP with several transition state analogs showed an unusual geometric arrangement of three oxygens in a close stack. We propose that internal protein motions in hPNP cause this stack to squeeze together and push electrons towards the purine ring, stabilizing the oxacarbenium character of the transition state. Increased electron density in the purine ring improves electrostatic interactions with nearby residues and facilitates the abstraction of a proton from a nearby residue, making the purine a better leaving group, thus accelerating catalysis.

We used a hybrid QM/MM method and identified protein vibrations in the sub-ps range that compress the 3-oxygen stack, and found that the activation energy decreases when the stack is compressed. (JACS, vol. 126, p 15720-15729, 2004)

POSTER II-2
HYDRATION AND TAUTOMERIZATION OF NUCLEIC ACID BASES: AB INITIO AND MOLECULAR DYNAMICS STUDY IN THE GAS PHASE, IN A MICROHYDRATED ENVIRONMENT AND IN AQUEOUS SOLUTION

<u>Jaroslav Rejnek</u>[1,2], Michal Hanus[1,2], Martin Kabelác[1,2], Filip Ryjácek[1,2], Pavel Hobza[1,2]

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Nucleic acid bases are dominantly present in the most stable canonical form, but their rare tautomers may be involved in various biological processes including point mutations. Their presence in biomolecules is nevertheless rather rare. The situation is different in gas-phase experiments where various tautomers coexist. Although gas-phase is very far from the native environment, the first more native insight is passing from the gas-phase to bulk water. Water can dramatically change the relative stability of various tautomers, which requires a description of hydration effects.

Different tautomers of guanine, adenine, thymine and uracil were studied in the gas phase, in a microhydrated environment and in bulk water environment using the molecular dynamics-thermodynamic integration method (MD-TI), conductor-like polarizable continuum model (C-PCM,COSMO) and a hybrid model (C-PCM + explicit water molecules). This work is another theoretical prediction of coexistence of several tautomers in the water phase as well as introduction of new method (hybrid model) used for determining relative stabilities of tautomers in the water phase.

POSTER II-3
AB INITIO FREE ENERGY PROFILES FOR ENZYMATIC REACTIONS USING MODEL POTENTIALS

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Our goal is to evaluate activation free energies in order to reproduce experimental k_{cat}/K_M values in enzymatic reactions. Standard ab initio calculations of transition states usually do not involve proper sampling of the environment because of the high cost of exploring many configurations.

Here we propose alternatives to the expensive ab initio potential of mean force calculations (PMFs) by generating the PMF profile on a fast empirical potential and determine ab initio energies based on this model force field. We used the EVB method for the low-level system and applied DFT calculations for the high-level ab initio model. Our method is based on a thermodynamic cycle from the low-level potential to the high-level one. We also present another approach where we simply replace the EVB ground state energies with the corresponding ab initio values in the evaluation of the PMF profile.

The results indicate that the presented methods are robust enough to perform well with model potentials that were not directly parameterized on the ab initio energies and structures, however in case of large qualitative differences between the model potential and the ab initio surfaces, one can easily identify the problems and correct the parameterization.

POSTER II-4
HOW WELL DOES PB CONTINUUM SOLVENT COMPARE WITH EXPLICIT SOLVENT?
Chunhu Tan, Lijiang Yang, Ray Luo
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The Poisson-Boltzmann (PB) implicit solvent has become increasingly popular due to its computational efficiency and accuracy. However, there have been relatively few attempts to optimize the PB solvent for its applications. Even if it is optimized, its transferability to larger systems has barely been discussed. In the present study, the PB solvent was first optimized by fitting charging free energies of 42 small molecules (including 29 amino acid side-chain analogs, 5 bases and 8 phosphates analogs of nucleic acids), which were calculated by Thermodynamic Integration in explicit solvents. The performance of PB was tested on salt-bridging pairs, hydrogen-bonding pairs, and short peptides. Our study shows that, in most cases the free energy differences in explicit solvents can be reproduced by PB with reasonable accuracy, but for hydrogen-bonding process, PB can not capture the subtle dependence of free energy upon configuration.

POSTER II-5
ESTIMATING EFFECTS OF MUTATIONS ON P53 STABILITY WITH POISSON-BOLTZMANN THEORY

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Molecular Biology and Biochemistry, University of California, Irvine, CA 92697

The effects of mutations on stability of the p53 core domain were studied by the Poisson-Boltzmann model, and compared with experiment. Different from other works, both ionic and neutral, even hydrophobic mutants can be modeled with reasonable accuracy. This is so even if we assume that mutations do not change the overall protein structure. The self and short-range interaction energies in the unfolded state were modeled with a native-like structure: the unfolded state were obtained by "carved" out the mutated residues and its closer neighbors from the folded protein structure. The electrostatic energies of folded states and of short range of unfolded states were calculated by Finite-Difference Poisson-Boltzmann, the long range interactions are treated by the Gaussian-chain model. The ionization energies upon folding were considered by the HYBRID multiple-site titration program. The hydrophobic effect is considered by the solvent-accessible surface area model. This model considers key physical contributions to protein stability and is computationally simple and fast, but it correlates very well with experiment.

POSTER II-6
COMPUTED ENERGETICS OF PROTEINS AT THE DIFFERENT LEVELS OF THE
PROTEIN STRUCTURE
<u>Ivan Y Torshin</u>
Bioinformatix Consulting LLC, Moscow, Russia

Unified models for analysis of structure-function relationship are essential for post-genomic biology, biochemistry and biophysics. The three-dimensional structure of a protein is one of the important pieces of information that can be used as a starting point of research in the post-genomic era. It is, however, rarely available and the methods of extracting functional information directly from sequence are being elaborated. This presentation will analyze the novel concept of the molecular energetic profiles in relation to the levels of the protein structure. The data illustrate that many functional residues in various test sets can be predicted using amino acid sequence and a secondary structure prediction without any data on the tertiary structure of a protein. Consequently, the method can, potentially, be applied directly to amino acid sequence which is one of the most important output data of the genomic projects.

POSTER II-7
THE CONCEPT OF MOLECULAR ENERGETIC PROFILES IN APPLICATION TO TRNA STRUCTURES.

Ivan Y Torshin
Bioinformatix Consulting LLC, Moscow, Russia

Molecular energetic profiles is a novel unifying model of biomolecular structure and function. The analysis of the individual contributions of the residues of a macromolecule to the stability open new ways in the post-genomic biology. The concept is applicable as to proteins as well as to the RNA. This presentation reports an analysis of the structures of transfer RNAs (tRNA) using the method of the molecular energetic profiles. One of the most important results was the uniform picture that emerged after comparative analysis of the profile of tRNA of quite low sequence identities. In particular, the most stabilizing nucleotides formed the essential parts of the anticodon loop and of the acceptor stem, while the least stabilizing nucleotides formed the central core of the tRNA. The presentation will also discuss other biochemical and biophysical implications (such as energetic aspects of the protein- and aminoacyl-binding) in the framework of the tRNA structure-function studies.

POSTER II-8
FINDING REARRANGEMENT PATHWAYS
Semen A. Trygubenko, David J. Wales
University Chemical Laboratories, Cambridge, United Kingdom

We report a new algorithm for constructing pathways between local minima that involve a large number of intervening transition states on the potential energy surface. A significant improvement in efficiency has been achieved by changing the strategy for choosing successive pairs of local minima that serve as endpoints for the next search. We employ Dijkstra's algorithm to identify the `shortest' path corresponding to missing connections within an evolving database of local minima and the transition states that connect them. The metric employed to determine the shortest missing connection is a function of the minimised Euclidean distance.

We also present a new method of sampling for the most kinetically relevant pathways. Rates information is obtained using discrete paths sampling approach. The method is used to analyse the potential energy surface of a number of effective two-state systems.

POSTER II-9
CATECHOL TO SEMIQUINONE TO QUINONE: A THEORETICAL STUDY OF THE FEATURES RESPONSIBLE FOR RADICAL INITIATION, PROPAGATION, ANTI/PRO-OXIDANT CHARACTER AND CELL TOXICITY

James S. Wright, Leonid L. Chepelev
Dept. of Chemistry, Carleton University, Ottawa, Canada K1S 5B6

This work is a theoretical study of the title reaction, which is an important biochemical reaction responsible for many aspects of free radical-induced cell toxicity. Catechol (1,2-dihydroxybenzene) is easily oxidized under biological conditions forming the semiquinone radical, which in turn is oxidized to form the 1,2-benzoquinone. This is a major pathways for benzene metabolism, and in general the quinones are cytotoxic by one of two mechanisms: 1) Michael addition to the carbon-carbon double bond in the quinone, with subsequent depletion of protein thiols, or 2) redox cycling between quinone and semiquinone, producing superoxide radicals and eventually hydrogen peroxide. Calculation of all possible reaction paths is a theoretical challenge, since it requires accurate calculation of bond dissociation enthalpies (BDEs), pK's, ionization potentials and a good solvation model for all of the above. We will describe our work using a B3LYP-based methodology coupled to a PCM solvation model, and discuss the relevance to molecular toxicity of the catechol and naphthalenediol family. These molecules are also of interest as biological antioxidants, and we will show the relation between the computed properties and the anti/pro-oxidant property.
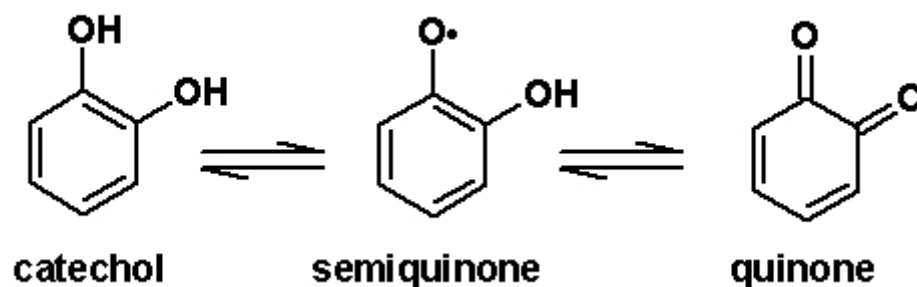
catechol ⇌ semiquinone ⇌ quinone

**A COMPUTATIONAL PLATFORM FOR STUDYING THE MULTIDIMENSIONAL
COHERENT VIBRATIONAL SPECTROSCOPY OF PROTEIN DYNAMICS**

Wei Zhuang, Darius Abramavicius, Tomoyuki Hayashi, Shaul Mukamel
University of California at Irvine

The response of complex molecules to sequences of infrared pulses provides multidimensional femtosecond snapshots of their structure and dynamical processes. Due to the large broadening effect, The peak pattern is much less resolvable compared with multidimensional NMR. A computational package has been developed for predicting the Infrared spectra of peptides and proteins based on their structures.

The code combines Molecular Dynamics simulation, Density Functional Theory and Green Function description of optical response functions. Two main methods of nonlinear spectroscopy simulation: Cumulant expansion of Gaussian Fluctuation (CGF) and Nonlinear Exciton Equation (NEE), have been used and an ab initio electrostatic map is constructed to generate fluctuating vibrational Hamiltonians. Linear absorption, Circular Dichoism, and three third order techniques (photon echo, double quantum excitation and pump probe) can currently be simulated. Polarization of the imposed optical pulses can be tuned to achieve better resolution of the spectra. Quantitative agreement with the experiments have been achieved in simulating several peptides and protein systems.

The exciton scattering matrix and sensitivity analysis which can simplify complex spectra and retrieve and enhance desired features have been applied to structure determination of peptides and protein folding dynamics probing.
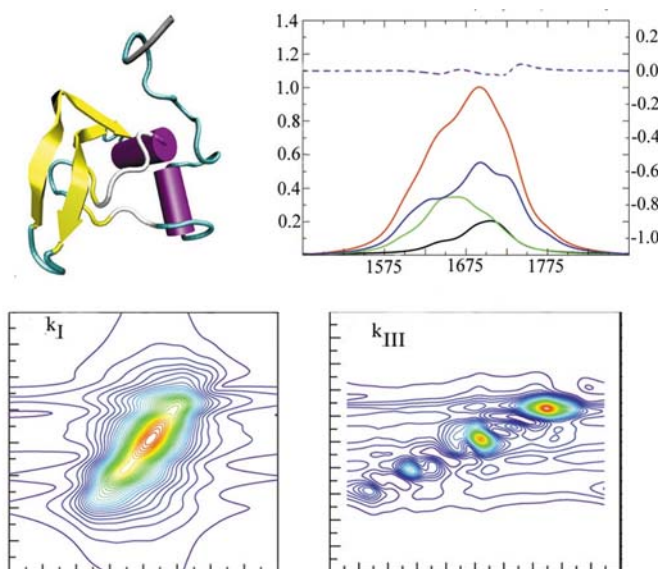
POSTER II-11
REACTIVE MOLECULAR DYNAMICS SIMULATIONS OF PROTON TRANSFER PROCESSES

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Proton transfer reactions are of fundamental importance in a wide range of chemical and biological processes. Theoretical investigations of these dynamical processes are therefore of great interest. The energetic barrier for proton and hydrogen transfer is often so high that transfer events happen only rarely. The long time scales complicate application of accurate dynamical studies using QM/MM molecular dynamics simulations.

Based on prototype systems such as the protonated water dimer, protonated ammonia dimer and protonated ammonia water hetero-dimer, multidimensional potential energy functions have been calculated. Using these, a force field representation has been developed to study the dynamics of the transfer events by molecular dynamics simulations. The flexible implementation of the force field makes it transferable to a variety of systems with hydrogen bonding patterns.

We present applications of the reactive force field to the dynamics of single and double proton/hydrogen bonds in systems of chemical and biological interest. Results are discussed for both, prototype systems and systems of biological interest (proton transfer in ferredoxin I). For the former, infrared spectra are calculated that can be compared to experimental results, while for the latter proton transfer rates from protein side chains to a buried [3Fe-4S] cluster are of interest.

POSTER II-12
FULL CONFIGURATION-INTERACTION MIXED QUANTUM/CLASSICAL NONADIABATIC MOLECULAR DYNAMICS SIMULATIONS OF A HIGHLY CORRELATED TWO-ELECTRON SYSTEM: DYNAMICS AND THERMODYNAMICS OF THE HYDRATED DIELECTRON

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We present the results of extensive molecular dynamics simulations of the hydrated dielectron, a system in which two electrons are solvated by liquid water in a single solvent cavity. The two electron problem is solved at every timestep of the simulations with full configuration interaction, using a highly efficient algorithm we have recently introduced [J. Chem. Phys. 119, 7272 (2003)]. We examine the dynamics of spin-singlet and spin-triplet dielectrons following photoexcitation and find that dielectrons relax on a sub-picosecond timescale and are stable to photodissociation. We use thermodynamic integration ("charging") to examine the thermodynamic stability of dielectrons relative to the single hydrated electron. When the simulated Helmholtz free energy differences are converted to enthalpies (to correct for differences in the simulated pressure in our fixed-volume simulations), we find that the singlet dielectron is thermodynamically stable. We introduce also a generalization of umbrella sampling that allows the umbrella potential to be applied directly to the quantum mechanical degrees of freedom, a feature absent from previous "quantum umbrella sampling" methods. We use this quantum umbrella sampling formalism to study the kinetic stability of dielectrons by forming the potential of mean force for the root-mean-squared separation between the two electrons.

POSTER II-13
FIRST PRINCIPLES DYNAMICS OF ELECTRONICALLY EXCITED *TRANS*-1,3-BUTADIENE: UNDERSTANDING ULTRAFAST TIME RESOLVED PHOTOELECTRON SPECTRA

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As the smallest conjugated organic molecule, butadiene has attracted great attention from theoretical and experimental physical chemists alike. Several time resolved photoelectron spectroscopy studies have been reported for this molecule, all reporting lifetimes on the order of tens of femtoseconds. The observed decay is often assigned to nonadiabatic conversion from the bright 1 ^1B_u state to the dark 2 ^1A_g state or from the dark 2 ^1A_g state to the ground state, but many possible explanations must be entertained before a definitive assignment can be made. We have studied the photodynamics of *trans*-1,3-butadiene using a combination of Ab Initio Multiple Spawning (AIMS) dynamics and ab initio quantum chemical calculations. From our dynamics simulations we have calculated the time resolved photoelectron signal and find good agreement with experiment. In our simulation, however, the decay is not the result of a nonadiabatic process, but instead it is caused by an increase in the ionization potential resulting from nuclear relaxation along a terminal carbon-carbon bond twisting coordinate. Our simulations suggest that two oppositely polarized charge transfer states play an important role in the photodynamics of butadiene.

POSTER II-14
ROTATION OF THE ECKART FRAME DUE TO
INTERNAL MOLECULAR MOTIONS

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By changing its shape while conserving angular momentum, a polyatomic molecule can return to its initial shape with a different orientation (as a gymnast or a diver can do), corresponding to a rotation of the Eckart frame of the molecule. The net angle of rotation is explicitly described using generalized Eckart coordinates, which include various "internal" coordinates, such as Jacobi coordinates, interatomic distances, and hyperspherical coordinates, as special cases. Thus this result is applicable to collision dynamics as well as to the dynamics of van der Waals complexes, molecular clusters, polyatomic molecules, and macromolecules. In particular, the overall rotation of an atom-diatomic molecule van der Waals complex is described in terms of molecular rotational constants. Using geometric mechanics, the net angle of overall rotation is expressed as the sum of a dynamic phase plus a geometric phase.

POSTER II-15
BOHMIAN DYNAMICS FROM TRAJECTORY STABILITY PROPERTIES IN BOTH REAL AND IMAGINARY TIME

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It is shown that the quantum force in the Bohmian formulation of quantum mechanics can be related to the stability properties of the given trajectory. In turn, the evolution of the stability properties is governed by higher order derivatives of the quantum potential, leading to an infinite hierarchy of coupled differential equations. Neglecting derivatives of the quantum potential beyond a certain order allows truncation of the hierarchy, leading to approximate Bohmian trajectories. The lowest-order version of the truncated hierarchy can capture large corrections to classical mechanical treatments and yields (with fewer trajectories) results that are somewhat more accurate than those based on quasiclassical phase space treatments.

Bohm's hydrodynamic formulation is employed to solve the diffusion equation. Quantum trajectories are found to behave differently in imaginary time, exhibiting caustic singularities. A wavefunction repartitioning methodology is introduced to prevent the imaginary-time crossing events, leading to stable evolution that does not suffer from the numerical obstacles in real time. Use of an approximate technique based on trajectory stability properties to solve Bohm's equations in imaginary time leads to accurate prediction of the energy of a low-lying eigenstate from a single quantum trajectory.

SIMULATION OF DYNAMICAL PROPERTIES OF NORMAL AND SUPERFLUID HELIUM

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The formation of a superfluid when ^{4}He is cooled below the characteristic lambda transition temperature is accompanied by intricate quantum mechanical phenomena, including emergence of a Bose condensate. The forward-backward semiclassical dynamics (FBSD) method in conjunction with an imaginary time path integral representation of the Boltzmann operator is employed to calculate the single-particle velocity autocorrelation function across the normal-to-superfluid transition. We find that the inclusion of particle exchange alters qualitatively the shape of the correlation function below the characteristic transition temperature. The incoherent structure factor extracted from the velocity autocorrelation function is in very good agreement with neutron scattering data, reproducing the width, height, frequency shift, and asymmetry of the curves, as well as the observed increase in peak height characteristic of the superfluid phase. Our simulation results reveal the distinct roles of zero-point motion and quantum statistical effects in the dynamics of the quantum liquid.

POSTER II-17
ELECTRON DYNAMICS OF SILVER CLUSTERS IN PULSED LASER FIELDS:
LASER-FREQUENCY DEPENDENCE AND THE SCREENING EFFECT OF *D* ELECTRONS

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We present theoretical studies of electron dynamics of harmonic generation from Ag_2 and Ag_8 in pulsed laser fields. A time-dependent N-electron interacting system is solved through a set of electronic wave functions satisfying the time-dependent Kohn-Sham equation. We have found that the harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. This resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence *s*-electrons are shaken effectively and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have also found that the polarizable core *d*-electrons significantly screen the valence *s*-electrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The figure illustrates an increase (red) and a decrease (blue) in the Ag_2 electron density, respectively. We can see that the *s* and *d* electrons move reciprocally.

References:
[1] K. Nobusada and K. Yabana, Phys. Rev. A 70, 043411 (2004).
[2] K. Shiratori, K. Nobusada and K. Yabana, Chem. Phys. Lett. 404, 365 (2005).
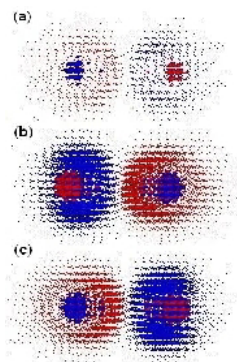
POSTER II-18
MIXED QUANTUM-CLASSICAL EQUILIBRIUM

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We present an analysis of the equilibrium limits of the two most widely used approaches for simulating the dynamics of molecular systems that combine both quantum and classical degrees of freedom - namely mean field (Ehrenfest) and surface hopping. For a N-level quantum system connected to a classical bath of oscillators at constant temperature, we derive the analytical expression for the equilibrium mean energy attained by the mean field method, and show that it is substantially higher than that given by the Boltzmann distribution of quantum state populations, but does not correspond to "infinite temperature", i.e., equal population of all states. In addition, the mean energy diverges as N increases. By contrast, "fewest switches" surface hopping achieves Boltzmann quantum state populations. These analytical results are verified with simulations.

POSTER II-19
DIRECT QM/MM SIMULATIONS OF THE PHOTODYNAMICS OF RETINAL PROTONATED SCHIFF BASE IN ISOLATION AND SOLVATED ENVIRONMENTS

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Retinal Protonated Schiff Base (RPSB) is the chromophore of rhodopsin family, including bacteriorhodopsin-bR and halorhodopsin-hR. Photoisomerization of PSBR from the all-trans to 13-cis conformation triggers ion transport across the cell membrane in hR and bR. In the protein environment, this isomerization occurs exclusively about the C13=C14 bond. However, in solution environments, a variety of isomerization products are observed. An unresolved question is the role of the environment in photochemical mechanism. We have investigated the photochemical mechanism of RPSB using an analogue having all isomerizable bonds. Simulations are performed in isolation and a solvated (methanol) environment. We use the multiple spawning method to describe quantum mechanical effects of the nuclear degrees of freedom. A reparameterized multireference semiempirical method is used to describe the ground and excited electronic states of the chromophore and the environment is represented with an empirical force field (QM/MM). The potential energy surfaces and their couplings are determined "on the fly". We find that the isomerization occurs in hundreds of femtoseconds for the isolated case, but is slowed down to multiple picoseconds in methanol. The quantum yield is strongly decreased in a solvated environment. Good agreement is obtained with experimental results in solution.

TWO-DIMENSIONAL CONDENSATION OF ORGANIC ADSORBATES AT ELECTROCHEMCIAL INTERFACES: A SPIN-1 ISING MODEL FORMALISM

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Various organic adsorbates such as coumarin, adenosine, adamantane etc. undergo two-dimensional condensation at electrochemical interfaces and two pits are obtained in the differential capacitance-potential (C-E) plot. This is due to change in the orientational states of an adsorbate, where an adsorbate may undergo condensation by the adsorption in two different positions at an electrochemical interface. To explain such systems the available classical model of two parallel capacitor is inappropriate, since it is phenomenological and not molecular, hence spin-1 Ising model is used.

In this model, adsorbate molecules are considered with two different orientation states A1 and A2, the sites of a two-dimensional lattice is occupied by the adsorbate in any one of the orientation state or solvent molecule. The interaction picture at the interface would include, the energitics arising from permanent or induced dipolar effects, discreteness of charge effects, electrostatic and non-electrostatic interactions of the adsorbate with the electrode surface. By incorporating various interactions the total Hamiltonian (H_T) can be written as

Equation (1)
where K_1, L, J are the interaction energies, D and H are the field parameters. The mean field solution for the above Hamiltonian Eq.(1) yields the following two expressions for order parameteris viz the total surface coverage of the adsorbate theta $=(theta_1 + theta_2)$ and the net orientation of the adsorbed dipolar states, R=(theta$_1$-theta$_2$)
Equation (2)
and
Equation (3)

The above expressions are used for the simulation of differential capacitance-potential(C-E) plot as shown in fig-1.

Fig-1:Differential capacitance – potential plots (a) Two pits when p_{A1} p_{A2} and alpha$_{A1}$ alpha$_{A2}$, L=0;K_1=3.9kT and J=0.01K_1;(b)Two dips when J=K_1=L=0; (c)one dip when H=J=K_1=L=0, Δ_{UA2}->∞ and (d)one pit when H=J=L=0,Δ_{UA2}->∞ and K_1=-3.9kT. (where Δ_{UA2} denotes the non electrostatic interaction energy).
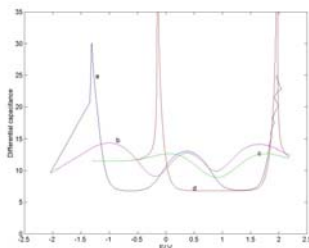
$$H_s = -K_1 \sum_{i,j} s_i^z s_j^z - L \sum_{i,j} \left(s_i s_j^z + s_j s_i^z \right) - J \sum_{i,j} s_i s_j - D \sum_i s_i^z - H \sum_i s_i \qquad (1)$$

$$\theta = (\theta_1 + \theta_2) \text{ and } R = (\theta_1 - \theta_2)$$

$$R = \theta \tanh \left[(H + 2JR + 2L\theta)/kT \right] \qquad (2)$$

and

$$\frac{\theta}{1-\theta} = \frac{\exp\left[(D + H + 2(J+L)R + 2(K_1 + L)\theta)/kT \right]}{\left[1 + \exp\left[-2(H + 2JR + 2L\theta)/kT \right] \right]} \qquad (3)$$

POSTER II-21

REASSIGNED TO PI-100

POSTER II-22
SEMICLASSICAL LIOUVILLE METHOD FOR THE SIMULATION OF ELECTRONIC TRANSITIONS WITH A SINGLE ENSEMBLE OF CLASSICAL TRAJECTORIES.
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The semiclassical Liouville method used in the simulation of electronic transitions is applied to the problem of nonadiabatic molecular dynamics on coupled electronic surfaces. While previous implementations of the method require the use of a different ensemble of classical trajectories for each element of the semiclassical density matrix, the approach outlined in the present work supports the evolution of all density matrix elements with a single ensemble of trajectories. Such simplification makes the method more suitable for general applications, and at the same time the computational cost involved in the calculations becomes more manageable. The ensemble of trajectories evolves under classical laws on a reference potential, whose value is dictated by the initial state and the nature of the underlying system. A set of coefficients determines the weight of the classical trajectories on the different surfaces, and the errors made by using a reference Hamiltonian for the propagation have been compensated in the calculation of these coefficients by explicitly including a correction term that involves the difference between the true and the reference potential. Accurate results were obtained for a variety of benchmark models, and the limits of validity of the approximation have been identified.

POSTER II-23
PRONOUNCED NON-CONDON EFFECTS IN THE ULTRAFAST INFRARED
SPECTROSCOPY OF WATER

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In the context of vibrational spectroscopy in liquids, non-Condon effects refer to the dependence of the vibrational transition dipole moment of a particular molecule on the rotational and translational coordinates of all the molecules in the liquid. For strongly hydrogen-bonded systems such as liquid water, non-Condon effects are large. That is, the bond dipole derivative of an OH stretch depends strongly on its hydrogen-bonding environment. Previous calculations of non-linear vibrational spectroscopy in liquids have not included these non-Condon effects.

We use a combined electronic structure/molecular dynamics approach to calculate both the linear and non-linear response for the OH or OD stretches of dilute HOD in D_2O or H_2O, respectively. We find that for water, inclusion of non-Condon effects is important for an accurate calculation of, for example, homodyned and heterodyned three-pulse echoes. Such echo experiments have been ``inverted'' to obtain the OH stretch frequency time-correlation function, but by necessity the Condon and other approximations are made in this inversion procedure. Our conclusion is that for water, primarily because of strong non-Condon effects, this inversion may not lead to the correct frequency time-correlation function.

POSTER II-24
A SEMI-CLASSICAL TREATMENT OF NONADIABATIC DYNAMICS

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We focus on the development of fast semi-classical methods for dynamics that involve transitions between electronic states.

Using spin-coherent states, we are able to map the discrete matrix mechanics of the electrons to an equivalent but classical-like dynamics. The semi-classical coherent state propagator is then used to calculate approximate time correlation functions. The solutions to the boundary conditions are found using the Newton-Raphson method starting from a real trajectory.

Our method is tested using 3 model systems proposed by Tully. For most situations, our semi-classical results agree quantitatively with the quantum results over a wide energy range. However, when strong branchings of classical paths exist, the semi-classical results deteriorate. The origin of these errors will be discussed.

POSTER II-25
ENERGY TRANSFER AT A GAS-LIQUID INTERFACE

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Although energy transfer at a gas-solid interface has been a topic of interest for several decades, only recently has the gas-liquid interface attracted interest. We describe here simulations of energy transfer and surface trapping occurring when a hot gas impinges on a liquid surface. Of particular interest is on the dependence of the energy transfer on the temperature of the liquid and on the degrees of freedom available for accepting the incident kinetic energy. Our initial investigations of atomic and molecular liquids suggest that there are significant similarities between the energy transfer to liquid surfaces and the analogous processes at a gas-solid interface.

POSTER II-26
AB INITIO PHOTODYNAMICS OF BENZENE: MODELING PHOTOELECTRON SPECTRA

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The photophysics of benzene has been extensively studied, including topics such as channel three processes and time dependent decays of the photoionization signal. Photoelectron spectroscopy experiments on benzene indicate decay of this signal occurs with two very different time constants: one process has a decay constant of about 40 fs and the other has a time constant of about 5-10 ps. We examine the dynamics of benzene excited to the low-lying bright electronic state (S_2) using an ab initio multiple spawning (AIMS) technique. From these dynamics simulations, we see population transfer from S_2 to S_1 within about 50 fs. Soon after population reaches S_1, the population begins to transfer to the ground state, which has nearly half of the total population by about 400 fs. The efficiency of this transfer may be due to the similarities between the S_2S_1 and S_1S_0 conical intersection geometries. Using these dynamics simulations, we model the time-dependent photoelectron spectra using ionization potentials calculated using CAS*PT2. Our simulated spectra show both the long and short time components seen experimentally, and we have examined the physical origin of the different components.

POSTER II-27
ADSORPTION OF GLYPHOSATE ON MONTMORILLONITE INTERLAYER SURFACES
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Glyphosate (N-phosphonomethylglycine) is the most popular herbicide in the world. Glyphosate is rapidly adsorbed and tightly bound to most soils through constituents such as clay minerals, metallic oxides, organic materials and humic substances. Glyphosate can be adsorbed on clay silicates like montmorillonite or bound to octahedral cations, specifically iron and aluminum, exposed on the edges of the mineral surface. Glyphosate also interacts with this octahedral smectite and penetrates into the interlayer space, which expands in aqueous solution. As the exact binding mechanism is not fully understood we develop and implement a theoretical structural model of these interactions using the molecular modeling software Spartan Pro. This model reproduces the expansion of the interlayer in presence of water adequately and shows a correlation between the minimization of the energy of the system and the proximity of the sulfonate moiety of glyphosate with the mineral surface.

QUANTUM INSTANTON EVALUATION OF THE KINETIC ISOTOPE EFFECTS

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A general quantum-mechanical method for computing kinetic isotope effects is presented. The method is based on the quantum instanton approximation for the rate constant and on the path integral Metropolis Monte-Carlo evaluation of the Boltzmann operator matrix elements. It computes the kinetic isotope effect directly, using a thermodynamic integration with respect to the mass of the isotope, thus avoiding the more computationally expensive process of computing the individual rate constants. The method is more accurate than variational transition-state theories or the semiclassical instanton method since it does not assume a single reaction path and does not use a semiclassical approximation of the Boltzmann operator. We first present numerical results for the Eckart barrier and for the collinear and full three-dimensional isotope variants of the hydrogen exchange reaction H+H2->H2+H. In all seven test cases, for temperatures between 250 K and 600 K, the error of the quantum instanton approximation for the kinetic isotope effects is less than ~10%. Finally, we apply the method to a model of hydrogen transfer in enzymatic reactions: the [1,5]-sigmatropic hydrogen transfer in 1,3-cis-pentadiene. The reaction is modeled using an empirical valence bond potential based on modified AMBER force field. Numerical results agree with experiment.

CALCULATION OF TIME CORRELATION FUNCTIONS USING THE SEMICLASSICAL INITIAL VALUE REPRESENTATION

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Real-time correlation functions play a key role in the theory of dynamic processes in many-body systems. However the exact calculation of real-time correlation functions for a quantum system is extremely difficult. Hence we use Semiclassical theories to provide an approximate description of the quantum dynamics of the system.

Semiclassical Initial Value Representation (SC-IVR) techniques incorporate quantum effects into molecular dynamics simulations. Extensive applications of the IVR techniques have been shown to be quite accurate in describing quantum effects. However these techniques are still not feasible for very large systems because of the computational difficulty in dealing with oscillatory integrands. One can use Filinov filtering schemes to reduce the oscillations. We try and explore these filtering techniques on the SC-IVR approximation to the real-time correlation functions restricting ourselves to the dipole and flux-side correlation function.

POSTER II-30
INTERNAL ROTATIONAL MOTIONS OF METHYL, TRIFLUOROMETHYL AND *TERT*-BUTYL GROUPS IN CRYSTALLINE SOLIDS

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Recently we have studied the internal rotational motions of methyl, trifluoromethyl, *tert*-butyl groups in a series of aromatic crystalline solids with a combination of multiple techniques. A few representative compounds are shown below. With measuring the ^{1}H and/or ^{19}F spin relaxation rate as a function of temperature and magnetic field strength, the information on the internal rotation dynamics of methyl, trifluoromethyl and *tert*-butyl groups were obtained. With the crystal packing structure elucidated by single crystal x-ray crystallography, we were able to model the internal rotational process of these groups through *ab initio* and density functional theory computations. Through quantum mechanics calculations, we targeted to interpret the rotational barrier in terms of *intra*- and *inter*-molecular interactions and to understand the relationship between the rotational barrier with the molecular and crystal structure. The role of structural relaxation and the coupling of rotational motions, e.g. intra-*tert*-butyl motions coupling and intermolecular coupling between neighboring rotor groups, were also addressed. Our recent progress on the project will be presented.
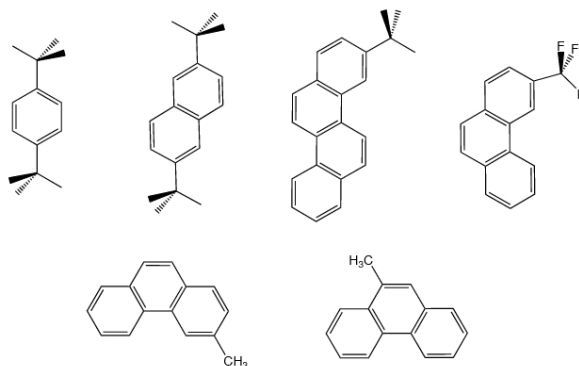
POSTER II-31

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POSTER II-32
ELECTRON TUNNELING OF PHOTOCHEMICAL REACTIONS ON METAL SURFACES: NEGF-DFT APPROACH TO PHOTON ENERGY DEPENDENCE OF REACTION PROBABILITY

Koichi Yamashita, Hisao Nakamura
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We have developed a theoretical model of photo-induced reactions on metal surfaces initiated by the substrate/indirect excitation mechanism using the non-equilibrium Green's function (NEGF) approach. We focus on electron transfer, which consists of (1) electron-hole pair creation, (2) transport of created hot electrons, and (3) tunneling of hot electrons to form an anion resonance. We assume that steps (1),(2), and (3) are separable. By this assumption, the electron dynamics might be restated as a tunneling problem of an open system. Combining the Keldysh time-independent formalism with the simple transport theory introduced by Berglund and Spicer, we present a practical scheme for for first-principle calculation of the reaction probability as a function of incident photon energy. The method is illustrated by application to the photo-induced desorption/dissociation of O_2 on a Ag(110) surface by adopting density functional theory.

QUANTUM INSTANTON MODEL FOR CHEMICAL REACTION RATE CALCULATION USING PATH-INTEGRAL MONTE-CARLO METHODS

Siyang Yang, William Miller

Berkeley

Recently, a quantum mechanical theory for chemical reaction rate calculation was proposed which is herein referred to as the quantum instanton (QI) approximation because of its relation to an earlier semi-classical transition state theory (SC-TST) which became known as instanton model. QI is a new and more rigorous quantum version of TST which incorporates the desirable aspects of the instanton picture that involves only properties of the Boltzmann operator and thus is feasible for even quite complex molecular systems via Path-Integral Monte-Carlo (PIMC) method.

Some new developments have been made recently to incorporate zero-time information of flux autocorrelation function into the QI model. Some new and effective PIMC methods have been invented and implemented to apply the QI model for multi-dimensional problems.

The new models have been applied to several testing and real chemicle reactions including: 1-dimensional Eckart potential, 2-dimensional collinear reactions H+H2 and D+H2, proton abstraction H+CH4 in 3-dimensional Cartesian coordinate, and Borgis problem for proton transfer reaction in solution.

**ANOMALOUS TEMPERATURE-ISOTOPE DEPENDENCE IN PROTON-COUPLED
ELECTRON TRANSFER**

Steve Presse, Robert J Silbey
M.I.T.

A novel proton-coupled electron transfer, *PCET*, mechanism which has been motivated by an anomalous *T*-isotope dependence observed in ongoing experiments is presented. The proposed mechanism, involving no proton transfer, provides a physical interpretation for the unexpected *T*-dependence of the k_H/k_D ratio of the experiments, where k_H and k_D are the *ET* rates when the electron is coupled to the motion of the proton and deuteron respectively. In this model, the *ET T*-isotope dependence is microscopically attributed to the modulation of the electron tunneling dynamics by bath-induced fluctuations in the proton coordinate. A simple explanation for the relative *T*-stability of the rates over a wide *T*-range, as observed experimentally, emerges based on the magnitude of the fluctuation required to induce *PCET*. We argue that this mechanism is particularly relevant in understanding *PCET* processes for which there exists a sufficient timescale separation between electron and proton transfer. Incidentally, this *T*-isotope dependence cannot be reconciled on physical grounds with the *T*-isotope dependence of the Marcus formula for simple *ET*.

AB-INITIO QUANTUM TRANSPORT STUDIES: APPLICATIONS AND METHODOLOGY.

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With the success of experiments to measure charge transfer through molecular wires the need for accurate theoretical models describing these systems has been highlighted. The Landauer based scattering theory is currently widely used to define the theoretical formalism describing molecular conductivity. According to this view, electrons are originating from one electrode flowing to the second through the connecting molecule, where each electrode is in different thermodynamic equilibria as defined by their electrochemical potentials. Conductivity then can be described by concentrating on the molecular scattering state.

Within this approach different approximations and modeling choices have to be defined to describe the open system characteristics inherent in conductivity. In the presented research, these choices are carefully analyzed to produce a set of recommendations necessary to achieve a model, which reliably describes the conductivity properties of the investigated system. In addition, we present results demonstrating a molecular junction which acts as an electronic switch based on changes induced by photo excitation and relaxation processes.

EFFECT OF THE POTENTIAL PARAMETERS ON THE ELECTRON TRANSFER MECHANISM IN DONOR-BRIDGE-ACCEPTOR SYSTEMS

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Using a modified on-the-fly filtered propagator path integral formalism, effect of the donor-bridge energy gap, donor-acceptor energy gap and electronic coupling constants between states is thoroughly investigated in electron transfer of a double mutant photosynthetic purple bacterial reaction center. Pathways connecting the donor and the acceptor are separated to three groups; incoherent hopping, coherent superexchange, and partially coherent hopping mechanism. By decomposing the reduced density matrix of a system into three partial density matrices, relative contribution of each transport mechanism to the overall charge transfer is evaluated and the role of potential parameters is discussed.

POSTER II-37
TIME-INDEPENDENT SCATTERING WITH CHEBYSHEV POLYNOMIALS

Burçin Temel, Greg Mills, Horia Metiu

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Time-independent scattering problems can be formulated with different asymptotic boundary conditions, having different functional forms and different unknown quantities. In our work, we use a least-squares functional which has a minimum when the wave function satisfies Schrödinger equation on a grid.

The wave function on a grid and the phase-shifts are obtained by minimizing the functional. The minimization is performed with a preconditioned conjugate gradient; using an iterative method such as a preconditioned conjugate gradient ($\sim O(N)$) is more efficient than matrix inversion ($\sim O(N^3)$). We use Chebyshev polynomials to calculate, fast and accurately, the derivatives at the grid points.

This method allows the use of real (as opposed to complex) boundary conditions without the instabilities that are inherent in the Kohn Variational Principle (KVP). In addition, we obtain accurate wave functions and phase-shifts, unlike the KVP which only provides accurate phase-shifts.

POSTER II-38
CHARGE TRANSFER IN PROTEINS:
A VARIATIONAL APPROACH
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Charge transfer (CT) plays an important role in biology and chemistry: Photosynthesis, respiration and protection against oxidative damage are central to life on our planet. Here, we present numerical results for CT processes for simple model proteins with characteristic secondary structure elements and a C60 molecule and its antibody.

In our work, we describe polarization (outer sphere) and vibronic (inner sphere) degrees of freedom by a chemically specific, atomistic Su-Schrieffer-Heeger Hamiltonian which has been extended by a frequency-independent reaction field. The inherent many-body problem is solved by a mean-field approach, which permits the diagonalization of the Hamiltonian in a self-consistent fashion. We obtain constants for CT in alpha-helices, isolated beta-sheets and a C60 –antibody complex.

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TRIPLET-TRIPLET ENERGY TRANSFER COUPLING: THEORY AND CALCULATION

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The triplet-triplet (TT) energy transfer is a process where molecules exchange spin and energy. The electronic coupling in triplet-triplet energy transfer involving two molecular fragments with different theoretical models is shown here. We showed that Direct-Coupling (DC) scheme, traditionally used for electron transfer, is applicable to calculate TT coupling. Results from the DC scheme are very similar to that from CI-Singlet (CIS) in the model systems studied. The distance dependence of TT coupling is roughly twice as steep as that of electron transfer coupling, which is characteristic for the Dexter's exchange mechanism. For application to large molecules, we have developed the Unperturbed Initial Guess (UIG) method, for a simplified and intuitive route to calculate the electronic coupling. The use of UIG in electron transfer and TT couplings will be presented and discussed.

ELECTRON AND ENERGY TRANSFER IN DNA PHOTOLYASE: A THEORECTICAL STUDY

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Photolyase enzyme repairs DNA damages caused by the base pair dimerization upon exposure to the sun's UV rays. Recently obtained crystal structure of DNA and photolyase complex near their repair conformations agrees well with the theoretical model previously proposed in our laboratory. In this work we corroborate ZINDO/S calculation with the forward electron transfer results from our previous results. We further study back electron transfer based on conformational changes of the reactive center. Coupled with the electron transfer we examine energy transfer in terms of excited states configurations that form the basis of spectroscopic calculations. Mechanistic aspects of DNA photo repair are presented in connection with electron transfer, energy transfer and protein dynamics of the DNA and its photolyase complex

VARIATIONAL REDUCED-DENSITY-MATRIX CALCULATIONS ON RADICALS: A NEW APPROACH TO OPEN-SHELL AB INITIO QUANTUM CHEMISTRY

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A new approach to open-shell calculations using variational reduced-density-matrix (RDM) theory will be presented. We will report ground-state energies and properties for radicals both near and far from equilibrium. Unlike unrestricted wave function methods, the RDM method produces 2-RDMs without spin contamination.

POSTER II-42
THE IMPORTANCE OF G FUNCTIONS TO THE EXCITATION ENERGIES OF THE FIRST ROW TRANSITION METALS

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Excitation energies of transition metals in their d-shells describe many important physical phenomena, and as of yet a satisfying prescription for the level of theory needed to determine the non-relativistic excitations has not been offered. In our research, the $s^2 d^n$ $s^1 d^{n+1}$ excitation energies of the transition metals have been computed using CCSD with two levels of perturbative correction ((T) and (2)) using two large basis sets both containing g functions. Previous literature sources have reported deviations from the experimental values for the excitation energy, and in our work we assess the nature of these deviations. We have examined the importance of higher angular momentum functions, saturation of the basis set for given levels of angular momentum, and the effect of the level to which the correlation is computed to discover the nature of these deviations. The understanding of the correlation of transition metals provided by this work has also motivated a look into the potential curve of the chromium dimer.

PROGRESS IN KINETIC ENERGY DENSITY FUNCTIONAL THEORY

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The first Hohenberg-Kohn theorem guarantees that the electron density ρ of any quantum mechanical system determines its ground-state energy. Unfortunately it does not provide the actual form of the energy density functional, leading to decades of research concerned with constructing the unknown exchange-correlation (most commonly) and kinetic energy density functionals (KEDFs). Kohn and Sham (KS) introduced one-electron orbitals to express the kinetic energy as an implicit functional of the density. It is our goal to derive an explicit functional of ρ for the kinetic energy.

Current KEDFs lack general applicability, although their performance is encouraging. The Thomas-Fermi (TF) KEDF is exact for the uniform electron gas. One may consider this to be the local density approximation for the kinetic energy. Unfortunately, this crude approximation breaks down in realistic systems where ρ is not free-electron-like. In order to account for fluctuations in ρ, we scale the TF KEDF using a weight function whose value is based on the fluctuation rate, defined by the ratio of the von Weiszäcker functional to the TF functional. The weight function exhibits similar behavior for different elements, suggesting its possible generality, and can be fine-tuned to reproduce the KS kinetic energy for the same electron density.

POSTER II-44
SCALED OPPOSITE-SPIN SECOND ORDER MΦLLER–PLESSET CORRELATION
ENERGY: AN ECONOMICAL ELECTRONIC STRUCTURE METHOD.

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Separate scaling of the same-spin and opposite-spin contributions (Spin-Component-Scaled (SCS)-MP2) to the second order MφllerPlesset energy can yield statistically improved performance for a variety of chemical problems including atomization energies and derivative properties. If only the opposite spin contribution (Scaled-Opposite-Spin (SOS)-MP2) is scaled up, while completely ignoring the same-spin contribution, it is possible to reduce the computational complexity from 5th order to 4th order in system size, without exploiting spatial locality, by using a combination of the Laplace approach and resolution-of-identity (RI) approximation that results in very little degradation of results. However neither of these scaled MP2 energies recovers the full MP2 result for the dispersion energy of non-overlapping systems. This deficiency is addressed by using a distance-dependent scaling of the opposite spin correlation energy in the Modified-Opposite-Spin (MOS)-MP2 method that can get the long-range description correct by construction. The added advantage of these Opposite-Spin-MP2 methods (employing the Laplace-RI formalism) is that the analytical gradient can be evaluated in a fourth order scaling algorithm that would permit faster evaluation and push the limit of system size currently feasible for geometrical optimization techniques that systematically include electron correlation.

POSTER II-45
REACTIONS OF HYPERTHERMAL OXYGEN ATOMS WITH GRAPHITE

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In low Earth orbit (LEO), at 300 km altitude, the faint atmosphere interacts with satellites leading to the degradation of metal, hydrocarbon and ceramic surfaces. $O(^3P)$, the predominant species in LEO, collides with surfaces with a kinetic energy of 5eV. We study the interaction of atomic O and graphite, as a model for the satellite surface. We have performed ab initio calculations using VASP and Gaussian. We varied oxygen coverage and position and considered perfect and defective graphite planes. We have calculated transition state energies and geometries as well as many other points on the oxygen-graphite potential energy surface. These ab initio points are being used as input to construct a global potential energy surface that will then serve as the basis for dynamics simulations.

TRUNCATION OF THE CORRELATION CONSISTENT BASIS SET: A MEANS TO REDUCE THE COMPUTATIONAL SCALING OF AB INITIO METHODS?

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Truncation of the correlation consistent basis sets (cc-pVnZ, where n = D(2), T(3), Q(4), 5) for the hydrogen atom has been examined. Several molecules containing hydrogen along with first- and third-row molecules have been studied in order to determine if truncation is a viable means to reduce the computational scaling. The effects that truncation has on properties such as geometry, dissociation and ionization energies has been examined and compared to the overall time saved in the calculation. The ability to extrapolate a series of truncated basis sets to a complete basis set (CBS) limit that is comparable to the full CBS limit has also been addressed.

THEORETICAL AND INFRARED SPECTROSCOPIC STUDY OF THE BENZENE·O_2^- COMPLEX.

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The infrared spectrum of the benzene·O_2^- complex has been determined by means of Ar-atom predissociation spectroscopy. Several transitions due to CH stretch fundamentals and various combination bonds are observed in the 2875–3100 cm^{-1} region. In this study electronic structure calculations are employed to characterize the benzene·O_2^- complex. The potential energy surface of benzene·O_2^- is found to be quite flat with multiple minima separated by small barriers. The vibrational spectra were calculated allowing "near-degeneracy" mixing of the CH stretch with combination and overtone bands. Comparison of the calculated and experimental spectra reveals that the experimental spectrum most likely arises from two distinct isomers differing in the coordination of the superoxide molecule to the hydrogen atoms of benzene.

POSTER II-48
ELECTRONIC STRUCTURE STUDIES OF BENZENE-PALLADIUM INTERFACE USING DFT

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Metal-molecule interface in molecular electronic devices is currently one of the fundamental problems in molecular electronics. Density functional theory was used to investigate the benzene-palladium interface at B3LYP/LANL2DZ level. The geometries of the interfaces when they are used as the two terminals connecting single molecules are important in evaluating their electrical properties. The analysis is based on the ability of the Kohn-Sham molecular orbitals to predict the electron transport characteristics of single molecules attached to metallic contacts. Our work provides insight on the nature of these interfaces.

AB INITIO STABILITY INVESTIGATION OF IONIC CLATHRATE HYDRATES

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We performed *ab initio* structural optimization simulations on *tetramethylammonium hydroxide* (TMA) clathrates $Me_4NOH.7.5H_2O$ and their alkali metal analogs $Cs(Me_4N)_2(OH)_3.14H_2O$. Experimentally, addition of Cs^+ ions into the empty small cages increases the melting temperature by 53 ^{o}C, but the molecular mechanisms involved are subtle. Our DFT simulations indicate three-fold coordinate OH^- in the 4-coordinate polyhedral (water) lattice, with the hydroxide proton not effectively hydrogen bonded. Geometry optimized configurations were not stable in the initial tetragonal space group, with all heavy atoms shifting well outside their equivalent harmonic displacements. Besides a widely expanded distribution of O...O...O angles in the relaxed configurations, numerous cage edges with $r_{OO} \geq 3.25$ Angstroms were found, only ~35% of which corresponded to the long $(O^*$--H$)^-$...O distances through the weakly interacting hydroxide protons, in contrast to the X-ray data. Addition of Cs^+ ions shortened the O^*--H$)^-$...O distances by ~0.2 Angstroms, but left the remaining O^*...O distances unaffected. The open, proton deficient framework of these optimized structures is similar to a low temperature, semiclathrate phase of TMA, suggesting a link between clathrate stability and high proton mobility, i.e. alkali hydroxide content and orientational water dynamics. LA-UR-05-3237

AB INITIO ELECTRONIC STRUCTURE OF DIMETALLOCENES M$_2$L$_2$ WITH M = SC, TI, V, CR, MN, FE, CO, NI, CU, ZN, CD, HG AND L = H,F,CH$_3$,(CH)$_5$, (CH$_3$C)$_5$

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Dimetallocene compounds M$_2$L$_2$ are studied for all metals in the first transition series (Sc, .., Cu) and group twelve (Zn, Cd, Hg) using the Wien *ab initio* simulation package (ultra-soft pseudo-potentials, 394eV cut-off, spin polarized density functional with generalized gradient approximation, conjugate gradient geometry optimization, cubic cell 1.50 nm edge, periodic boundaries, Γ point). The focus is on recently synthesised dizincocene with pentamethyl-cyclopentadienyl (CH$_3$)$_5$C$_5$ ligands. Its geometry by X-ray crystallography is well predicted by these calculations: short Zn-Zn bond 239pm, almost "ideal" dimetallocene geometry with metal axis perpendicular to parallel rings. Chosen metals explore 3d electron *aufbau* and atomic size. Ligands explore bonding through electronegativity, orbital shape-size and delocalization. The calculations for C$_5$H$_5$-, C$_5$(CH$_3$)$_5$- dizincocenes are similar, providing a reason for exploring across the transition metals with the smaller ligand. Dizincocene shows no significant energy difference (< 0.1eV) amongst staggered D$_{5d}$, eclipsed D$_{5h}$ and the other intermediate geometries examined. Not all transition elements attain the "ideal" dimetallocene geometry, some are slipped, some edge bonded. Many but not all, appear physically stable in vacuum with singlet S = 0 ground state.

POSTER II-51
MOLECULES OF IRON FE$_N$ (N = 2, 3, 4, 6, 8)

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Ab initio electronic structure calculations are presented for neutral iron molecules Fe$_n$ (n = 2, 3, 4, 6, 8). Properties include total binding energy and geometric structure as a function of the total spin S. Unpaired electrons in the ground state are: Fe$_2$ (6), Fe$_3$ (10), Fe$_4$ (14), Fe$_6$ (20), Fe$_8$ (24). These molecules are interesting for catalysis, magnetism, information storage, molecular electronics, bioinorganic chemistry. Starting with Fe$_4$ chiral geometries are possible. In small molecules geometric changes include angle bending, bond stretching to bond fission, torsion angle changes to planarity. Shortest bonds (< 200pm) are found the states with lowest total spin. Molecule Fe$_8$ ($0 \leq S \leq 16$) exhibits shape and volume change properties not possible in smaller systems. Calculations were performed with the Wien *ab initio* simulation package (plane wave basis, ultra soft pseudo-potentials, spin polarized, DTF with generalized gradient approximation, cubic unit cell length 1.50 nm, periodic boundaries, Γ point, energy cut off 300eV, geometry optimization by conjugate gradient). Relevant comparison with the Gaussian calculations of Gutsev and Bauschlicher show good overall agreement.

OM-IP-CC AND EOM-EA-CC METHODS APPLIED TO CHARGE TRANSFER REACTIONS

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Accurate calculation of energy profiles for charge transfer (CT) reactions, i.e., Marcus curves, is a difficult task due to: a) symmetry breaking of the Hartree-Fock wave function at the transition state, b) near-degeneracies of the two CT states. These problems can be remedied by employing the stable Hartree-Fock wave function for an ionized or electron attached system (N-1 or N+1, respectively) as a reference, and describing the target N-states by the corresponding EOM methods. EOM-IP/EA-CC provide most satisfactory treatment of this class of problems. We present benchmark calculations of an ionized ethylene dimer and other prototypical systems.

DIFFUSION MONTE CARLO STUDY OF LI-NE USING TRANSCORRELATED VARIATIONAL MONTE CARLO TRIAL FUNCTION

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In the fixed node approximation of the diffusion Monte Carlo (DMC) method, the quality of the obtained solution depends upon the accuracy of the nodal hypersurface of the many body trial function. A common practice in DMC is to use a trial wave function that is a determinant or linear combination of determinants, multiplied by a correlation function (such as the Jastrow factor), which is symmetric with respect to particle exchange. The determinant expansion is usually obtained from other ab initio methods. This procedure generates a nodal hypersurface optimized without considering the influence of the correlation function. However, the transcorrelated variational Monte Carlo (TC-VMC) method [J. Chem. Phys. 119, 10015 (2003)], suggests a procedure for optimizing the determinant orbitals in presence of the correlation function. A wave function obtained in this way, may be expected to have a more accurate nodal hypersurface. The TC-VMC wave function has been shown to give improved variational Monte Carlo energies, but its effect on DMC energies has not been fully investigated. Here we compare DMC energies for Li-Ne obtained using Hartree-Fock Jastrow and TC-VMC Jastrow type trial functions.

POSTER II-54
A COMPUTATIONAL STUDY OF HEAVIER DIHALOGEN-M-DICHALCOGENIDES: THE FOOF ANALOGS

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Dihalogen-µ-dichalcogenides (XYYX, X=F,Cl,Br; Y=S,Se) are studied using both CCSD(T) and B3LYP methods. Several familes of the correlation consistent basis sets, including cc-pVnZ, aug-cc-pVnZ, cc-pV(n+d)Z, and aug-cc-pV(n+d)Z have been employed. Optimized structures and vibrational frequencies are reported and compared with known experimental data. The central Y-Y bond length in the fluorides is shown to be shorter than in the analogous Y2 compounds. A similar trend exists in the well-studied FOOF molecule. Further, a trend exists with respect to increasing halogen size (decreasing electronegativity) where the Y-Y bond increases compared with the analogous Y2 compound. The mean absolute errors (MAEs) as compared with experiment are smaller with CCSD(T), but comparable to B3LYP as the differences are 0.001 angstrom and 0.017 angstrom in the X-Y and Y-Y bond lengths, respectively, 0.03 degree and 1.12 degree difference in the Y-Y-X and X-Y-Y-X angles, respectively. Additionally, vibrational frequencies at the aug-cc-pVTZ level contain MAEs of 3.7-12.2 and 2.7-20.7 wavenumbers for B3LYP and CCSD(T), respectively.

QUANTUM MONTE CARLO FOR ELECTRONIC STRUCTURE: APPLICATION TO PHOTOPROTECTION.

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As our understanding of biological systems has advanced, the need for models and theories with which these systems can be treated accurately has increased. The typically large size of these systems renders unfeasible the application of all but a limited number of computational methods. Density functional theory (DFT) has been used for a broad range of molecular applications with reasonable success. At present, however, DFT appears not to be sufficiently accurate to answer some questions owing to uncertainties in the exchange-correlation functional. Among these is the accurate computation of the ground-state singlet to lowest triplet-state excitation energies of the molecules involved in the photoprotection mechanism needed to characterize fully the process in bacteria and plants. For answering these questions a more rigorous electronic structure method that accurately treats electron correlation is needed. The growth in computational effort with available ab initio correlated methods scales too steeply with system size to be applicable. Diffusion Monte Carlo (DMC) presently offers a feasible option for the accurate calculation of these quantities. Our efforts in progress to address the mechanism of photoprotection will be described.

POSTER II-56
INTERMOLECULAR BONDING IN CONJUGATED POLYMERS

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Soluble conjugated polymers may enable the development of fast sensitive biosensors. However, the tendency of these molecules to aggregate even at low concentrations has a profound effect on the fluorescence signal that these sensors rely on. We propose that the aggregation of doped conjugated polymers occurs due to the formation of weak interpolymeric bonds resulting from intermolecular electron tunneling at crossing points of the chains. Although these bonds are essentially covalent in character, they are significantly weaker (~2 kT) due to poor the intermolecular overlap of the electron wavefunctions as well as the delocalization of the pi-electrons along the polymer backbone. We show that the aggregates resulting from these bonds form either loosely bound braids or tight bundles of parallel chains depending on the strength of the electrostatic repulsion between the polymers. Surprisingly, we find that undoped polymers are unable to form parallel bundles. We also explore the interaction of SSH solitons on the chains with these intermolecular binding sites and demonstrate a roughly a four-fold enhancement of the binding strength when each chain has a soliton at the binding site.

NUCLEAR-ELECTRONIC ORBITAL NONORTHOGONAL CONFIGURATION INTERACTION METHOD FOR CALCULATING TUNNELING SPLITTINGS AND COUPLINGS

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The nuclear-electronic orbital (NEO) method treats specified nuclei quantum mechanically on the same level as electrons in molecular orbital calculations. Both electronic and nuclear molecular orbitals are expressed as linear combinations of Gaussian basis functions. For hydrogen transfer systems, the hydrogen nuclei, as well as all electrons, are treated quantum mechanically. This approach enables the calculation of tunneling splittings and couplings for hydrogen transfer systems. The NEO-FCI (full configuration interaction) method accurately describes the ground and excited state nuclear-electronic wavefunctions but is computationally impractical for most chemical systems. To address this issue, we have developed a NEO-NOCI (nonorthogonal configuration interaction) method to calculate tunneling splittings and couplings. In this approach, the total wavefunction is represented as a linear combination of a small number of nonorthogonal NEO-HF (Hartree-Fock) localized nuclear-electronic wavefunctions. The NEO-NOCI method has been benchmarked against the NEO-FCI and Fourier Grid Hamiltonian methods for model hydrogen transfer systems.

POSTER II-58
INTERPOLATION MODEL RELATING THE ELECTRON DETACHMENT ENERGIES IN HIGH-SYMMETRY ALKALI HALIDE SOLVATED-ELECTRON ANIONS TO THE DIPOLE MOMENTS AND POLARIZABILITIES OF THE SPECIES THE CLUSTERS CONSIST OF

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We decompose the vertical electron detachment energies (VDEs) in solvated-electron clusters of alkali halide in terms of (i) an electrostatic contribution that correlates with the dipole moment (μ) of the individual alkali halide molecule and (ii) a relaxation component that is related to the polarizability (α) of the alkali halide molecule. Detailed ab initio numerical results for twelve species $(MX)_n^-$ (M=Li,Na; X=F,Cl,Br; n=2,3) are used to construct an interpolation model that relates the clusters' VDEs to their μ and α values as well as a cluster size parameter *r* that we show is closely related to the alkali cation's ionic radius. The interpolation formula is then tested by applying it to predict the VDEs of the systems that were not used in determining the parameters of the model. The average difference between the model's predicted VDEs and the ab initio calculated electron binding energies was found to be less than 4%.

POSTER II-59
TOWARD CHEMICAL ACCURACY FOR EXCITED STATES: EQUATION-OF-MOTION
COUPLED CLUSTER METHOD WITH TRIPLE EXCITATIONS (EOM-CC(2,3))

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We report the implementation of the single-reference excited state method which includes single and double excitations in the coupled cluster (CC) part and single, double, and triple excitations in the equation-of motion (EOM) part, i.e., EOM-CC(2,3). This method significantly improves the accuracy of traditional EOM-CCSD and its spin-flip (SF) counter-part, SF-CCSD. Moreover, the inclusion of triples allows one to accurately treat molecules with highly-degenerate electronic structure, such as radicals and weakly bonded complexes. To reduce the computer cost and widen the applicability of EOM-CC(2,3), an active space variant with "semi-internal" triples has been implemented. I will present applications of EOM-CC(2,3) and active-space EOM-CC(2,3) to interesting chemical problems, e.g., the singlet-triplet gap in the TMM diradical and the effect of the spin-contamination on excitation energies of σ-π diradicals and triradicals.

POSTER II-60
DENSITY FITTING USING THE ATTENUATED COULOMB OPERATOR

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Our research seeks to employ the resolution of the identity (RI-J) method to build the Coulomb matrix, J, in effort that scales linearly with system size. Multipole expansions of the far-field are employed, similarly to Ahlrichs' multipole accelerated RI-J method. However, instead of using the Coulomb metric for density fitting, we use an attenuated version of this metric. Properly attenuated, the resulting density expansion coefficients are sparse, yet retain accuracy typical of RI-J. The method is demonstrated for systems of 1-, 2-, and 3-dimensions.

COMPUTATIONAL STUDIES OF THE INTERACTION OF SULFUR TRIOXIDE WITH WATER CLUSTERS

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Intermolecular complexes of sulfur trioxide and water are important species in atmospheric chemistry, for example in the formation of acid rain. Most previous computational work on these systems has focused on interactions of sulfur trioxide with one or only a few water molecules. However, heterogeneous chemistry, including reactions taking place on ice surfaces, plays a key role in reactions of sulfur oxides in the atmosphere. It is estimated that about 50 percent of atmospheric sulfur dioxide reactions occur heterogeneously; thus, it is important also to understand heterogeneous reactions involving sulfur oxides. In this work, we report the results of ab initio and density functional studies of sulfur trioxide interactions with 3-6 water molecules as well as studies of sulfur trioxide interactions with larger clusters containing up to 26 water molecules. Geometries, binding energies, and charge distributions have been determined. Results for the smaller systems indicate that the activation barrier for formation of sulfuric acid approaches zero at approximately four water molecules, in accord with previous work. For the larger systems, the results indicate that sulfur trioxide can occupy a variety of binding sites, including top sites and sites in which the sulfur trioxide molecule is partially embedded in the water cluster.

POSTER II-62
DUAL-BASIS SCF THEORY
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The use of dual basis sets allows for the capture of large-basis effects for roughly small-basis cost. After performing a full SCF calculation in a small basis, a single SCF step is performed in the large basis. A correction is subsequently formed from the new density matrix. This theory has been applied to HF and DFT energies, and analytic gradients have been implemented. Relative to full large basis calculations, savings are roughly 90% (energies) and 80% (gradient). Recent extensions to MP2 theory show drastic savings in the SCF portion of the calculation, with negligible error in the total energies.

POSTER II-63
SMOOTH WELL-DEFINED LOCALIZED ORTHONORMAL VIRTUAL ORBITALS FOR USE IN LOCAL ELECTRON CORRELATION THEORY
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The localization of the virtual space from an electronic structure calculation into orthonormal orbitals has the potential to greatly speed up local correlation algorithms by simplifying the working equations one needs to solve iteratively. However, producing a set of such orbitals in a smooth and well-defined manner has been a stumbling block in most local electron correlation schemes thus far. The Boys' orbitals for the virtual space are both computationally expensive and most likely not unique (hence not smooth functions of nuclear coordinates). Most local correlation schemes avoid the complexity of the virtual space by projecting atomic orbitals into the virtual space, and then working with a localized redundant basis for the virtual space. We demonstrate in our work that one need not work with a redundant basis set, that localized orthonormal virtual orbitals can be constructed in a well-defined manner, and the cost for that construction is negligible.

IMPACT OF NUCLEAR QUANTUM EFFECTS ON HYDROGEN-BONDED CLUSTERS

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We investigate the structural impact of nuclear quantum effects on hydrogen-bonded clusters using the nuclear-electronic orbital (NEO) method. In the NEO approach, selected nuclei are treated quantum mechanically on the same footing as the electrons, and the mixed nuclear-electronic wavefunction is calculated variationally using molecular orbital methods. Electron-electron and electron-proton dynamical correlation effects are included with the NEO-MP2 (second-order perturbation theory) method. In hydrogen-bonded clusters, all hydrogen nuclei are treated quantum mechanically. Our results indicate that nuclear quantum effects stemming from the hydrogen atoms can alter heavy-atom distances on the same order as electron correlation effects. The NEO-MP2 method is a computationally efficient approach for incorporating nuclear quantum effects into electronic structure calculations.

INTEGRAL DIRECT MULTI-REFERENCE CONFIGURATION INTERACTION

Andrew B. Szilva, Emily A. Carter

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We have developed a local multi-reference singles and doubles configuration interaction (CI) method, which asymptotically reaches linear scaling in the large molecule limit. Linear scaling is achieved through localization and integral prescreening. Following the strategy of Saebo and Pulay, we first locally truncate the internal configuration space, limiting excitations out of widely separated internal orbitals (the Weak Pairs approximation). We then localize the virtual orbitals and restrict excitations from internal orbitals to spatially close virtuals (the Truncation of Virtuals approximation). The final step toward a linear scaling algorithm requires efficient integral transform prescreening that includes information from subsequent transformation steps. Our recent work suggests that due to the multi-reference nature of our method, we can extract smooth potential energy surfaces for processes such as bond breaking. Additionally, we have demonstrated in our earlier work that our size extensivity correction (averaged coupled pair functional correction) allows us to reliably study large systems. Consequently, we expect our new method to be quite robust in exploring chemical phenomena at the small to medium molecular size scale (0 to approximately 400 electron systems), which was previously not accessible with multi-reference methods.

MOLCAS 6: A PROGRAM PACKAGE FOR QUANTUM CHEMISTS AND CODE DEVELOPERS

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The program system MOLCAS is a package for calculations of electronic and structural properties of molecular systems in gas, liquid, or solid phase. It contains a number of modern quantum chemical methods for studies of the electronic structure in ground and excited electronic states, including Hartree-Fock, Density Functional Theory, Coupled-Cluster, and multiconfigurational approaches, including second order perturbation theory. MOLCAS runs on almost all UNIX-like platforms and has straightforward installation from a single source code for 32- and 64- bit architectures, as well as for serial and parallel execution.

MOLCAS also offers an environment for developing new software for quantum chemistry. The key features of the MOLCAS environment include: a modular structure, an easy to use environment, an Application Programming Interface library for solving common computational and system-oriented problems, documentation, a solid verification control system, and tools for a distributed development. The MOLCAS environment allows to include in a simple way new codes, integrated with libraries and other MOLCAS modules.

In order to demonstrate the major possibilities of the MOLCAS code, two selected applications are presented:
- The chemical bond in U-U complexes
- Interaction between two charged C60 molecules.

A DIRECT OPTIMIZATION METHOD TO STUDY CONSTRAINED SYSTEMS WITHIN DENSITY FUNCTIONAL THEORY

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MIT

Consider a system with an arbitrary constraint on its electron
density (e.g. that there are N charges on a certain group of atoms). We show that in Kohn-Sham density
functional theory, the *minimum energy* state consistent with the constraint is actually a *maximum* with
respect to the constraint potential, and that this solution is unique. This leads us to an efficient algorithm
for calculations on constrained systems. Illustrative studies are shown for charge transfer in: the
zincbacteriochlorin--bacteriochlorin complex, polyene and
alkane chains.

POSTER II-68
WAFERS, PLATELETS, AND SPHERES: GROWTH PATTERN OF COPPER CLUSTERS

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The ground-state structures of neutral copper clusters (Cu_n) for n = 3 – 20 are identified with a combined tight-binding and density functional theory approach. A new growth pattern, from planar (n ≥ 6) to platelet-like (n = 7 – 16) and to compact structures (n = 17 – 20) is presented. This evolution in shapes complies qualitatively with the prediction from the spheroidal jellium model. The platelet structures consist of two layers with atoms on each layer forming a trigonal bonding network similar to that found in the small planar clusters. The lowest-energy structures of the anionic and cationic clusters are also presented. The calculated electronic properties based on the optimal structures, such as ionization potentials, electron affinities, dissociation energies, HOMO-LUMO gaps, etc, are in good agreement with available experimental data. The present study demonstrates the importance of using extensive and unbiased search techniques, coupled with accurate, first-principles theory to find optimal cluster structures.

POSTER II-67
DYNAMICAL CORRELATION EFFECTS IN ELECTRON
TRANSFER COUPLINGS

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We have proposed and tested the use of Spin-Flip (SF) scheme to calculate the energy gap between adiabatic states, half of which gives electron transfer coupling strengths.

With a high-spin reference state, the SF scheme allows us to determine the state energies without problems arising from near-degenerate molecular orbitals. The SF-CIS model is more robust than the traditionally used Hartree-Fock Koopmans Theorem, and its coupling dependence on intermolecular separation is correct even in diffuse basis sets. The SF approach allows for a systematic inclusion of dynamical correlation effects. We have investigated the dynamical correlation effects in electron transfer coupling both with and without a bridge fragment. Our results indicate a relatively small dynamical correlation effect for electron transfer couplings. For donor-bridge-acceptor systems, the dynamical correlation effects are more significant than those in donor-acceptor systems. We show that correlation through changes in energy gaps between the donor (acceptor) and the bridge fragment is not dominant. Instead, the effects of correlation in donor-acceptor correlation are through the donor-bridge and bridge-acceptor couplings.

POSTER II-70
THE 3-VINYLMETHYLENECYCLOBUTANE – 4-METHYLENECYCLOHEXENE REARRANGEMENT: A STEREOSELECTIVE STEPWISE COPE REARRANGEMENT

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The potential energy surface (PES) of the rearrangement of 3-vinylmethylenecyclobutane to 4-methylenecyclohexene has been studied computationally, using density functional theory (B3LYP), complete active space self-consistent field [(6,6)CASSCF], and complete active space second-order perturbation theory [(6,6)CASPT2] calculations with the 6-31G* and 6-31+G* basis sets. The parent reaction is non-concerted and occurs through several parallel biradical pathways. Transition structures and biradical intermediates are highly comparable in energy, with no deep potential energy well on the potential energy surface. In the substituted system, stereoelectronic effects of the trialkylsiloxyl group regulate torquoselectivity in the bond-breaking processes, promoting the compact transition state that leads to a stepwise Cope rearrangement. Dynamic effects on the stepwise Cope rearrangement may explain the highly selective nature of the reaction.
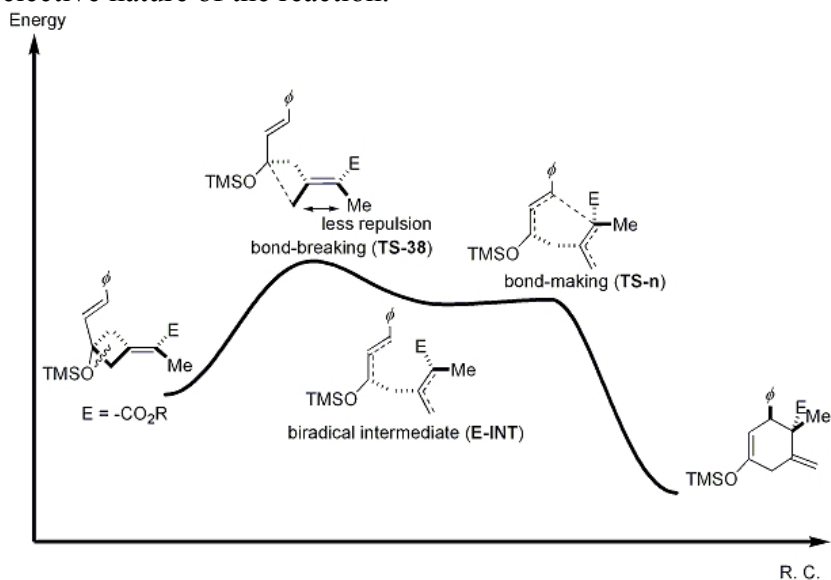
ELECTRONIC STRUCTURE STUDIES ON INTERACTIONS OF ORGANIC MOLECULES WITH NANOPARTICLE SURFACES

Linlin Zhao, George C Schatz

Chemistry Department, Northwestern University, 2145 Sheridan Road, Evanston, IL, 60208

In this research, the interactions of organic molecules with nanoparticle surfaces are studied by electronic structure calculations. Two systems are of main interests: pyridine-silver metal cluster and catechol-titanium oxide complex. (Figure 1.) The first system is chosen to study the chemical enhancement mechanism of surface-enhanced Raman scattering (SERS).[1] Raman spectra of pyridine and pyridine in the molecule-metal cluster with silver are calculated by density functional theory. The effects of molecule orientation, molecule-metal distance, and applied electric field on the Raman spectra and the corresponding Raman enhancement factors are investigated. The second system is chosen to study the mechanisms for adhesions of DOPA(3,4 - dihydroxyphenylalanine) containing proteins onto titanium oxide nanoparticle surface.[2] The binding energies of the molecular complex for Ti atom clusters are calculated using both ab initio molecular orbital theory and density functional theory. The effect of the distance between the molecule and the Ti atom clusters on the binding energies is investigated, and the corresponding pull-off curve is plotted.
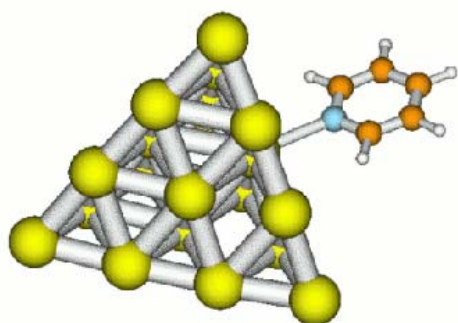
Fig 1a: pyridine-silver metal cluster
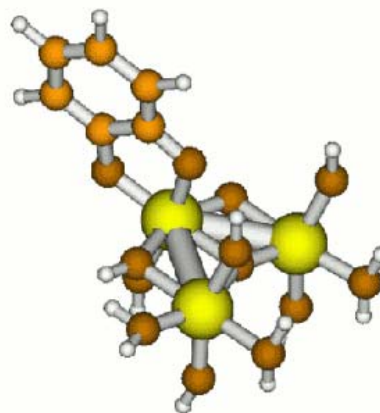
Fig 1b: catechol-titanium oxide molecule complex

[1] Zhao, L; Jensen, L; Schatz, GC; "Density Functional Study on the Adsorption of Pyridine onto Silver Nanoparticles", in prepration,
[2] Dalsin, JL; Messersmith, PB; et al; Langmuir, 2005, 21, 640-646.

FORMULATION, ASSESSMENT, AND PARAMETRIZATION OF THE ANALYTIC AND VARIATIONAL Xα METHOD

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We have formulated a fully analytic and variational density-functional method based on Slater's Xα approximation to Hartree-Fock theory. It uses linear combination of atomic orbitals to express both the molecular orbitals and the Kohn-Sham potential. The method allows arbitrary scaling of the exchange-correlation potential around each atom. Being analytic, it is free from numerical integration and delivers machine-precision, basis-set-dependent energies that are stationary in all respects. One choice of scaling uses the α's that give exact atomic energies. This choice gives total molecular electronic energies that are precisely the sum of atomization energies and experimental atomic energies. We assess the performance of this method by calculating the atomization energies and total energies of the G2 and extended G2 sets of molecules. The MAE in total energies for the G2 set of molecules is 17 kcal/mol. This is comparable to or better than almost all pure and hybrid density functional models. This error is reduced by a factor of one third by finding the α's that minimize the G2-set MAE, but this improvement comes at the expense of no longer having a quantum-mechanical energy that dissociates to exact atomic energies.

THE EFFECT OF HYDRATION ON THE STRUCTURE AND REACTIVITY OF α-Fe$_2$O$_3$ (0001) AND α -Fe$_2$O$_3$ (1-102)

Cynthia S Lo[1,2], Anne M Chaka[1], Thomas P Trainor[2]
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[2]University of Alaska Fairbanks

The structure and reactivity of metal oxides such as α-Fe$_2$O$_3$ depends on several factors, including the composition of the bulk material, crystallographic orientation, and local coordination of the surface atoms. In particular, interactions at the solid-liquid interface play major roles in catalysis, chemical sensors, and environmental processes such as contaminant sequestration and remediation. Unfortunately, these oxide surfaces have largely been characterized experimentally and theoretically only under UHV conditions. Therefore, it is important to understand the adsorption and dissociation of water on the α-Fe$_2$O$_3$ surface. We have computed, using density functional theory and *ab initio* thermodynamics, the structure and Gibbs free energy of several terminations of α-Fe$_2$O$_3$ (0001) and α-Fe$_2$O$_3$ (1-102). We have found that the most stable termination in the presence of water is not the bulk stoichiometric termination, but rather one missing the top layer of Fe atoms; these results correlate well with experimental crystal truncation rod diffraction data. We show thermodynamically how the presence of a water monolayer serves to pull these Fe atoms out of the surface, and present a possible mechanism for water dissociation. Finally, we discuss the possible reasons for the differences in reactivity between α-Fe$_2$O$_3$ and α-Al$_2$O$_3$.

WITHDRAWN

POSTER II-75
HYDROGEN STORAGE IN MAGNESIUM BASED ALLOYS

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[2]Chemistry Department, University of Washington, Seattle WA 98195, USA

We have carried out DFT calculations to study how binding energy and diffusivity of hydrogen atoms in magnesium hydride can be improved by addition of other elements. The calculations make use of a plane wave basis set, ultrasoft pseudopotentials and the PW91 functional. The results indicate that the addition of more electronegative elements reduces the binding energy. For example, the addition of 15% Al brings the desorption temperature of 1 bar hydrogen gas down from 700 K to 350 K. Experimental measurements have indicated that the addition of a small amount of a transition metal, for example titanium, can speed up the unloading of hydrogen. Our calculations on the magnesium-titanium hydride predict a large increase in diffusivity of hydrogen as compared with pure magnesium hydride because of greatly reduced formation energy of hydrogen interstitials even far from the Ti-ions. An electron gets transfered from the Ti-ion to the H-interstitial, as can be seen from the maximally localized Wannier functions (see figure). Preliminary results indicate that ternary alloys can both have reduced binding energy and fast diffusion, but the question is whether a material can be found where both the alloy and the hydride are stable with respect to decomposition.
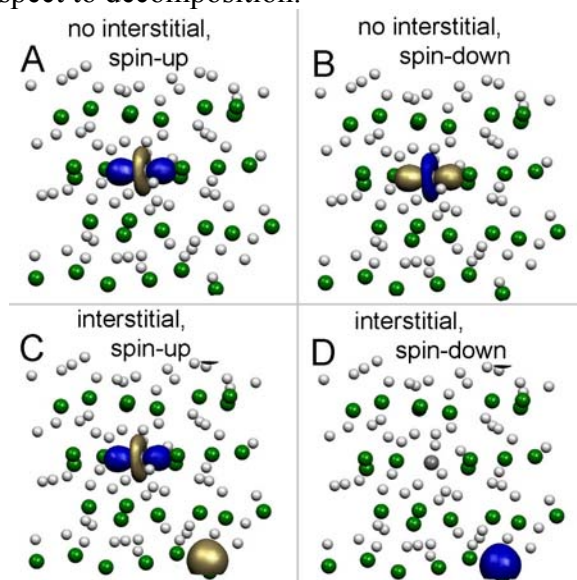
A NEW THEORETICAL FRAMEWORK FOR STUDYING THE STRUCTURE AND CHEMISTRY OF WATER AT THE ELECTRIFIED METAL/WATER INTERFACE

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Direct observation of the structure of water at a metal surface has been noted for only a few well-defined ultra-high vacuum systems. Recent surface science experiments have been able to observe in situ transitions in the metal/electrolyte structure to hydroxyl overlayers and oxide structures. An understanding of the role played by environmental water at the interface, however, and methods to predict the formation of such overlayers are in demand. In this poster we present predictions of surface structure on Ni(111) as a function of pH, electrochemical potential and temperature calculated using density functional theory. Electrochemical potentials are tuned by varying the surface charge and its corresponding countercharge. In this way we map regions in (pH,V,T) space over which water is electrochemically activated to form OH or H on the surface, and also regions over which OH will also be activated to form surface oxides (Figure 1). The formation of surface oxides is found to correlate with structural features indicative of metal dissolution. We also present data derived from ab initio molecular dynamics simulations that illustrate the dynamic fluctuation in electrochemical potential at the interface resulting from the thermal motion of water near the electrode.
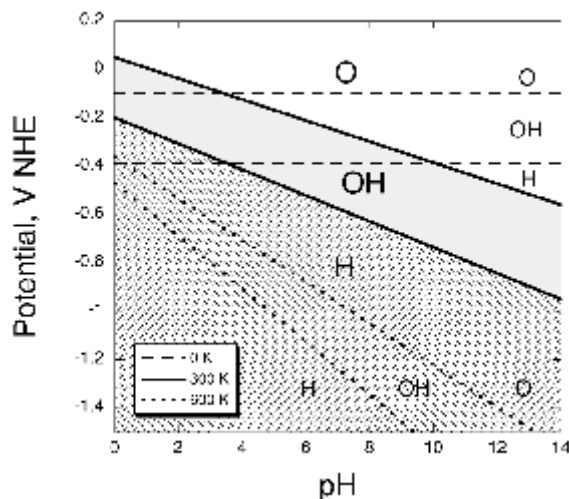
POSTER II-77
SELECTIVE OXIDATIONS OF METAL DOPED ZEOLITES

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Incorporation of heteroatoms (Ti, Fe etc.) in zeolites opens new opportunities in the field of heterogeneous catalysis, however, the catalytic mechanisms often remain unknown. Reactivity of metal centres in oxide materials presents serious challenges to current computational techniques. Our theoretical investigation of a $[AlO_4]^0$-centre in α-quartz proved the reliability of the BB1K functional designed for accurate thermochemical and kinetics.

TS-1 is an extremely active catalyst in oxidation reactions with aqueous H_2O_2. Tripodal Ti incorporated into the zeolite framework by silanol inversion reacts favourably with H_2O_2. We focus on elucidating the transition states, and the most energetically favourable pathways of catalytic reactions of linear and cyclic alkenes over TS-1.

Fe-S-1 is selective and active in the oxidation of benzene to phenol using N_2O. Experiments suggest the high activity of Fe-S-1 is attributed to a α-Fe-site, however, the nature of this site remains unclear. We propose a bipodal model for α-Fe, again realised by the silanol inversion mechanism. We re-assess the three-step mechanism, and propose an unified model for the full catalytic cycle based on the exposed Fe(II) site for N_2O decomposition, and a silyl hydroperoxide site for benzene conversion.

INTERACTION OF Au CLUSTERS AND DEFECTIVE TiO$_2$ SURFACE

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[2]*Faculty of Liberal Arts and Science, Kasetsart University, Kampaeng Saen, Nakorn Pathom, 70193, Thailand*

The interaction of Au clusters with the O-vacancy of the TiO$_2$ rutile (110) surface has been studied by the embedded cluster model at DFT/B3LYP level of calculation. O-vacancy is the active center of the TiO$_2$ surface and it can stabilize small Au clusters on the surface. The electron density of Au cluster increases significantly due to the excess electrons transfer from the vacancy site to the Au cluster. We also found that the electron density on the TiO$_2$ surface is perturbed by the Au cluster as well. The mulliken charge on nearby Ti(5f) atom is increases significantly and behaves as another active center for another Au atom. The change in electron density at the surface of TiO$_2$ could attract more Au atom to from a bigger stable cluster. The effect of Au cluster on the nearby TiO$_2$ surface may have the significant role in high catalytic reactivity of the Au-TiO$_2$ interface for CO oxidation.

THREE-BODY EFFECTS ON PHASE EQUILIBRIUM PROPERTIES OF NOBLE GASES

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Intermolecular interactions determine the phase behaviour of fluids. Generally two-body intermolecular interactions dominate the total intermolecular interactions, but an increasing number of studies have shown that three-body interactions play an important role in the phase behaviour of pure fluids and mixtures. The effect of three-body interactions on the vapour-liquid equilibria of pure noble gases has been investigated. However, little work has been done for mixtures and solid-liquid equilibria have not been studied. In this work, three-body effects on vapour-liquid, solid-liquid phase equilibrium properties of argon, krypton, xenon and vapour-liquid phase equilibrium properties of argon-krypton mixtures are investigated by molecular simulation. The simulations were performed using a true two-body potential (Barker-Fisher-Watts potential) with or without the three-body interactions (Axilrod-Teller term) included. The main simulation techniques involved are the Gibbs ensemble, the Gibbs-Duhem integration Monte Carlo method, and equilibrium and non-equilibrium molecular dynamics. The calculated results have been compared with experimental data, which shows that simulations with accurate two-body and three-body interactions can be used to provide a reasonably good agreement with experiment.

FUTURE POLYNITRAMINE EXPLOSIVES

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Energetic materials, particularly high explosives are among the few products that take years of effort to develop and yet disintegrate in a few millionth of a second on demand. Despite the short lifespan, new high explosives are still a valued commodity and finding new energetic materials with lower sensitivity to shock and friction while maintaining the high performance is a goal of wide interest. employing new tools to the search for novel high explosives can provide better and faster results opposed to the intuitive trial and error approach that is still common.

Recently the synthesis of new tricyclic tetraaza cage was reported by a simple rearrangement of the tetracyclic hexaaza cage **1**, the condensation product of glyoxal and benzylamine. Two polynitramines, a tetranitro (**2**) and a hexanitro (**3**) derivatives, based on the new skeleton are being considered as possible candidates for synthesis of new explosives.

Towards evaluation of the explosive properties of the new candidates, *ab-initio* calculations were performed for structure elucidation and stability estimation. Thermochemical simulations, from solid state density and heat of formation calculations, were performed to evaluate the performance characteristics of these proposed energetic materials.

POSTER II-81
THE ORIGIN OF THE HALOGEN EFFECT IN DIELS-ALDER REACTIONS INVOLVING FURAN

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Intramolecular Diels-Alder reactions involving furan have higher yields when furan is substituted with chlorine, bromine, or iodine. Intermolecular Diels-Alder reactions involving furan, cyclopentadiene, and butadiene were studied with CBS-QB3 level of theory. Chlorine or bromine substitution on these dienes increases cycloaddition exothermicity that in turn decreases activation enthalpy relative to unsubstituted reactions. Halogenation has the greatest effect on reactions involving furan. The origin of these effects was deduced from a series of isodesmic reactions calculated at the same level of theory, and was found to be the preference of halogens to be bound to a more electropositive carbon skeleton. This accounts for the decreased diene stabilization and increased product stabilization. Intramolecular Diels-Alder reactions involving furan have been reported to have a tendency for retrocycloaddition, but halogenation can eliminate retrocycloaddition by making the reaction more exergonic.

SMALL Pd CLUSTERS, UP TO THE TETRAMER AT LEAST, ARE HIGHLY MOBILE ON THE MgO(100)SURFACE

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Density functional theory calculations predict that small clusters of Pd-atoms, containing up to at least 4 atoms, are highly mobile on the MgO(100) surface with the tetramer (Figure 1) having the largest diffusion rate at room temperature - larger than the monomer. Surface vacancies are found, however, to bind the larger clusters strongly enough to trap them. These are important considerations when analyzing the growth and sintering of metal islands on oxide surfaces, in particular the role of point defects.

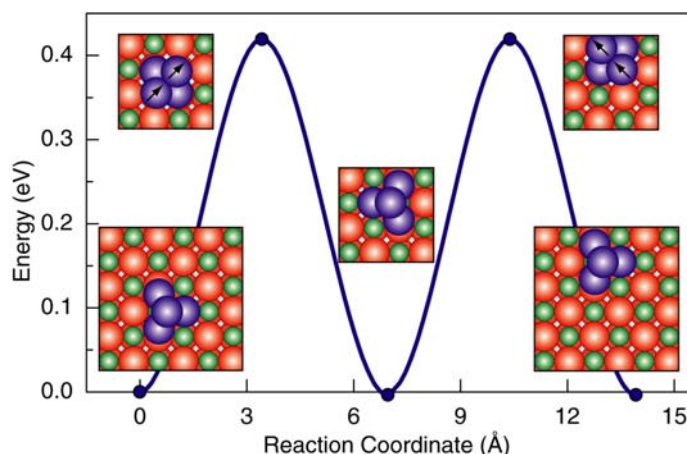FIG: Tetramer diffusion mechanism. The top-atom and one of the base atoms move in a concerted way as shown in the inset. This 'rolling' mechanism is surprisingly efficient with an activation energy that is lower than for trimer diffusion and a prefactor that is anomalously large mainly because of two soft vibrational modes in the transition state. The tetramer is predicted to diffuse faster than a monomer at room temperature.

MOLECULAR DYNAMICS SIMULATIONS OF THE MECHANICAL UNFOLDING OF PROTEINS

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Department of Chemistry and Biochemistry, Institute for Theoretical Chemistry, University of Texas at Austin, Austin, Texas 78712

A number of proteins perform load-bearing functions in living organisms and often have unique mechanical properties. In recent years, there has been considerable effort to understand the relationships between the molecular structure of such proteins and their mechanical response. Several of them have been studied in great detail through single molecule mechanical pulling experiments. Interpretation of these experiments requires the use of atomistic simulations. However typical simulation time scales are many orders of magnitude shorter than relevant experimental and/or physiological time scales. We have developed a procedure that allows prediction of the outcome of single molecule pulling experiments based on molecular dynamics simulations. Here we report on our studies of the mechanical unfolding of the I27 domain of the muscle protein titin, ubiquitin, and protein G and compare them with the existing experimental data. In particular we demonstrate that the mechanical unfolding pathway can be altered by changing the pulling geometry and that the presence of a hydrogen bonded clamp between terminal parallel strands of these domains is the key property that is responsible for their high mechanical stability.

POSTER II-84
CHEMICAL REACTION OF SMALL GAS MOLECULES WITH THE 5-1DB DEFECT ON THE SIDEWALL OF THE SINGLE-WALLED CARBON NANOTUBES

Lei Vincent Liu, Wei Quan Tian, Yan Alexander Wang
Department of Chemistry, University of British Columbia

Normally, a SWCNT is not perfect: it contains many defects, which can be categorized as topological, rehybridization, and incomplete bonding defects. Defects may tailor the intrinsic properties and broaden the applications of the SWCNT. Single vacancy as an incomplete bonding defect exists as a native defect and can be introduced by ion and electron irradiations. But it is only metastable: two of its three two-coordinated carbon atoms will combine to form a more stable structure, the so-called 5-1DB defect (one pentagon and one dangling bond). We studied the electronic structure of the 5-1DB defect on the (5,5) SWCNT within density functional theory and found that the 5-1DB defect strongly destructs the conjugated pi-system and creates localized electronic states, thus it should be a chemical reactive center. In order to verify this, we studied several chemical reactions between the 5-1DB defect and some small gas molecules (e.g. NO, O_2, O_3, etc) by applying semi-empirical and ONIOM methods. We found some very interesting results. For example, the reaction of NOs with the 5-1DB defect may produce the N-substitutionally doped SWCNT, which implies a new way to fabricate the position controllable N-substitutionally doped SWCNT at mild conditions.

POSTER II-85
MONTE CARLO SIMULATION OF ACTIN SELF-ASSEMBLY
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Using grand canonical Monte Carlo simulations we study the equilibrium properties of actin self-assembly. The statistics of actin polymerization is described by a mechanism involving monomer activation and chain propagation with bond association constants derived from experimental free energy parameters. For efficiency in representing systems of very long, stiff chains we use a coarse-graining based on spherocylinders. We will present results pertaining to the isotropic-nematic transition in this equilibrium polymer system.

POSTER II-86
SIMULATION OF VIBRATIONAL RESONANCES IN INELASTIC ELECTRON TUNNELING

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Department of Chemistry, University of California-Irvine

Nonequilibrium Greens function theory is applied to STM currents of chemisorbed molecules. We outline a strategy for calculating the inelastic current through a molecule based on a perturbative expansion of the electronic self-energy. Inelastic effects due to electron-phonon interactions introduce a finite broadening into the molecular electronic eigenspectrum. The first order corrections to the molecular orbitals are calculated by solving the coupled perturbed Hartree-Fock (CPHF) equations as implemented within the Gaussian 03 quantum chemistry package using a DFT or HF level of theory. The coupling matrix elements are related to the magnitude of the discontinuous change in the STM current when the sample bias is resonant with the vibrational transition energy. Numeric results for the inelastic electron tunneling (IET) signal and simulated spatial profiles are compared with the experimental spectrum and STM images of a distryl-benzene derivative of [2.2]paracyclophane. The symmetry selection rules of the IET spectroscopy are also discussed.

PRINCIPLES OF INTERACTIONS AND MOLECULAR BIOMECHANICS OF PACKING OF MALACHITE GREEN BY THE RNA APTAMER

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RNA plays a central role in many biological processes. In recent years, an increasing wealth of structural and functional information about small molecule - RNA complexes has been obtained either using *in vitro* selection (aptamers) or *in vivo*. It has been shown that these complexes can be used to build biological switches for controlling gene expression in the era of synthetic biology. Therefore, understanding principles underlying molecular interactions and recognitions of small molecules by RNA is a crucial step for engineering appropriate RNA with desired properties. In this work, we will present a set of principles governing observed physical properties of malachite green and another structurally similar dye tetramethylrosamine upon binding to the RNA aptamer determined by using both *ab initio* electronic structure and classical molecular dynamics methods. In addition, we will present the molecular biomechanics of the packing of malachite green by the RNA aptamer observed over the course of 0.6 microsecond of dynamics.

ON COARSE-GRAINING ANISOTROPIC SYSTEMS: NEW ELLIPTIC POTENTIALS

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The importance of coarse-grained models for the dynamics of supramolecular assemblies is well established. In such models, groups of atoms are typically considered as a unit whose interactions are taken into account in an "effective" average manner. Most existing models use spherical sites to represent group of atoms interacting through effective potentials estimated form atomistic simulations or experiments. This representation is simple but ignores the fact that many of the molecules of interest have in effect anisotropic shapes or interact through effectively anisotropic potentials.

We have developed a new general geometrical framework for coarse-grained molecular dynamics of arbitrary mixtures of molecular or supramolecular units of any size or elliptic shape. The framework is based on the "elliptic contact function approach", which predicts correctly the point of contact of any two ellipsoids. The potential is flexible and simpler than previous potentials in the literature with fewer fitting parameters and numerically efficient, due to the algebraic representation of ellipsoids as quadratic forms.

Prelimin ary result show the spontaneous formation of micellar self-assembly in water and the rich dynamical behaviour of the phases of lipid bilayers

CHARGE DEPENDENCIES FOR ATOM AND PAIR ENERGIES

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LA-UR-05-4570

It is common practice to view atoms in a molecule as fractionally charged, and equally common to assume an electrostatic model for the energy of pairs of those atoms. A recently-developed approach using an ensemble representation of a potential energy surface [1] yielded a novel charge model for the interaction energy of an atom pair whose charges sum to an integer. However, if the sum of the charges on an atom pair is not an integer, that pair may be viewed as an open system in the sense of Perdew, Parr, Levy, and Balduz (PPLB) [2]. A generalization of the PPLB charge dependence of the interaction energy for an open pair was addressed by invoking a diatomics-in-molecules (DIM) representation [3] of a polyatomic hamiltonian [4]. When an atom pair is open, an second charge dependence has been found beyond the one discussed by PPLB and implied by electrostatic models. Similar reasoning is applied to the atomic components of the DIM hamiltonian. There are again two charge dependencies for a chosen atom, but the second charge dependence involves the charges of at least two other atoms, thereby constituting an explicit three-body effect, but does *not* involve charge transfer with the chosen atom.

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POSTER II-90
COMPUTATIONAL STUDY OF FOLDING PATHWAYS OF COLD SHOCK PROTEINS

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In this work, we present atomically detailed simulations describing the folding paths of members of the Cold Shock protein family. We used the Stochastic Difference Equation in length to obtain trajectories connecting unfolded conformations of the proteins to their native structures. In this method there is no need to solve differential equations in the form of Newton's law but instead the classical action is optimized as functional of the trajectory. This method can be used to study conformational transitions even when there is a significant structural change.

Our target is Cold Shock protein Bc-CspR3E (Protein Data Bank 1I5F) which is a mutant species of Bc-CspB from Bacillus subtilis (PDB 1C90). Both proteins have the same amino acid sequence with the only difference being the presence of a glutamic acid in position 3 in Bc-CspR3E instead of arginine. In total, 25 complete trajectories were obtained at room temperature and each of them has 400 intermediate slices. We present detailed results of the folding process for this protein that indicates an early collapse event without a complete formation of the beta turns. Finally, the role of the glutamic acid in position 3 is also analyzed.
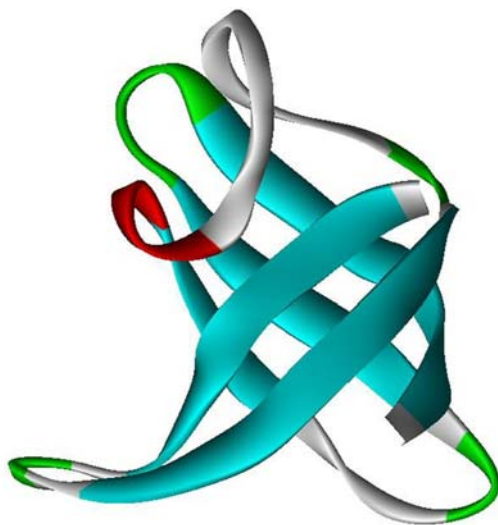
Side View of Bc-CspR3E protein.

POSTER II-91
SCATTERING FROM AN IMPURITY IN A QUANTUM WIRE: THE HALL OF MIRRORS WAVEFUNCTION

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We present a compact, intuitive picture of elastic scattering from s -wave point defects in multimode quantum wires. Impurity scattering in waveguides arises in multiple contexts, including two-dimensional electron gases, carbon nanotubes, and atom waveguides. Our problem has thus been the subject of experimental and theoretical work in condensed matter and atomic physics.

We revisit the problem unconventionally, using the method of images. A central result of our work is that the problem reduces to scattering of a single renormalized "mirror" wavefunction off an array of images. This simplification enables us to explicitly understand how multiple scattering events from the wire walls affect transport phenomena, such as the conductance. Furthermore, we are able to simply explain certain complex transport phenomena which have already been observed (such as conductance dips and confinement-induced resonances), and predict other new ones.

POSTER II-92
DYNAMIC SPIN MODEL FOR DNA PULLING EXPERIMENT

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We develop and study a one-dimensional spin model caricaturing the DNA pulling experiments of Mao and Bustamante. Our model is an extension of the Bragg-Zimm model, and possesses three states: B-phase (helical), S-phase and molten. Two experimentally accessible parameters describe the tendency of the molecule to extend (the B to S transition) and to melt. The interplay of the three states renders the dynamics of the model asymmetric, in a similar fashion to the dynamics observed experimentally. Upon pulling, the model executes a relatively smooth transition from a B-rich to an S-rich phase. The reverse transition, which occurs when the pulling force is relaxed, is much rougher, because the advance of the helical phase is thwarted entropically by the presence of molten sections. We study our model numerically and analytically.

POSTER II-93
BEYOND LINEAR RESPONSE THEORY OF HELIUM TO ROTATION

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The response of helium to the rotation of molecules embedded in superfluid helium droplets has been a topic of interest in recent years. The coupling of helium to molecular rotation has been accepted as the cause of the decreased rotational constants for heavy rotors, such as CO_2 and OCS, in helium droplets. Previous theoretical models for the rotation of molecules in helium droplets are based on ideas from macroscopic linear response theory, in which a non-superfluid component of the helium density is assumed to rotate rigidly with the molecule. We have recast the problem of the coupled motion of helium to rotation within the body-fixed molecular frame, leading to a completely microscopic model which does not require any assumptions regarding rigid coupling. A perturbative analysis of the body-fixed Hamiltonian leads to an effective moment of inertia which is seen to reduce to the linear response form in certain limits. We investigate the range of validity of this "beyond linear response" model here through its application to a simple model for which the eigenstates can be evaluated exactly.

QUANTUM DIFFUSION IN LIQUID PARA-HYDROGEN FROM RING-POLYMER MOLECULAR DYNAMICS

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We have used the ring-polymer molecular dynamics method to calculate approximate Kubo-transformed velocity autocorrelation functions and self-diffusion coefficients for low-pressure liquid para-hydrogen at temperatures of 25 and 14 K. The resulting diffusion coefficients are shown to be consistent with experimental shear viscosities and the established finite-size relation $D(L)=D(\infty)-2.837/6\pi\beta\eta L$, where β is the reciprocal temperature, η is the shear viscosity, and L is the length of the (cubic) simulation cell. The diffusion coefficients $D(L)$ obtained in simulations with finite system sizes are therefore too small. However, the extrapolation to infinite system size corrects this deficiency and leads to excellent agreement with experimental results. This both demonstrates the influence of system-size effects on quantum mechanical diffusion coefficients and provides further evidence that ring-polymer molecular dynamics is an accurate as well as practical way of including quantum effects in condensed phase molecular dynamics.
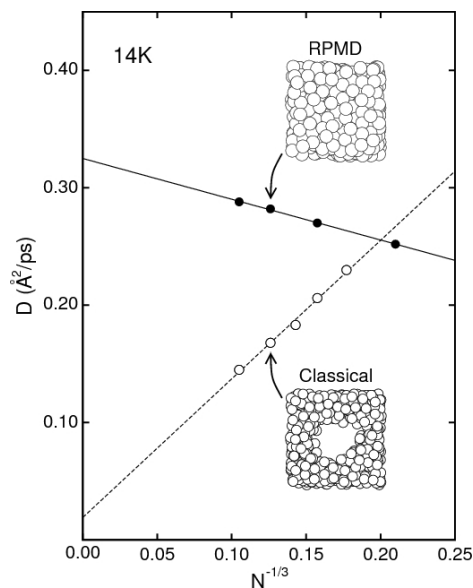
INTERFACIAL FREE ENERGIES BETWEEN A CRYSTAL AND ITS MELT FROM COMPUTER SIMULATIONS

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We developed a reliable method to define the interfacial particles for determining the crystal-melt interface position, which is the key step for the crystal-melt interfacial free energy calculations using capillary wave approach. Using this method, we have calculated the free energies of the fcc crystal-melt interfaces for the hard-sphere system as a function of crystal orientations by examining the height fluctuations of the interface using Monte Carlo simulations. The results are in good agreement with the simulation results based on the calculations of the reversible work required to create the interfaces. Combining with previous results for the Lennard-Jones system, we show that the capillary wave approach is a reliable and efficient technique to compute the crystal-melt interfacial free energies with rough interfaces. We have applied this method to calculate the plastic crystal-melt interfacial free energies for the hard-dumbbell system and results will be presented.

DECOUPLING OF STRUCTURAL RELAXATION AND DIFFUSION IN A MODEL GLASSFORMER

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The viscosity of glassformers may increase by several orders of magnitude upon cooling near the glass transition temperature despite a small change in temperature. For strong glassformers, this increase is Arrhenius, that is, the viscosity increases exponentially with inverse temperature, whereas, for fragile glassformers, this increase is super-Arrhenius. Recent experimental and theoretical evidence indicate that fragile glasses can undergo a crossover to strong behavior at low enough temperatures. Here, we show that a fragile-to-strong crossover can be modeled by a union of two kinetically constrained lattice gas models, and that, for this model, the variation of the product of the self-diffusion constant and the structural relaxation time is non-monotonic with temperature as a result of the crossover.
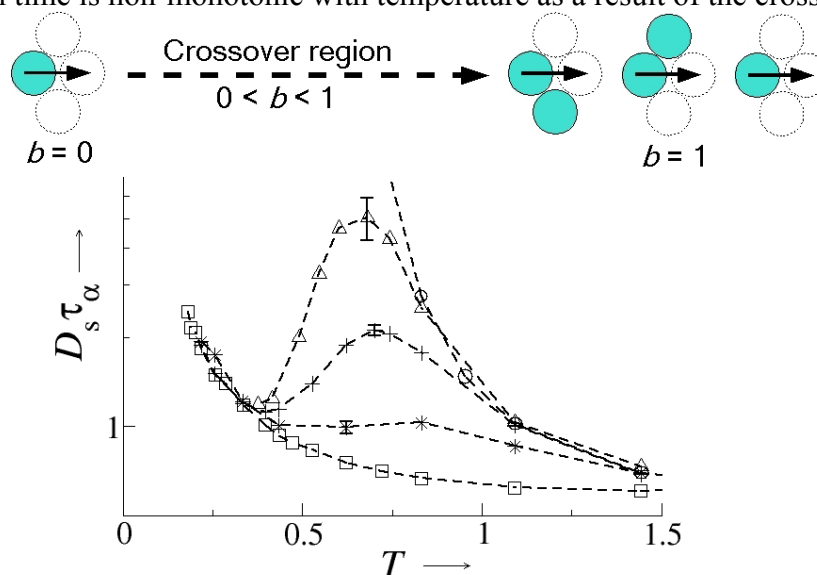
A FAST SAMPLING ALGORITHM FOR PATH-INTEGRAL SIMULATIONS

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I present a recently developed algorithm (PRE, **71**, 045701, 046707, 2005) for Monte Carlo sampling in path integral simulations. The algorithm is based on the observation that the simultaneous sampling of independent random variables results in a loss of statistical efficiency proportional to the number of variables. Therefore, the sampling of independent variables is best conducted independently. Using the Levy-Ciesielski representation of the Brownian motion, I show that any Lie-Trotter product can be put in a form that groups the path variables in $\log_2(n)$ layers, with the variables from a same layer being statistically independent. I conclude that the computational cost of the sampler is $n*\log_2(n)$, as number of calls to the potential vs. number of path variables. Some numerical results are presented, to illustrate the behavior of the new sampling technique.

TORSIONAL MODES IN BIOLOGICAL MOLECULES : AN ANHARMONIC TREATMENT FOR SIMPLE SUGARS.

Yvette K. Sturdy, Chris-Kriton Skylaris, David C. Clary

Physical and Theorertical Chemistry Laboratory, University of Oxford, UK.

Schemes to include a treatment of torsional anharmonicity in the conformational analysis of biological molecules are considered. The approaches combine *ab initio* electronic energies and harmonic frequencies with anharmonic torsional partition functions calculated using the torsional path integral Monte Carlo (TPIMC) method on affordable potential energy surfaces.

An application to the conformational preference of the monosaccharide β-D-galactose in the gas phase is considered. A large number of conformers are found to be populated at ambient temperatures (300K). Both quantum mechanical and anharmonic effects in the torsional modes have little effect on the populations and it is therefore expected that standard harmonic treatments are satisfactory for the conformational study of monosaccharides. Previous studies in our group have, however, shown large anharmonic and quantum mechanical effects for other biological molecules, and the methods are expected to be useful in future applications.

POSTER II-99
**FINITE-SIZE SOLVATION EFFECTS IN MAGNESIUM AND CALCIUM DOPED HELIUM
CLUSTERS**

G L Warren, R J Hinde
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Diffusion Monte Carlo (DMC) is a powerful computer simulation technique for numerically solving the many-body Schrodinger equation. DMC calculations provide a full quantum mechanical treatment and may in principle be carried to arbitrary precision. In addition, the computational expense of these calculations scales very favorably with the system size. These features make diffusion Monte Carlo an ideal method for the investigation of doped helium clusters which exhibit large, anharmonic zero-point motions and substantial quantum effects.

Using DMC methods, we examine the solvation behavior of neutral calcium and magnesium impurities attached to helium nanodroplets. Energy optimized Mg-He and Ca-He pair-product wavefunctions are employed to accurately determine the energetics and solvation structures of these highly quantum systems. We observe strong deformations of the helium density for both dopants, with calcium preferentially solvated further from the interior of the cluster than magnesium. Finite size effects in small clusters appear to prevent the interior solvation of magnesium in clusters with 20 or fewer helium atoms. This contrasts with experimental observations in larger clusters indicating the full interior solvation of magnesium atoms.

Invited Speaker Changes

July 17, 2005
Session II: Multiscale Modeling
Orlando Guzman, coworker of Juan de Pablo, will be speaking in his place.

Poster Session Changes

Posters Withdrawn

PI-21 CHARACTERIZATION OF THE TIP4P-EW WATER MODEL: VAPOR PRESSURE AND PROPERTIES IN THE NEAR- AND SUPER-CRITICAL REGION
Hans W. Horn

PI-64 THE ART OF BOND BREAKING. AN ODYSSEY THROUGH THE COMPUTATIONAL AND INTERPRETATIONAL PROBLEMS OF MC, M=SC, TI, V, AND MN.
Apostolos Kalemos

PII-74 ION-INDUCED CHARGE TRANSFER EXCITATIONS IN PARACYCLOPHANE CHROMOPHORES
Artem E. Masunov

PII-89 HEAT RECTIFICATION IN MOLECULAR JUNCTIONS
Dvira Segal

Posters Added (abstracts attached)

PI-21 CALCULATION OF THE QUANTUM MECHANICAL THERMAL RATE CONSTANT FOR THE $OH + H_2 \rightarrow H_2O + H$ REACTION USING FLUX AUTOCORRELATION FUNCTION
Arindam Chakraborty

PII-89 CHARGE DEPENDENCIES FOR ATOM AND PAIR ENERGIES
Steven M. Valone

Posters Reassigned

PII-31 is now PI-64 THE DECOMPOSITION OF PETN AT EXTREME CONDITIONS
Christine J. Wu

PII-21 is now PI-100 SEMICLASSICAL SIMULATION OF THE VIBRATIONAL DEPHASING OF IODINE IN A CRYOGENIC KRYPTON MATRIX
Jeanne M. Riga

Poster Abstracts on CD

The CD included with the conference abstract booklet contains files with the poster abstracts. The abstracts for posters PI-65 through PI-99, whose titles are listed in the conference booklet, are unfortunately labeled as PI-64 through PI-98 on the CD. For the most up-to-date Poster Session Abstracts from ACTC 2005, please visit: http://www.conferences.ucla.edu/ACTC/PosterAbstracts.pdf

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