

DIVISION OF PHYSICAL CHEMISTRY

Final Program, 226th ACS National Meeting, New York, NY, September 7-11, 2003

Thursday Program

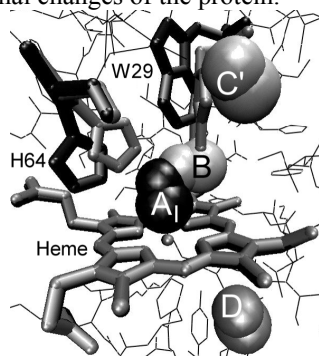
Abstracts

PHYS 431 [639920]: Smaller but slower: Folding kinetics of a β -hairpin and a three-helix bundle
Feng Gai¹, William F. DeGrado², Yongjin Zhu¹, and Deguo Du¹. (1) Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, gai@sas.upenn.edu, (2) Department of Biochemistry & Biophysics, University of Pennsylvania

The folding kinetics of a 16-residue miniprotein (Trpzip4) and a de novo designed, 73-residue three-helix bundle (a3D) were studied by time-resolved infrared spectroscopy coupled with T-jump initiation method. For both proteins, the T-jump induced relaxation signals follow first order kinetics. However, their folding rates exhibit non-Arrhenius temperature dependence. A two-state model predicts a folding time constant of ~ 5 microseconds for a3D and ~ 26 microseconds for Trpzip4 at 298 K, respectively. Detailed comparison of properties associated with the hydrophobic core/cluster of these two systems revealed that the folding rate depends on the details of hydrophobic side chain packing.

PHYS 432 [641894]: Ligand dynamics and binding in myoglobin
Gerd Ulrich Nienhaus, Department of Biophysics, University of Ulm, 89069 Ulm, Germany, Fax: 49-731-50-23059, uli@uiuc.edu

Ligand binding to heme proteins is a comparatively simple biological reaction. Yet, it is actually quite complicated when studied in detail, as seen from the presence of several intermediate states in kinetic experiments. In recent years, cryocrystallography and time-resolved crystallography on carbonmonoxy myoglobin (MbCO) under photolyzing conditions have related kinetic intermediates to different photoproduct structures, in which CO ligands reside in different protein internal cavities. With a variety of infrared and visible spectroscopy techniques, we have investigated the functional role of these cavities in the ligand binding reaction of MbCO and a large number of mutants. Each metastable location of the CO within the protein is associated with its individual CO stretch spectrum, and therefore, we have employed the CO bands as markers to observe ligand migration between the cavities, ligand dynamics within a cavity, and conformational changes of the protein.



PHYS 433 [644580]: Nature of structural inhomogeneities during folding of a helix: Manifestation in IR
S Gnanakaran¹, Robin M. Hochstrasser², and Angel E. Garcia¹. (1) Theoretical Biology and Biophysics Group, Los Alamos National Laboratory, T-10, MS K710, Los Alamos, NM 87545, gnana@lanl.gov, (2) Department of Chemistry, University of Pennsylvania

We report the first comprehensive study on the origin and nature of structural inhomogeneities that give rise to the changes in amide I band during the folding/unfolding of a helical peptide. The peptide is simulated in explicit aqueous solution by a highly parallel replica-exchange approach that combines MD trajectories with a temperature (T) exchange MC process. This efficient sampling technique has been used to capture the relevant structural ensembles of the peptide over a wide range of T (275K to 551K). The model system considered is AA(AAKAA)₃AAY, which along with its isotopomers have been the focus of linear IR, 2D-IR and VCD experiments. The manifestation of hydrogen bonding and conformational variability of solvated helix on amide I band is examined. We present a microscopic picture which provide the reasons for the differences between the amide I of solvated and buried helices and explain the behavior of amide I band upon thermal denaturation.

PHYS 434 [641250]: Watching a protein as it functions with picosecond X-ray crystallography

Philip A. Anfinrud¹, Friedrich Schotte¹, and Michael Wulff². (1) Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, MD 20892, anfinrud@nih.gov, (2) European Synchrotron and Radiation Facility, Grenoble FRANCE

To understand in mechanistic detail how proteins function, it is crucial to know the time ordering of events that give rise to their designed (or modified) function. We have developed the method of picosecond time-resolved macromolecular crystallography on the ID09B beamline at the European Synchrotron and Radiation Facility, and used this technique to acquire time-resolved protein structures with 150 ps time resolution and < 2 Å spatial resolution. We investigated the structural dynamics of L29F MbCO, a mutant of myoglobin that exhibits unusually rapid ligand escape dynamics. The frame-by-frame structural evolution unveils sub-nanosecond conformational changes that are far more dramatic than the structural differences between the static carboxy and deoxy states. The correlated motion of CO and several side chains provides a structural explanation for the rapid expulsion of this toxic ligand from the primary ligand docking site. The ejected ligand migrates through several internal cavities before escaping from the protein.

PHYS 435 [639763]: Protein dynamics from computer simulations compared to time-resolved X-ray crystallography

Gerhard Hummer, Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Building 5, Room 116, 9000 Rockville Pike, Bethesda, MD 20892-0520, Fax: 301-496-0825, hummer@helix.nih.gov

Recent studies of protein dynamics using time-resolved X-ray crystallography provide an increasingly detailed picture of the dynamics of proteins. Such measurements also form a unique basis for quantitative comparisons with molecular dynamics simulations. We will present results from computer simulations of myoglobin dynamics induced by carbonmonoxide photodissociation, and compare the simulations to recent Laue diffraction measurements with a time resolution near 100 ps (Schotte et al., Science, 2003). This comparison highlights how the combined approach using time-resolved crystallography and simulation can provide new insights into the functional dynamics of proteins.

PHYS 436 [652225]: Crystal structures and molecular mechanism of a light-induced signaling switch: the Phot-LOV1 domain

Ilme Schlichting¹, Roman Fedorov¹, Elisabeth Hartmann¹, Tatjana Domratcheva¹, Markus Fuhrmann², and Peter Hegemann². (1) Biophysikalische Chemie, Max Planck Institut für Molekulare Physiologie, Otto Hahn Str. 11, Dortmund, Germany, ilme.schlichting@mpi-dortmund.mpg.de, (2) Institut für Biochemie I, Universität Regensburg

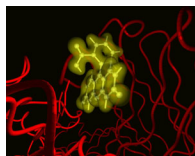
Phot-proteins (phototropin and homologues) are blue light photoreceptors that control mechanical processes like phototropism, chloroplast relocation or guard cell opening in plants. Phot-receptors consist of two FMN-binding LOV (Light Oxygen Voltage) domains and a C-terminal serine/threonine kinase domain that autophosphorylates upon absorption of a blue light photon. The approaches used and difficulties encountered in determining the structures of the resting dark state and the unstable photoproduct of the LOV1-domain of Phot1 from the green alga *Chlamydomonas reinhardtii* will be described. Light absorption causes formation of a proposed active signaling state that is characterized by a covalent bond between the flavin C4a and the thiol of Cys57. In the resting dark state of

LOV1 Cys57 is present in two conformations. The structures are interpreted in the light of the spectroscopic data and used as a basis for quantum chemical calculations to obtain insight in the reaction mechanism. It will be presented and compared to previously suggested mechanisms.

PHYS 437 [640042]: From molecules to proteins: Possibilities for data and algorithmic integration using HPC technologies

Kim K. Baldridge, Integrative Computational Sciences, San Diego Supercomputer Center, 9500 Gilman Drive, Mail Code 0505, La Jolla, CA 92093-0505, Fax: 858-534-5117, kimb@sdsc.edu

To deepen our understanding of natural and synthetic processes and to support current experimental progress, there is an increasing need for affordable theoretical calculations of chemical reactions in complex systems like solutions, biomolecules and materials. Intricacies of dynamical motion in protein and enzymatic systems, mechanistic aspects of biochemical reaction processes in solution, and determination of key dielectric phenomenon all require careful use of methodology if accurate and reliable results are to be expected. In the last few years, many efforts have been undertaken to combine techniques involving quantum mechanics with other less expensive approaches, most notoriously, QM/MM. This presentation will focus on strategies for hybrid techniques that are being developed in this group, based on algorithmic modifications and extensions to our quantum mechanical approach for the inclusion of solvent effects, COSab. Features of the methods will be highlighted using several examples of calculations performed on biochemical systems of interest.



PHYS 438 [639142]: Artificial intelligence for electronic structures: Automated parallel implementations of configuration-interaction, coupled-cluster, and many-body perturbation theories

So Hirata, William R Wiley Environmental Molecular Sciences Laboratory, Battelle, Pacific Northwest National Laboratory, K8-91, P.O.Box 999, Richland, WA 99352, Fax: 509-376-0420, So.Hirata@pnl.gov

Many-electron theory offers a variety of converging approximations to tackle chemical problems including bond breaking and formation. However, such studies are often deterred not only by limited computational resources but to a greater extent by the complexity of the process of deriving the working equations and implementing efficient programs of the approximations, which can even take man-years of efforts. We present a symbolic manipulation program that abstracts and automates the derivation and parallel implementations of second-quantized models of many-electron theory and its applications to parallel implementations of CI up to CISDTQ, CC up to CCSDTQ, and non-canonical MBPT up to fourth order. These computer-generated programs fully take advantage of spin, spatial, and index permutation symmetry, adjust memory usage by tiling algorithm, and balance parallel workload dynamically, and can compete with carefully hand-coded programs in performance.

PHYS 439 [642702]: Parallel multiconfigurational self-consistent field

Graham D. Fletcher, Computational Chemistry Group, NAS Division, Eoret Corporation, NASA Ames Research Center, Moffett Field, Mountain View, CA 94035, gletcher@arc.nasa.gov

A distributed data multiconfigurational self-consistent field (MCSCF) algorithm based on the full Newton-Raphson orbital update method, with an augmented Hessian, is presented. Scalability up to 512 processors is demonstrated. Application is made to the fragmentation of guanine (a basic component of DNA) under electron attachment.

PHYS 440 [645641]: Bond dissociations associated with GTP hydrolysis

Theresa L. Windus¹, Yuri Alexeev¹, and D. Dixon². (1) Molecular Science Software Group, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MSIN: K1-96, Richland, WA 99352, Fax: 509-375-6631, theresa.windus@pnl.gov, (2) PNL

GTP-binding proteins (GTPases) play an important role in a variety of biological processes such as cell growth control and control of transcription. Particularly, the Ras family proteins of GTPases play an important role in linking receptors on the plasma membrane to signaling pathways. Ras mutants, which are found in 25-30% of human tumors, are believed to encourage uncontrolled cell growth. When GTPases are bound to GTP these proteins are active. Later, when GTP is hydrolyzed to GDP, these proteins become inactive:



The hydrolysis can be catalyzed by GTPase-activating proteins. In spite of the obvious importance of GTP hydrolysis, the mechanism is still controversial. We will present bond dissociation energies and other thermodynamic properties for GDP, GTP, Ras-GTP, and other related chemical compounds.

PHYS 441 [640461]: Analytic energy second derivatives for MCSCF wavefunctions: Implementation and parallelization

Timothy J. Dudley, and Mark S. Gordon, Ames Lab/Iowa State University, 207 Spedding Hall, Ames, IA 50011, Fax: 515-294-5204, tim@si.fi.ameslab.gov

MCSCF techniques are widely used in describing bond breaking due to the inherent multiconfigurational nature of the process. Analytic MCSCF energy gradients have seen widespread use in characterizing stationary points on electronic potential energy surfaces, due to their superiority in both accuracy and efficiency over their numerical counterparts. Use of analytic MCSCF second derivatives, however, has been severely limited due to increased complexity and computational demands required to generate such quantities. Analytic second derivatives for the determinant-based complete active-space variant of MCSCF have been recently implemented into GAMESS. General aspects of the current implementation will be discussed. A more detailed analysis of issues pertaining to parallelization will also be presented.

PHYS 442 [641179]: Polyelectrolyte-surfactant complexes: phase diagrams and novel microemulsions

Helmut H. Strey, Michael J. Leonard, and Waiken Wong, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Conte Polymer Science Building, 120 Governors Drive, Amherst, MA 01003-9263, Fax: 413-545-0082, strey@mail.pse.umass.edu

When a water-soluble polyelectrolyte is combined with an oppositely-charged surfactant solution at a stoichiometric charge ratio, self-assembly into a highly ordered, water-insoluble complex occurs. We have established general phase diagrams for nanostructured CTax - poly[(sodium acrylate)-co-acrylamide] complexes by studying phase structure as a function of ionic strength, salt type, polyelectrolyte charge density, applied osmotic pressure, and temperature with small-angle X-ray scattering (SAXS). In addition, we present the discovery and characterization of complexes of polyelectrolyte, oppositely-charged surfactant, co-surfactant, and oil displaying long-range order. We have succeeded in swelling these hydrophobic domains by first introducing a co-surfactant to counteract the surfactant's spontaneous curvature, thus giving the complexes the flexibility to incorporate up to 50% oil. Such complexes have potential application in encapsulation of hydrophobic or non-polar species within an aqueous medium as well as in recovery of organic solvents from aqueous wastes.

PHYS 443 [643378]: Controlling the size of nanoscale toroidal DNA condensates with static curvature and ionic strength

Nicholas V. Hud, Christine Conwell, and Igor Vilfan, School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State St., Atlanta, GA 30332, Fax: 404-894-2295, hud@chemistry.gatech.edu

The condensation of DNA molecules into well-defined nanometer-scale particles by multivalent cations is an excellent example of a polymer phase transition in solution. We present a quantitative study of DNA toroids formed by the condensation of DNA with hexammine cobalt (III). The presence or absence of static loops within this DNA molecule demonstrates the effect of nucleation loop size on toroid dimensions, and that nucleation is principally decoupled from toroid growth. A comparison of DNA condensates formed at low ionic strength with those formed in the presence of additional salts (NaCl or MgCl₂) shows that toroid thickness is a salt-dependant phenomenon. Together, these results have allowed the development of models for DNA toroid formation in which the size of the

nucleation loop directly influences the diameter of the fully formed toroid, while solution conditions govern toroid thickness. The data presented illustrates the potential that exists for controlling DNA toroid dimensions. Furthermore, this study provides a set of data that should prove useful as a test for theoretical models of DNA condensation.

PHYS 444 [644222]: Monte Carlo simulations of self-assembled polymers and networks

James T. Kindt, Xinjiang Lv, and Jian Ni, Department of Chemistry, Emory University, 1515 Pierce Drive, Atlanta, GA 30322, Fax: 404-727-7412, jkindt@emory.edu

Off-lattice Monte Carlo methods have been developed and used to investigate the structure and phase diagrams of equilibrium polymers and networks. These simple model simulations are used to investigate general principles relevant to living polymers, wormlike micelles, and self-assembled protein fibers. Specific topics to be addressed include the coupling of equilibrium chain length distributions to nematic ordering and the influences of chain flexibility and junction geometry on the gelation of living networks.

PHYS 445 [642474]: Effect of mono- and multivalent salts on the interaction between two charged rods

Kun-Chun Lee¹, Itamar Borukhov², William M. Gelbart², Andrea J. Liu³, and Mark J. Stevens⁴. (1) Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Ave., Los Angeles, CA 90095-1569, Fax: 310-267-0319, klee@chem.ucla.edu, (2) Dept. of Chemistry and Biochemistry, UCLA, (3) Department of Chemistry, University of California, (4) Sandia National Laboratories

We calculate the effective potential between a pair of charged rods as a function of separation and angle using molecular dynamics simulations. We examine the effect of mixed mono- and multivalent salts on this interaction. At zero concentration of multivalent salt, the rods repel. We find that there is a threshold concentration of multivalent salt for an attraction to appear. Below this threshold, an attraction can be induced by adding enough monovalent salt. We also study whether sufficient multivalent salt can lead to charge reversal.

PHYS 446 [632485]: Osmotic force suppression of viral ejection

Alex Evilevitch¹, Martin Castelnovo¹, Laurence Lavelle¹, Charles M Knobler¹, Eric Raspaud², and William M. Gelbart¹. (1) Department of Chemistry and Biochemistry, University of California Los Angeles, 607 Charles E. Young Drive East, Box 951569, Los Angeles, CA 90095-1569, evilevit@chem.ucla.edu, (2) Laboratoire de Physique des Solides, Université de Paris-Sud

Bacterial viral capsids in aqueous solution can be opened in vitro by addition of their specific receptor proteins, with consequent full ejection of their genomes. We demonstrate that it is possible to control the extent of this ejection by varying the external osmotic pressure. In the particular case of bacteriophage lambda the ejection is 50% inhibited by osmotic pressures (of polyethylene glycol) comparable to those operative in the cytoplasm of host bacteria, while it is completely suppressed by a pressure of 20 atmospheres. Furthermore, our experiments monitor directly a dramatic decrease of the stress inside the un-opened phage capsid upon addition of polyvalent cations to the host solution, in agreement with many recent theories of DNA interactions. We also present a theoretical analysis of the forces that control the extent of DNA ejection, featuring the resisting force due to the osmotic stress agents.

PHYS 447 [643558]: Viral self-assembly as a thermodynamic process

Robijn Bruinsma, Department of Physics and Astronomy, University of California, Los Angeles, Hilgard Av, Los Angeles, CA 90095, bruinsma@physics.ucla.edu, Joseph Rudnick, Physics Department, University of California, Los Angeles, and William M. Gelbart, Department of Chemistry and Biochemistry, University of California, Los Angeles

The talk will present the results of the application of the statistical mechanics of self-assembly to the formation of viral shells ("capsids") and compare the results with measured self-assembly phase diagrams for viruses. Viral capsids constructed from structurally identical protein subunits are predicted to be characterized by certain "magic numbers" in terms of the number of constituent proteins. Actual sphere-like viruses adopt icosahedral symmetry

with a different sequence of magical numbers. We find that icosahedral symmetry requires (at least) two internal configurations for the protein subunits comprising the viral capsid (“switching”). For the two state model, we recover the sphere-to-rod structural transition that has been observed for a number of capsids. Our results indicate that icosahedral symmetry is not the unavoidable consequence of free energy minimization but instead an adaptation that maximizes surface coverage.

PHYS 448 [639573]: S-state to conduction band spectrum of the hydrated electron

Paul F. Barbara, Tak W. Kee, and Young Jong Lee, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, Fax: 512-471-3389, p.barbara@mail.utexas.edu

The s-state to conduction band (CB) absorption spectrum of the hydrated electron (e_{aq}^-) has been determined by a multi-color photo-detrapping experiment. Photo-detrapping has been observed indirectly by monitoring the effect of photo-excitation of e_{aq}^- on the electron/hole spatial separation, which is inferred from the e_{aq}^- /hole geminate recombination kinetics following photoionization of neat water. The yield of photo-suppression of geminate recombination (Y_{PS}) at 3.10 eV excitation has a high value of 0.92, corresponding to the 1-photon excitation of e_{aq}^- to the CB of water. The lower energy region of the spectrum (1.55 – 2.07 eV) shows a weaker but measurable Y_{PS} of ~ 0.18 . The results indicate that photo-excitation between 1.55 and 3.10 eV induces migration of e_{aq}^- by at least 30 Å, involving the CB of water.

PHYS 449 [639987]: The role of dispersion in the interaction of excess electrons with water clusters

Kenneth D. Jordan, Dept of Chemistry and Center for Molecular and Materials Simulations, University of Pittsburgh, Pittsburgh, PA 15260, Fax: 412-624-8611, jordan@pitt.edu

It has recently been established that dispersion interactions play an important role to the binding of an excess electron to water clusters. In this talk, the role of dispersion interactions in determining whether an excess electron prefers to be on the surface or interior of the cluster will be examined. In addition, the contribution of dispersion interactions to the excitation energies will be discussed.

PHYS 450 [644996]: Mapping the conduction band under CTTS Transitions: the photodetachment quantum yield of sodide in THF

Benjamin J. Schwartz¹, Erik R. Barthel¹, and Ross E. Larsen². (1) Department of Chemistry, UCLA, Los Angeles, CA 90095, schwartz@chem.ucla.edu, (2) Department of Chemistry, University of California, Los Angeles

When small anions are placed in solution, states in the continuum above the gas-phase detachment threshold can be stabilized to below the vacuum level, resulting in strongly allowed charge-transfer-to-solvent (CTTS) bands. Excitation of CTTS bands results in detachment of the electron from the anion, producing a solvated neutral atom or molecule and a solvated electron. By measuring the photodetachment quantum yield for electrons detached from sodium anions in THF, we are able to map out the point at which detachment above the liquid continuum begins. The results suggest the presence of three distinct sub-bands underlying the CTTS absorption spectrum; excitation into the low-energy sub-bands produce solvated Na atom:solvated electron contact pairs, whereas excitation into the highest-energy band results in electron ejection out into the solvent, a hallmark of the conduction band. The ejection quantum yields compare favorably with photoconductivity measurements made on related alkali metal anions by Levanon and co-workers.

PHYS 451 [672814]: Photoelectron spectroscopy of solute ions in water jets

Manfred Faubel, Max Planck Institut für Strömungsforschung, Bunsenstrasse 10, D-37073 Göttingen, Germany, Fax: +49-551-5176-704, mfaubel@gwdg.de

The photoelectron spectrum of bulk liquid solutions is probed at the free vacuum surface of thin, micron size, water jets, using 40 eV to 120 eV tunable photon energy. This allows to cover outer- and inner- valence shell electron bound states of the neat solvent and to measure the vertical ionization energies of solvated anions and cations of simple salt solutions in an extended range of concentrations. The photoelectron spectral intensities can show

elevated surface concentration of surface active solutes or ongoing solute reactions. In addition, observed weak secondary spectral peak structures of the neat liquid which seem not to correlate with gas phase features, tentatively, are attributed to water conductance band processes.

PHYS 452 [644993]: Electron Photodetachment from aqueous halide ions via CTTS States and the bulk conduction band

Xiyi Chen, Jeremiah A Kloepfer, and **Stephen E Bradforth**, Department of Chemistry, University of Southern California, 920 W 37th St, SSC716, Los Angeles, CA 90089, Fax: 213-740-3972, xiyichen@usc.edu, bradfort@usc.edu

Electron photodetachment from halide anions in aqueous solution has been systematically investigated as a function of excitation energy using femtosecond pump-probe spectroscopy. The excitation energies employed ranged from 4.7 eV to 8.3 eV, enabling us to excite each halide into its various CTTS states and/or the bulk conduction band. Excitation via one- and two-photon mechanisms is carefully verified. The ejection length as a function of detachment energy is mapped using the time-dependent geminate recombination profiles of the solvated electrons produced. The coupling to the bulk conduction band is observed as a higher escape probability of the ejected electron. In this way an action spectrum is generated - this is compared to bulk electronic structure calculations for the spectrum of vertical excited states of halide anions in water.

PHYS 453 [635604]: Conduction band in nonpolar fluids

Richard A. Holroyd, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, Fax: 631-343-5815, holroyd@bnl.gov

The existence of a band of states in which the electron is quite mobile and its wave-function is extended is common to all nonpolar liquids. The energy of the lowest state in this band relative to vacuum is designated V_0 . Values of V_0 for nonpolar molecular liquids range from +0.2 to -0.75 eV at room temperature, and V_0 increases with increasing density. The value of V_0 affects such phenomena as the mobility of electrons, the value of the work function of a metal immersed in the fluid, the ionization threshold of molecules in a fluid, and field ionization of Rydberg states of solutes. Consequently, studies of these phenomena provide ways of measuring V_0 . Recent studies provide accurate values of the conduction edge in nonpolar liquids and some results of these studies will be discussed.

PHYS 454 [642190]: Linear scaling quantum Monte Carlo: Applications to semiconductor nanomaterials

A. Williamson, Lawrence Livermore National Laboratory, Livermore, CA 94551, williamson10@llnl.gov

A method for performing QMC calculations where the computational time required to evaluate the local energy of a configuration of electron coordinates scales linearly with the number of electrons will be presented. Truncated, maximally localized Wannier functions are chosen to represent the single particle orbitals in the Slater determinant part of the many-body wavefunction. This choice of orbitals yields increasingly sparse Slater determinants as the system size is increased yielding a near linear scaling of the computational time.

The application of these QMC techniques to the evaluation of a variety of optical properties of semiconductor quantum dots will be presented. We present a comparison of the size dependence of optical absorption gaps predicted by QMC, density functional and semi-empirical techniques. We also present predictions of the energy difference between optical absorption and emission in quantum dots.

PHYS 455 [643555]: Electronic structure of systems with transition metals by quantum Monte Carlo

Lubos Mitas, Prasenjit Sen, Lucas K. Wagner, J-W. Lee, and Michal Bajdich, Department of Physics, North Carolina State University, 2700 Stinson Dr., Box 8202, Raleigh, NC 27695-8202, Fax: 919-515-4496, lmitas@unity.ncsu.edu

Recently, we have carried electronic structure calculations for several types of systems which contain transition metal (TM) atoms. This includes TMO molecules, TM@Si12 clusters, perovskite transition metal solids, and biomolecules. We focus on calculations of excited states such as low-spin/high-spin splittings especially for near-

degenerate states, optical excitations and electronic gaps in solids. For this purpose we use a combination of methods and developments which include optimizing mean-field approaches for generating one-particle orbitals, configuration interaction for analysis and building trial wave functions and correlated sampling in variational and diffusion Monte Carlo calculations. This enables us to shed new light on electronic structure challenges in these systems such as identification of ground states and stability of TM@Si₁₂ systems ahead of experiment and prediction of band gaps of solid materials for which experimental results are contradictory or inconclusive.

PHYS 456 [644868]: Diffusion Monte Carlo studies of excitation energies in solids and quantum dots

Cyrus J. Umrigar, Cornell Theory Center, Cornell University, 633 Rhodes Hall, Ithaca, NY 14853, Fax: 607-254-8888, cyrus@tc.cornell.edu

It is well known that commonly used density functionals tend to greatly underestimate the band gaps of solids. In contrast diffusion Monte Carlo yields band gaps and band widths that are in reasonable agreement with experiment and tend to overestimate these by about 10 - 20%. We discuss the likely reason for this overestimate.

Quantum dots containing one to several tens of electrons are analogous to atoms with tunable properties, exhibiting shell structure and obeying Hund's first rule. They are both of considerable technological interest and of theoretical interest because it is possible to go from a weak correlation to a strong correlation regime by tuning the relative strength of the external potential to the electron-electron potential. We find that the Hartree-Fock approximation is a poor approximation for dots and that the local spin density approximation is significantly better but nevertheless inadequate for predicting the correct ordering and values of the ground and excited state energies.

PHYS 457 [644036]: Diffusion quantum Monte Carlo studies of Wigner crystals

Richard J. Needs, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom, Fax: 44 1223 337356, rn11@phy.cam.ac.uk

We report diffusion quantum Monte Carlo (DMC) calculations for Wigner crystals in two and three dimensions. Very accurate calculations are required to obtain reliable values of the fluid/crystal transition densities. The orbitals within the Slater-Jastrow guiding wave functions are optimized within DMC, and finite size errors, time-step errors and population control errors are analyzed. In three dimensions we compare our crystal data with the recent fluid DMC data of Zong, Lin, and Ceperley, and find a transition density of $r_s \sim 106$. We compare our DMC data with Hartree-Fock results, which allows us to understand the effects of correlation on Wigner crystals.

PHYS 458 [641293]: QMC computations for homogeneous and inhomogeneous jellium systems

P. Ballone, Department of Physics, University of Messina, Contrada Papardo, 98166 Messina, Italy, p.ballone@fz-juelich.de

Jellium systems provide a suitable playground to check the predictions of many-body theories by QMC computations. I present Fixed-Node Diffusion MC results for homogeneous and inhomogeneous systems. In the case of homogeneous systems, the focus is on the paramagnetic to ferromagnetic transition, on the Wigner crystallization, and on glassy low density phases. I present new results, and I discuss the comparison with previous computations. In the case of inhomogeneous systems, I present results for isolated and for interacting jellium spheres. In the case of isolated spheres, total energy, electron and spin density have been computed for a wide range of sizes and background densities. The QMC results are compared to the predictions of recent approximations for the exchange and correlation energy proposed by J. P. Perdew and co-workers. Interacting jellium spheres provide benchmark results for non-local correlations in valence electron systems.

PHYS 459 [670500]: Molecular dynamics simulation of bacteriorhodopsin's photoisomerization using ab initio forces for the excited chromophore

Klaus Schulten, Department of Physics and Beckman Institute, U. of Illinois at Urbana-Champaign, Urbana, IL 61801, Shigehiko Hayashi, Department of Physics, University of Illinois, Urbana Champaign, and Emad Tajkhorshid, Department of Physics, University of Illinois, Urbana Champaign

Retinal proteins possess a common chromophore, retinal, that upon absorption of light isomerizes and, thereby, triggers biological functions ranging from light energy conversion to vision. The photoisomerization of retinal is extremely fast, highly selective inside the protein matrix, and characterized through optimal sensitivity to incoming light. We report the first ab initio quantum mechanical description of the in situ isomerization dynamics of retinal in bacteriorhodopsin. The description combines ab initio multi-electronic state molecular dynamics of a truncated retinal model with molecular mechanics of the protein motion and unveils in complete detail the photoisomerization process. The results illustrate the essential role of the protein for the characteristic kinetics and high selectivity of the photoisomerization; the protein arrests inhomogeneous photoisomerization paths and funnels them into a single path that initiates the functional process. Supported by comparison with dynamic spectral modulations observed in femtosecond spectroscopy, results identify the principal molecular motion during photoisomerization.

PHYS 460 [640904]: Transport mechanism from crystal structures of seven states in the bacteriorhodopsin photocycle

Janos K. Lanyi, Department of Physiology & Biophysics, University of California, Irvine, Irvine, CA 92697, Fax: 949-824-8540, jlanyi@orion.oac.uci.edu

We have trapped the K (1), L (2), M1 (3), M2 (4), M2' (5) and N' (6) intermediates of the bacteriorhodopsin photocycle in crystals at various temperatures and with various illumination regimes, and determined their structures by x-ray diffraction to 1.47-1.62 Angstrom resolutions. High-resolution structural information is therefore available for the initial bacteriorhodopsin state (1, 7) as well as six in-intermediates in the transport cycle of this light-driven proton pump. In these states the photoisomerized retinal undergoes configurational changes, the retinal Schiff base protonates Asp85, a proton is released to the extracellular membrane surface, a switch event occurs that allows reprotonation of the Schiff base from the cytoplasmic side, side-chain motions are initiated in the cytoplasmic region, a single-file chain of hydrogen-bonded water molecules is formed that conducts the proton of Asp96 to the Schiff base, and Asp96 is reprotonated from the cytoplasmic surface. The structural models describe the transformations of the retinal and its interaction with water 402, Asp85, and Trp182 in atomic detail, the displacements of functionally important residues, and the locations of water molecules transiently sequestered in the cytoplasmic region. The observed changes suggest a detailed atomic-level model for the critical steps in the transport, and describe it as the gradual relaxation of the distorted retinal that causes displacements of water and protein atoms that result in vectorial proton transfers to and from the Schiff base.

1. B. Schobert, J. Cupp-Vickery, V. Hornak, S. O. Smith and J. K. Lanyi. *J. Mol. Biol.* 321: 715-726, 2002.
2. J. K. Lanyi and B. Schobert. *J. Mol. Biol.* (in press).
3. J. K. Lanyi and B. Schobert. *J. Mol. Biol.* 321, 727-737, 2002.
4. H. Luecke, B. Schobert, J.-P. Cartailler, H.-T. Richter, A. Rosengarth, R. Nee-dleman and J.K. Lanyi. *J. Mol. Biol.* 300: 1237-1255, 2000.
5. H. Luecke, B. Schobert, H. -T. Richter, J. -P. Cartailler and J. K. Lanyi. *Science* 286: 255-260, 1999.
6. B. Schobert, L. S. Brown and J. K. Lanyi. (submitted).
7. H. Luecke, B. Schobert, H. -T. Richter, J. -P. Cartailler and J. K. Lanyi. *J. Mol. Biol.* 291: 899-911, 1999.

PHYS 461 [643917]: Measurements of fluctuations in DNA structure on the nanosecond to femtosecond time scales

Mark A. Berg¹, Daniele Andreatta¹, Catherine J. Murphy¹, Robert S. Coleman², Louis L. Pérez Lustres³, Sergey A. Kovalenko³, and Nikolaus P. Ernstring³. (1) Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, Fax: 803-777-1456, berg@mail.chem.sc.edu, (2) Department of Chemistry, The Ohio State University, (3) Institut für Chemie, Humboldt-Universität zu Berlin

Fluorescent dyes have long been used as static probes of local polarity in biological systems. We have synthetically incorporated a polarity sensitive dye (coumarin-102) into the interior of oligonucleotides. A combination of time-resolved absorption and fluorescence measurements reveal dynamic fluctuations of the DNA structure through the resulting changes in the electric field at the dye position. Dynamics extend over an extremely wide time range extending throughout the nanosecond and picosecond time ranges. The most recent measurements extend these dynamics into the femtosecond time regime. Specific results include: (1) Sodium counterions have specific binding modes with lifetimes extending into the nanosecond range. (2) A transition from solvent-controlled dynamics at short times to intrinsically DNA controlled dynamics at long times. (3) A deleted base does not disrupt the basic

dynamic of the oligonucleotide, but does cause an extra 16 ns relaxation, which may be due to a sugar flipping motion.

PHYS 462 [639351]: New technique to detect energy and conformational changes of proteins in time-domain
Masahide Terazima, Department of Chemistry, Kyoto University, Sakyo-ku, Kyoto city 606-8502, Japan, Fax: +81-75-753-4000, mterazima@kuchem.kyoto-u.ac.jp

In science, thermodynamic properties have been very important to understand the nature of material or the state of molecules for a long time. On the other hand, kinetics is another large and important field for studies of chemical reactions. However, these two fields have been developed almost independently and the connection between these fields is not clear. For example, there have been almost no data on the thermodynamical properties of any transient species. Recently, we are interested in making a connection between these two large fields. We have succeeded in measuring the thermodynamical quantities of short lived species and tracing the kinetics of molecular energy, molecular volume, as well as the diffusion coefficients in time-domain based on the transient grating technique. Here we will show some examples of protein reaction and protein folding dynamics by monitoring the energy, molecular volume and the diffusion process.

PHYS 463 [644404]: Nanosecond time-resolved macromolecular crystallography: blue light photoperception
Keith Moffat, Sean Crosson, and Spencer Anderson, Department of Biochemistry & Molecular Biology, and Institute for Biophysical Dynamics, University of Chicago, 920 East 58th Street, Chicago, IL 60637, Fax: 773-702-0439, moffat@cars.uchicago.edu

By exploiting the intensity and pulsed nature of third-generation synchrotron sources such as the Advanced Photon Source at Argonne National Laboratory, pump-probe experiments can be conducted on single crystals of biological macromolecules with sub-ns time resolution. These experiments reveal the time course of the structural evolution of the reaction, whether or not it conforms to a simple chemical kinetic model, and the structures of time-independent intermediate states. Application of plausible structural constraints may enable certain candidate reaction schemes to be ruled out, and the structures of individual intermediates associated with these states to be identified. Conventional crystallographic and unconventional, time-resolved experiments on blue light photoreceptors such as photoactive yellow protein and the LOV2 domain of phototropin will be presented, to demonstrate how certain biological systems harness the energy derived from photon absorption to generate a biological signal.

PHYS 464 [642943]: Initial steps in biological signal generation: ultrafast isomerization and structural changes in the photoactive yellow protein

ML Groot¹, DS Larsen¹, KJ Hellingwerf², and **R. Van Grondelle**¹. (1) Department of Biophysics, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1081, Amsterdam 1081 HV, Netherlands, marloes@nat.vu.nl, rienk@nat.vu.nl, (2) Laboratory for Microbiology, Swammerdam Institute for Life Sciences, University of Amsterdam

We describe the first steps of signal generation in the Photoactive Yellow Protein of the xantopsin family. The isomerization of its chromophore upon light absorption is the first step in a photocycle that leads to the signalling state and ultimately to a negative phototactic response of the bacterium. Using visible pump/mid-infrared probe spectroscopy with <200 fs time resolution, we have characterized the structural changes that initiate the photocycle in WT PYP. Upon photoexcitation, PYP's intrinsic chromophore undergoes an excited state isomerization within ~200 fs. We observe that the flipping of the C=O group of the chromophore around the ethylene bond of the chromophore determines whether a stable cis ground state can be formed, and the subsequent reactions of the photocycle can proceed. Instantaneous changes involving the chromophore also include the strengthening of the hydrogen bond with residue Glu46 and charge redistribution on the phenol ring. Our results indicate that instantaneous changes of Arg52 occur, probably due to changes in the hydrogen-bonding network on the distal side of the chromophore. Relaxation of the coumaryl tail of the chromophore occurs on the 850-ps time scale.

PHYS 465 [641896]: Electron correlation treated using time-dependent approaches

Roi Baer, Shlomit Yacobi, and Yair Kurzweil, Institute of Chemistry and the Lise Meitner Center for Quantum Chemistry, The Hebrew University of Jerusalem, Givat Ram Campus, Jerusalem 91904, Israel, Fax: 972-2-6513742, roi.baer@huji.ac.il

Electron correlation in molecules can be described using time dependent methods. We will discuss two approaches. First, the use of auxiliary fields to replace electron-electron interactions will be discussed. This method will be shown to yield very highly accurate electronic energies in molecules. We will next discuss how correlation over time should be incorporated into time dependent density functional theory. This can be elegantly done via functionals that depend on the current density. The non-adiabatic part of the electron correlation is rigorously manifested in a transverse vector potential. This is then a "exchange-correlation magnetic field" which is always present even when there is no real magnetic field in the problem.

PHYS 466 [643192]: Can density functional theory provide a reliable description of bond making/breaking processes?

Elfi Kraka, Jürgen Gräfenstein, and Dieter Cremer, Department of Theoretical Chemistry, University of Göteborg, Reutersgatan 2, Göteborg S-41320, Sweden, Fax: 46-31-7735590, Kraka@theoc.gu.se

DFT is presently the only method, which can reasonably describe chemical processes involving large molecules at acceptable cost. Nevertheless, there are also many examples of its failure: Reaction barriers are underestimated, false intermediates are predicted or an erroneous asymptotic behavior for bond dissociation is calculated. It is shown that pitfalls and shortcomings of DFT can be avoided by an educated use of the method. This implies careful handling of the self-interaction error of approximate XC-functionals or the suppression of a double counting of non-dynamic electron correlation when using multi-reference DFT. For the purpose of assessing the performance of DFT more clearly, the detailed mechanism of bond making / breaking processes is discussed.

PHYS 467 [638732]: The spin-flip approach within time-dependent density functional theory

Yihan Shao, Q-Chem, Inc, Four Triangle Lane, Export, PA 15632, yihan@q-chem.com, Anna I. Krylov, Department of Chemistry, University of Southern California, and Martin Head-Gordon, Department of Chemistry, University of California at Berkeley

Krylov's spin-flip approach is extended from wavefunction based methods to density functional theory framework. This extension naturally combines the strengths of both the spin-flip approach, which is suitable for describing non-dynamical correlation, and density functional theory, which well accounts for dynamical correlation. This new method (SF-DFT) is implemented within the Tamm-Dancoff approximation to the time-dependent density functional theory within the Q-Chem electronic structure software package. We will present some results on bond-breaking, diradicals, and other interesting problems.

PHYS 468 [651120]: Excited states via linear response in DFT and HF free of basis set error

Robert J. Harrison Harrison, and Takeshi Yanai, Oak Ridge National Laboratory, PO Box 2008 MS6367, Oak Ridge, TN 37831-6367, harrisonrj@ornl.gov

We will describe the computation of excitation energies and transition densities using multiresolution in multiwavelet bases. These results, for general polyatomic systems, are free of basis set error (more precisely have guaranteed precision) and are compared with computations in conventional atom-centered Gaussian bases.

PHYS 469 [644556]: Bond-breaking in density functional theory

Kieron Burke, Department of Chemistry and Chemical Biology, Rutgers, 610 Taylor Road, Piscataway, NJ 08854, Fax: 732-445-5312, kieron@rutchem.rutgers.edu, and Martin Fuchs, Fritz-Haber-Institute der MPG

We review the basic difficulties of bond-breaking within KS density functional theory, using H₂ as the canonical example. We will discuss why spin-contamination of KS wavefunctions is a good thing, if correctly interpreted. We

will discuss recent work on RPA calculations of ground-state energies, corrected by either TDDFT or short-range GGA, showing how such calculations correctly dissociate.

PHYS 470 [643598]: Cell cytoskeletal actin-bundle assembly in-vitro

Cyrus R. Safinya, and Linda Hirst, Department of Materials & Physics, University of California at Santa Barbara, MRL 2208, Santa Barbara, CA 93106, Fax: 805-893-7221, safinya@mrl.ucsb.edu

With the completion of the Human Genome Project and the emerging proteomics era, the biosciences community is beginning the daunting task of understanding the structures and functions of a large number of interacting proteins. Cellular activity, which is tightly regulated, results from protein-protein and protein-nucleic acid interactions, which often lead to the formation of large assemblies of biomolecules for distinct functions. Examples include DNA condensation during the cell cycle, and bundle and network formation of filamentous proteins in cell attachment, motility, and cytokinesis. We present recent confocal imaging and synchrotron x-ray diffraction data, in cell-free systems of actin filaments and the actin bundling protein alpha-actinin. The data, spanning lengths from the nanometer to scales larger than the cell size, reveal supramolecular assemblies with unexpected patterns and morphologies, which are distinct from actin networks and bundles described in current textbooks. Supported by NSF-DMR-0203755, NIH-GM-59288-05.

PHYS 471 [643736]: Force generation by polymerization of actin filaments

Julie A. Theriot, Department of Biochemistry, Stanford University School of Medicine, 279 West Campus Drive, Stanford, CA 94305-5307, theriot@stanford.edu

Actin is a major protein component of the eukaryotic cytoskeleton. Actin monomers self-assemble to form helical filaments. Polymerizing networks of actin filaments are capable of exerting significant mechanical forces. Certain intracellular bacterial pathogens can induce the polymerization of human host cell actin filaments on their surfaces to generate movement. Moving bacteria are associated with a characteristic actin structure that resembles the tail of a comet. Comet tails can also be assembled on artificial particles including polystyrene beads and lipid vesicles. Actin polymerization in comet tails generates nanonewton-scale forces, largely directed perpendicular to the direction of motion, compressing the cargo. Surprisingly, speed is independent of particle surface properties such as fluidity, shape and curvature. Particles that nucleate actin polymerization uniformly over their surface are able to break symmetry spontaneously to form polarized actin comet tails. The physical parameters governing movement initiation are distinct from the physical parameters governing steady-state movement.

PHYS 472 [632358]: Linker-assisted biopolymer aggregation

Itamar Borukhov¹, Robijn Bruinsma², William M. Gelbart¹, and Andrea J. Liu¹. (1) Dept. of Chemistry and Biochemistry, UCLA, 607 C. Young Dr. East, Los Angeles, CA 90095-1569, Fax: 310-206-4038, itamar@chem.ucla.edu, (2) Department of Physics and astronomy, University of California, Los Angeles

The cellular cytoskeleton relies on structural elements formed from F-actin, a highly charged, stiff biopolymer, linked together by actin-binding proteins (linkers) that can bind two actin filaments together. The resulting structures can have very different morphologies, depending on the concentrations of biopolymers and linkers. In crawling cells such as blood platelets, F-actin primarily assembles into a network but can alternatively assemble into bundles; this is important to cell motility and adhesion. This suggests that the system could be near a phase transition between networks and bundles. I will present a theoretical study that elucidates the physical mechanisms that control these structures and their stability. The study is based on a generalized Onsager theory that includes linker-mediated attractions between charged filaments, and that yields phase diagrams as a function of actin concentration and linker concentration.

PHYS 473 [644728]: Programming colloidal interactions with DNA hybridization

John C. Crocker¹, Anthony J. Kim¹, and Paul Biancaniello². (1) Dept. of Chemical and Biomolecular Engineering, University of Pennsylvania, 220 S. 33rd St., Philadelphia, PA 19104, jcrocker@seas.upenn.edu, (2) Dept of Physics and Astronomy, University Of Pennsylvania

The hybridization of complementary DNA molecules has been used successfully to self-assemble well ordered crystals of DNA subunits, to reversibly aggregate nanoparticles and to assemble polyhedral colloidal clusters. Several groups are currently pursuing the formation of colloidal alloy crystals using short-ranged DNA-based interactions; for potential photonic applications. To date, however, no one has reported the assembly of large well-ordered colloidal crystals. We will discuss some of the challenges of such approaches, as compared with more 'traditional' self-assembly methods using charge-stabilized colloids or depletion interactions. We will also describe the novel temperature dependent phase behavior of these systems as well as direct measurements of the interactions employing optical tweezers.

PHYS 474 [644300]: Biophysical layers: elaboration of sensing surfaces using hydrophobin

Ewa Rogalska¹, Alain Walcarius², Rick Rink³, and Yohann Corvis¹. (1) Equipe Physico-chimie des Colloïdes, UMR 7565 CNRS/UHP, Université Henri Poincaré Nancy 1, Faculté des Sciences, 54506 Vandoeuvre-lès-Nancy cedex, France, Fax: +33 3 83 68 43 22, rogalska@lesoc.uhp-nancy.fr, (2) Laboratoire de Chimie Physique et Microbiologie pour l'Environnement UMR 7564 CNRS/UHP, Université Henri Poincaré Nancy 1, Faculté des Sciences, (3) Biomade Technology Foundation

Hydrophobins are small, naturally occurring proteins that have the remarkable property of adhering to almost any surface. Different hydrophobic and hydrophilic surfaces were modified with fungal hydrophobin films and, subsequently, functionalized using several enzymes. The enzymes adsorbed to the hydrophobin-modified surfaces maintain their activity for long periods of time, and allow detection of the enzyme substrates in aqueous solutions. Hydrophobin interfacial behavior and elaboration of biosensors based on this approach is discussed in this presentation.

PHYS 475 [644626]: Local friction and dynamics in aqueous poly(ethylene glycol) solutions

Benjamin J Lee, Eric G. Diken, and Edward W. Castner Jr., Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854-8087, Fax: 732-445-5312, benjlee@rutchem.rutgers.edu

Aqueous poly(ethylene glycol) (PEG) solutions are complex, having structures and dynamics that vary sharply with relative concentrations. Fluorescence probing using coumarin 102 (C102) provides molecular level details of the local friction and solute-solvent-polymer interactions. PEG molecular weights from 200 to 20,000 have been investigated using C102, for concentrations ranging from 0 to 50 wt % PEG. Fluorescence polarization anisotropies characterize the friction experienced by the C102 probe, and are somewhat non-exponential. Time-dependent fluorescence Stokes shift (TDFSS) experiments probe reorganization of the water and polymer in the solution surrounding the C102 molecule in response to a jump in its charge distribution. These dynamics show non-exponential character that fits well to a single stretched exponential (Kohlrausch) function; the degree of non-exponentiality increases with both increasing PEG concentration and molecular weight. The correlation between local structural features and the observed molecular dynamics will be discussed.

PHYS 476 [637699]: Transition from delocalized states of electrons at interfaces to localized states

Charles B. Harris, Department of Chemistry, University of California, Berkeley, CA 94720, Fax: 510-6426724, harris@socrates.berkeley.edu

Femtosecond time and angle resolved two-photon photoemission studies have been used to study electron solvation and localization at interfaces and to directly probe the development of a two dimensional band structure at the interface. This offers a powerful technique for obtaining the electronic structure of the interface. In addition, the energy relaxation measured in the photoemission spectra of molecules adsorbed on metal surfaces is due to a reorientation of the molecular dipole moments in the presence of the excess electron. This dynamical energy shift is a measure of a two dimensional solvation energy that occurs on a timescale of ~200 fs and corresponds to a transition from a delocalized to a localized state. From the time dependence of the square amplitude of the localized electron's wave function in momentum space, the time dependence of the electron's spatial extent in real space can be directly determined.

PHYS 477 [637314]: Atomically detailed description of metal-dielectric interfaces: The crossover from surface to bulk conducting properties

Brian Space, Chemistry, University of South Florida, 4202 E. Fowler Ave. SCA400, Dept. Chem.T, Tampa, FL 33620-5250, Fax: 8139743203, space@cas.usf.edu

An atomically detailed simulation method designed to be efficacious for modeling conduction properties of closed shell atoms or molecules resident at interfaces that was developed earlier is applied to a metal-dielectric interface of Ag-Xe. The effective mass of conduction electrons resident at Ag-Xe interfaces as a function of the number of layers of xenon present has been measured experimentally by the Harris group at Berkeley. Here a simple yet effective theoretical model of the interface is developed and the effective mass that results is in quantitative agreement with the empirical measurements. The effective mass of a conduction electron is calculated by solving the Schrodinger-Bloch equation using Lanczos grid methods to obtain the Bloch wave vector dependent energies. The metal is treated as a continuum within the effective mass approximation for the purpose of calculating the eigenenergies. This approach shows promise in modeling the conduction properties of more complex interfacial environments.

PHYS 478 [637967]: Electron-stimulated reactions at the interfaces of amorphous solid water films driven by long-range energy transfer from the bulk

Greg A. Kimmel, and Nikolay G. Petrik, Pacific Northwest National Laboratory, Mail Stop K8-88, P. O. Box 999, Richland, WA 99352, Fax: 509-376-6066, gregory.kimmel@pnl.gov

The electron-stimulated production of D₂ from amorphous solid D₂O deposited on Pt(111) is investigated as a function of film thickness. The D₂ yield has two components with distinct reaction kinetics. Using isotopically layered films of H₂O and D₂O demonstrates that the D₂ is produced in reactions that occur at both the Pt/amorphous solid water (ASW) interface and the ASW/vacuum interface, but not in the bulk. The *energy* for the reactions, however, is absorbed in the bulk of the films and electronic excitations migrate to the interfaces where they drive the reactions. A model based on the diffusion of electronic excitations to either interface accounts for the principle experimental observations.

PHYS 479 [644140]: Chemical dynamics of low energy electrons

Simon M. Pimblott, Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579, Fax: 574-631-8068, simon.m.pimblott.1@nd.edu, and Nicholas J. B. Green, Department of Chemistry, King's College London

Low energy electrons are ubiquitous in the radiolysis, and the photolysis, of liquids, solids and interfaces. The cross-sections for low energy electrons are strongly dependent on the phase of the medium, for instance, there are differences that are orders of magnitude in size between gaseous and ice water. Stochastic simulations are being used to understand the energy loss properties of low energy electrons in liquids and solids and thereby elucidate their thermalization and physico-chemical properties. Stochastic track structure simulations have been used to determine the energy distribution of daughter low energy electrons produced by ionizing radiation in water. Preliminary calculations of the attenuation of low energy electrons in condensed water are in progress. These calculations have reproduced experimental EELS data for ice and been used to investigate capture of, and ionization and excitation by, low energy electrons. About 53% of low energy electrons are captured with energy greater than 1 eV, about 28% are captured with energy greater than 5 eV, and about 10% with energy between 5eV and 8 eV through a dissociative electron attachment process. The energy distribution of ionizations and excitations is independent of the incident electron energy, except as it affects the maximum energy. The energy distribution of electrons ejected following ionization events is determined by incident electron energy. These findings are of considerable import in determining the effects of low energy electrons (< 25 eV) in the determining radiation damage, for instance the ultra-fast formation of molecular hydrogen.

PHYS 480 [642776]: Dynamics of photoinjected electrons in amorphous ice layers: Localization, solvation and the conduction band

Uwe Bovensiepen, Cornelius Gahl, and Martin Wolf, Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany, Fax: +49-30-83856059, uwe.bovensiepen@physik.fu-berlin.de

Two-photon photoelectron spectroscopy (2PPE) is used to investigate femtosecond dynamics of electron localization and solvation in amorphous ice layers adsorbed on Cu(111). Electrons, optically excited in the metal, transfer into the conduction band of the ice layer and generate a feature e_{CB} in the angle-resolved 2PPE spectra. Electrons localize within the first 50 fs to form a state e_s at 2.9 eV above the Fermi energy. The binding energy of e_s increases by 270 meV/ps which is attributed to electron solvation. By separating e_s and e_{CB} the bottom of the conduction band in the ice layer is determined to occur 1.05 eV below the vacuum level with an effective mass close to the free electron mass. The solvated state e_s is characterized by an apparently negative dispersion described by an electron momentum distribution with width $\Delta k_{||}$. From model calculations we conclude that $\Delta k_{||}$ changes simultaneously with electron solvation and is determined by the spatial extent of solvated electrons.

PHYS 481 [644664]: Probing electrical conductivity in liquids and solids by THz time-domain spectroscopy

Ernst Knoesel¹, Jie Shan¹, Feng Wang¹, Euan Hendry², Mischa Bonn², and **Tony F. Heinz**¹. (1) Department of Physics, Columbia University, 538 West 120th St., New York, NY 10027, Fax: 212-854-1909, tony.heinz@columbia.edu, (2) Leiden Institute of Chemistry, Leiden University

THz time-domain spectroscopy is a measurement scheme that uses ultrafast visible laser pulses to produce and characterize pulses of far-infrared radiation. The technique permits the determination of the complex conductivity of materials over a range of far-infrared (or THz) frequencies. Further, the method can be readily applied to probe non-equilibrium systems. We report here recent results for model liquids and insulating solids. Measurements in photoexcited n- and iso-hexane have provided a direct determination of the scattering time of quasi-free electrons, as well as of the dynamics of carrier recombination. These results will be compared with findings for model photoexcited crystalline insulators, such as sapphire. In these ordered systems, the scattering rate depends strongly on the sample temperature. This reflects scattering by phonons, rather than by the potential fluctuations present in a liquid. The influence of trap states in the liquid and solid samples will also be compared and contrasted.

PHYS 482 [643955]: Quantum Monte Carlo study of photoactive molecules

Claudia Filippi¹, Friedemann Schautz¹, and Francesco Buda². (1) Instituut-Lorentz for Theoretical Physics, Universiteit Leiden, Niels Bohrweg 2, NL-2300 RA Leiden, Netherlands, Fax: +31-71-5275511, filippi@lorentz.leidenuniv.nl, (2) Leiden Institute of Chemistry, Universiteit Leiden

In order to understand photochemical process in photoactive molecules, it is important to correctly describe the energetics of the primary photoinduced conformational changes in the excited state. While many studies have demonstrated the use and reliability of the diffusion quantum Monte Carlo (QMC) method for the description of ground state properties, relatively little experience exists concerning its application to low-lying excited states. Using QMC, we investigated photochemical reaction paths in prototypical molecules such as ethylene, formalimine and the protonated Schiff base $C_5H_6NH_2$. Our results indicate that the fixed-node approximation can accurately describe the energetics of the excited state along the reaction path if one makes an adequate choice of the trial wave function. We also compare our QMC results to those obtained with traditional quantum chemical and density functional based methods.

PHYS 483 [637162]: Diffusion Monte Carlo approaches for studying the structure of weakly bound complexes

Anne B. McCoy, Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, OH 43210, Fax: 614-292-2516, mccoy@chemistry.ohio-state.edu

In this talk, some of our recent work in which DMC approaches are used to investigate the structure and spectroscopy of weakly bound complexes will be presented. While DMC provides a powerful method for gaining information about states of the systems of interest for which there are no nodes or for which the positions of the nodes can be determined by symmetry, extracting information about vibrationally excited states or vibrational states that are delocalized among two or more diabatic potential surfaces is less straight forward. In particular, we will

show that DMC can provide an accurate description of the wave functions and energies of the ground and low-lying vibrationally excited states of weakly bound systems through comparisons of DMC and variational results for complexes of neon atoms with OH. In addition recent extensions of these approaches to studies of complexes of opened shell molecules will be presented and the role of the non-zero electron angular momentum on the structure of the cluster will be discussed.

PHYS 484 [644737]: Molecular thermochemistry via path integral Monte Carlo

Laurence E. Fried, Energetic Materials Center, Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-282, Livermore, CA 94551, fried1@llnl.gov, and Kurt R. Glaesemann, Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory

Most present-day approaches to molecular thermochemistry rely on a harmonic approximation to molecular vibrations. We present a method (1) for going beyond the harmonic analysis, which uses path integral Monte Carlo to calculate the vibrational and rotational contributions to molecular thermochemistry and properties. Anharmonic effects are found to be as large as 2.5 kcal/mol for the molecules studied. This presents a limit in the accuracy achievable in many present-day thermochemical calculations. We find that our method can calculate molecular heat capacities to within a few percent, even at temperatures of several thousand K.

Our method requires the evaluation of thousands of single-point energies with techniques such as MP2 or coupled cluster theory. The high computational cost is greatly reduced with a novel potential energy caching scheme.

1.) K. R. Glaesemann and L. E. Fried J. Chem. Phys. 118 (4): 1596-1603 (2003).

PHYS 485 [643733]: Simulations of impurity rotational dynamics in quantum cryogenic solids

Robert J. Hinde, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, Fax: 865-974-3454, rhinde@utk.edu

High-resolution infrared absorption spectra of solid parahydrogen containing impurities such as N₂, CO, and HCl reveal that these impurities undergo nearly free rotation in single substitutional sites in the H₂ matrix. The spectra provide information about molecular dynamics in highly quantum cryogenic condensed phases, information that complements that obtained from studies of molecular chromophores in helium nanodroplets by virtue of the well-defined crystal structure of the surrounding H₂ matrix. An impurity's rotational motion is hindered by the H₂ solid's crystal field, which is mediated by the highly-correlated large-amplitude zero point motions executed by H₂ molecules surrounding the impurity. Theoretical analysis of the impurity spectra could thus provide insight into the coupling between impurity rotations and the correlated translational motions of nearby H₂ molecules. We present quantum Monte Carlo simulations of diatomic chromophores in solid H₂ matrices, extracting from these simulations information about impurity rotational dynamics in highly quantum cryogenic solids.

PHYS 486 [671199]: Quantum Monte Carlo calculations of electronic structure of large molecules: C₂₀ and C₆₀

James B. Anderson, Department of Chemistry, Pennsylvania State University, University Park, PA 16802, Fax: 814-865-3314, jba@psu.edu

Quantum Monte Carlo (QMC) methods offer high accuracies and favorable N³ scaling for large molecules. But, QMC methods have not been useful in optimization of structures or determination of gradients. Some recent improvements overcome some of the difficulties. These are examined in all-electron calculations of structures and gradients for C₂₀ and C₆₀.

PHYS 487 [636866]: Estimating Bohm's quantum potential via expectation modelling

Jeremy Maddox, Department of Chemistry, University of Houston, jmaddox@uh.edu, and **Eric Bittner**, Department of Chemistry, Univ. of Houston, Fax: 713-743-2709, bittner@uh.edu

We will discuss our recent work involving the development of statistical methods for estimating the multidimensional density associated with a discrete bundle of de Broglie-Bohm trajectories. We show that by

constructing the quantum density as a discrete sum of non-equivalent gaussians, we can incorporate the ideas of Bayesian statistical analysis and an expectation maximization procedure to compute an approximate quantum force suitable for driving an ensemble of quantum trajectories. While our focus is on time-dependent dynamics, the method has strong parallels with QMC as we shall discuss in this talk.