

PHYS 301 [755345]: Formation of carbonaceous material in combustion conditions

Angela Violi, Chemical & Fuels Engineering, University of Utah, 1495 E 100 S - Room 109, Salt Lake City, UT 84112, Fax: (801) 585-1456, violi@eng.utah.edu, Adel F. Sarofim, Department of Chemical and Fuels Engineering, University of Utah, and Gregory A. Voth, Department of Chemistry and Henry Eyring Center for Theoretical Chemistry, University of Utah

Abstract

The growth of carbonaceous particles is analyzed using atomistic models, such as Molecular Dynamic (MD) and Kinetic Monte Carlo (KMC) methodologies. Aromatic growth is modeled through a sequence of different reaction pathways that include radical-molecule reactions involving cyclopenta-fused compounds, and acetylene addition. Dehydrogenation and internal rearrangement reactions of the carbonaceous material lead to the formation of aromatic graphitic structures. Reactions between aromatics occurring on the time scale of milliseconds are coupled to rearrangement reactions occurring on the time scale of picoseconds through the use of KMC/MD code. The growth process up to the formation of nano-sized compounds is analyzed retaining full atomistic detail of the structures formed. The methodologies will be used to study the early stages of formation of nanoparticles to rationalize experimental results available in the literature.

PHYS 302 [761806]: Structures of mismatch replication errors and observed in a DNA polymerase

Lorena S Beese, Department of Biochemistry, Duke University Medical Center, NanaLine Duke Building, Room 212, Research Drive, Durham, NC 27705, Fax: 919-684-8885, lsb@biochem.duke.edu

Abstract

One mechanism by which high-fidelity DNA polymerases maintain replication accuracy involves stalling of the polymerase in response to covalent incorporation of mismatched base pairs, thereby favoring subsequent mismatch excision. Some polymerases retain a “short-term memory” of replication errors, responding to mismatches up to four base pairs in from the primer terminus. Here I will discuss a structural characterization of DNA mismatches captured at the growing primer terminus in the active site of a polymerase. Our observations suggest four mechanisms that lead to mismatch-induced stalling of the polymerase. Furthermore, we have observed the effects of extending a mismatch up to six base pairs from the primer terminus, and find that long-range distortions in the DNA transmit the presence of the mismatch back to the enzyme active site, suggesting the structural basis for the short-term memory of replication errors.

PHYS 303 [754062]: Molecular origin of DNA polymerase fidelity

Samuel H. Wilson, Laboratory of Structural Biology, NIEHS-NIH, P.O. Box 12233, Research Triangle Park, NC 27709-2233, Fax: 919-541-3592, wilson5@niehs.nih.gov

Abstract

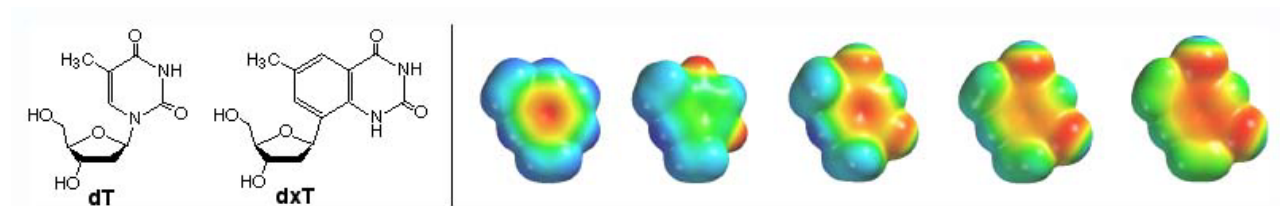
Comparison of pol β structures determined in different liganded states have revealed a major conformational difference between the binary complex of pol β /DNA and the ternary complex of correct incoming dNTP and DNA. The enzyme in the binary complex was in an “open” conformation, whereas in the ternary complex it was in a “closed” conformation. These observations lead our team to suggest that the enzyme closes down around the incoming dNTP when the new base pair conforms to Watson-Crick geometry and that the accompanying side chain motions in the vicinity of the 3'-oxygen and α -phosphorus subsequently induce efficient chemistry. This process was consistent with an “induced fit” mechanism. If a wrong dNTP binds at the active site, the substrate-induced conformational change either will not occur or will be different than it is when a right substrate dNTP binds. In these two cases, the atomic level mechanism of development of a bipyramidal pentacoordinated phosphorus transition state will be different; the side chains and location of the metal ions and solvent molecules that stabilize the transition state and leaving group will also be different. A series of new pol β crystal structures with mismatched and correct incoming dNTP and with altered template-primer base pairing will be described. This new information allows us to propose a model for contacts between side chains, metal ions, solvent molecules, and substrates in the pol β active site during transition state development.

PHYS 304 [744706]: Active site tightness: Steric effects in DNA replication and repair

Eric T. Kool, Department of Chemistry, Stanford University, Stanford, CA 94305, Fax: 650-725-0259, kool@stanford.edu

Abstract

New insights have been gained from studies in which we replace the natural DNA bases with nonpolar, non-hydrogen-bonding shape mimics. The surprising replication fidelity observed for such compounds has prompted us to present a model for DNA polymerization in which steric exclusion of incorrect nucleobase shapes plays a chief role in fidelity. A new strategy for testing shape and size effects in nucleic acid recognition is presented here. In this approach, DNA base analogues are “stretched” in size. In one such strategy, purines are replaced by benzo-purines and pyrimidines by benzo-pyrimidines (see dxT at left), giving bases that are longer by 2.4 Angstroms. These extended nucleosides retain natural hydrogen bonding ability, but their large size makes them useful as tools in biophysical studies. In a second approach, nonpolar DNA base shape mimics are gradually stretched in size (see models at right), by replacing bonds on the edges with progressively longer bonds. Some preliminary enzymatic studies of both sets of analogues will be described.



PHYS 305 [755385]: *In silico* investigation of the binding and chemical transformation of nucleoside triphosphates by DNA polymerases and adenylyl cyclases

Jan Florian, Department of Chemistry, Loyola University Chicago, 6525 N. Sheridan Rd., Chicago, IL 60626, jfloria@luc.edu

Abstract

Both DNA polymerases and adenylyl cyclases facilitate the nucleophilic attack of the 3'OH group of a sugar on the α -phosphorus of their nucleoside triphosphate substrates. These enzyme families have also in common the utilization of the Mg^{2+} metals in the active site and the presence of His or Asp aminoacid residues near the nucleophile, which are capable of abstracting the proton from this nucleophile. However, the aminoacid sequences and atomic details of the active site geometries are different in various proteins from these families. Correlations between the specific active site architecture and the enzyme function and substrate selectivity will be discussed in the light of the quantum mechanical/molecular mechanical calculations of transition state structures and the corresponding activation free energy barriers.

PHYS 306 [753453]: Unexpected properties of RecA protein required for *E. coli* DNA polymerase V-catalyzed SOS mutagenesis

Myron F Goodman¹, Katharina Schlacher¹, Phuong Pham¹, Michael M Cox², and Roger Woodgate³. (1) Biological Sciences and Chemistry, University of Southern California, 835 W. 37 St., University Park, Los Angeles, CA 90089-1340, Fax: 213-740-8631, mgoodman@usc.edu, (2) Biochemistry, University of Wisconsin, (3) Section of DNA Replication, Repair and Mutagenesis, NIH

Abstract

On a par with death and taxes, RecA nucleoprotein filaments are a fact of life and play an essential role during homologous recombination and for induction of the SOS response in response to DNA damage in *E. coli*. A third role for RecA was defined by mutants proficient in recombination and SOS induction, but which failed to cause pol V-dependent UV-induced mutations. It had been tacitly assumed that a RecA nucleoprotein filament was required for pol V-catalyzed translesion synthesis. Our experimental data, which include a comparison of wild type RecA with a mutagenesis-deficient RecA mutant, show that the elusive third role for RecA stems from its ability to form a complex with pol V that binds at a primer end upstream of a lesion, but does not involve assembly of a RecA filament on the DNA. All other RecA interactions with DNA occurring downstream of the lesion abrogate lesion bypass.

PHYS 307 [749298]: Role of vibrational entropy in enzyme catalysis

Giuseppe D. Ruggiero and **Ian H. Williams**, Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom, Fax: +44-1225-386231, i.h.williams@bath.ac.uk

Abstract

We assess the possible role of vibrational activation entropy in enzymatic catalysis by means of computational modelling using hybrid quantum-mechanical/molecular mechanical methods and the GRACE, CHARMM, DYNAMO and FOCUS codes. The molecules employed by physical

organic chemists to account for the rate enhancements characteristic of enzyme-catalysed reactions tend to be small, light and rigid. A typical model designed to illustrate intramolecular reactivity juxtaposes two reacting groups attached by strong covalent bonds to a small rigid ring. Such molecules possess little vibrational entropy in the first place, and therefore neither gain nor lose much on going to their transition states. In dramatic contrast, enzymes are large, heavy and floppy molecules possessing many very low-frequency entropy-rich modes of vibration; changes affecting these between a Michaelis complex and a transition state could contribute significantly to ΔS^\ddagger . We present results obtained by consideration of reactant complexes and transition structures calculated for several different enzymes.

PHYS 308 [760890]: Protein dynamics and its effect on enzyme catalysis

Jiali Gao, Department of Chemistry, University of Minnesota, Minneapolis, MN 55410

Abstract

Protein dynamics encompasses a wide range of time and length scales that are essential to biological processes including ligand binding, energy transfer, and catalysis. However, the relationship of protein dynamics and enzyme catalysis is still poorly understood. In this talk, I will describe a reactive flux molecular dynamics simulation study of the dynamic effects on the nucleophilic substitution reaction of dichloroethane by a carboxylate group in haloalkane dehalogenase and in water. We employ a combined QM/MM potential to model the chemical process. We found that protein dynamics accelerates the reaction rate by a factor of 2 over the uncatalyzed reaction. Compared to the thermodynamic effect in barrier reduction, protein dynamic contribution is relatively small. However, analyses of the friction kernel reveal that the origins of the reaction dynamics in water and in the enzyme are different. In aqueous solution, there is significant electrostatic solvation effect, which is reflected by the slow reorganization relaxation of the solvent. On the other hand, there is no strong electrostatic coupling in the enzyme and the major effect on reaction coordinate motion is intramolecular energy relaxation. I will also describe a study of the vibrational frequency shift and energy relaxation of an azide ligand in the active site of carbonic anhydrase as compared to an azide ion in aqueous solution.

PHYS 309 [754873]: QM/MM Car-Parrinello molecular dynamics study of selectivity in a potassium channel

Denis Bucher, Department of Computational Chemistry and Biochemistry, EPFL, SB-ICMB-LCBC BCH4121, Lausanne 1015, Switzerland, Fax: 0041-21-693-0320, denis.bucher@epfl.ch, Ursula Rothlisberger, Institute of Molecular and Biological Chemistry, Federal Institute of Technology EPFL Institute of Molecular and Biological Chemistry, Leonardo Guidoni, Institute of chemical sciences and engineering, Federal Institute of Technology EPFL, and Paolo Carloni, Condensed Matter Physics, S.I.S.S.A/I.S.A.S

Abstract

All biological ion channels are selectively permeable to specific ions. This mechanism needs to be understood in terms of the interaction of the permeating ions with the surrounding water and protein molecules. During the past several years, there have been enormous strides in our understanding of the structure-function relationships in biological ion channels. Classical MD simulations have been used to investigate the selectivity mechanism, but the importance of

polarization effects can hamper an adequate description of the potassium-protein interaction. In this context, quantum mechanics is the ultimate goal of any atomic modelling of ionic channels and will help reaching a new level of accuracy and a finer understanding. We have recently developed a QM/MM scheme in which the chemically reactive part of the system can be treated quantum mechanically using Car-Parinello molecular dynamics. This method paired with enhanced sampling techniques was used to investigate the mechanism of selectivity displayed by potassium channels.

PHYS 310 [755316]: Reaction path potential for simulation of chemical reactions in enzymes derived from ab initio QM/MM calculations

Weitao Yang, Zhenyu Lu, and Mingliang Wang, Department of Chemistry, Duke University, Durham, NC 27708, Fax: 919-660-1605, weitao.yang@duke.edu

Abstract

The reaction path potential (RPP) follows the ideas from the reaction path Hamiltonian of Miller, Handy and Adams for gas phase reactions but is designed specifically for large systems described with QM/MM methods. RPP is an analytical energy expression of the combined QM/MM potential energy along the minimum energy path. An expansion around the minimum energy path is made in both the nuclear and the electronic degrees of freedom for the QM subsystem, while the interaction between the QM and MM subsystems is described as the interaction of the MM charges with polarizable QM charges. The input data for constructing the reaction path potential are energies, frequencies and electron density response properties of the QM subsystem. RPP provides a potential energy surface for rigorous statistical mechanics and mixed quantum/classical reaction dynamics calculations of complex systems, as will be shown for several enzymes.

PHYS 311 [754651]: Quantum effects in protein-RNA interactions: A novel locking mechanism

Victor Guallar, Biochemistry and Molecular Biophysics, Washington University at St Louis. School of Medicine, 700 S. Euclid Ave., Room 112, St Louis, MO 63108, Fax: 314-659-2862, guallarv@biochem.wustl.edu

Abstract

Combining QM/MM and protein structure prediction methods we have explored the importance of quantum electronic effects in the interaction of various polar side chains with RNA/DNA base pairs. The results reveal the existence of stacking interactions, even for anionic side chains like ASP and GLU, stabilizing the RNA-protein complex. Wave function analysis indicates a delocalization of the electronic effect into other aromatic groups, enhancing neighbor stacking interactions. The overall electronic density is highly sensitive to the protein environment, responding to conformational changes which could determine the reversibility of the binding process. We propose a novel mechanism where small polar groups lock the RNA/DNA binding by stacking interactions, rather than ionic or hydrogen bond bonds. Several cases, including ATP and drugs binding, demonstrate that this mechanism appears to be ubiquitous in nature.

PHYS 312 [755096]: Reversible proton transfer dynamics in bacteriorhodopsin

Yong S. Lee, Center for Molecular Modeling, Center for Information Technology, National Institutes of Health, Bethesda, MD 20892, leeys@mail.nih.gov, and **Morris Krauss**, Center Advanced Research Biotechnology

Abstract

Proton transfer in bacteriorhodopsin from the cytoplasm to the extracellular side is initiated from protonated asp96 in the cytoplasmic region towards the deprotonated Schiff base. This occurs in the transition from the photocycle late M state to the N state. Ab initio dynamics using the CHARMM/GAMESS methodology is used to simulate the transfer of the proton through a hydrophobic channel. A quantum mechanics/molecular mechanics (QM/MM) model is constructed from the bacteriorhodopsin E204Q mutant crystal structure. Structural transformation occurs in the M state that results in a channel between the asp96 and Schiff base allowing a water chain between these groups. A chain of four waters from asp96 to the Schiff base N with one branching water supports proton transfer as a concerted event in about 3.5 ps with neutral asp85. Dynamic transfer of the proton from asp96 to the nearest water initiates the organization of a strongly hydrogen bonded ionic water chain conducive to the transfer of the proton to the Schiff base N. Proton transfer is also observed from the Schiff base back to asp96 demonstrating that there is no effective barrier to proton transfer larger than kT within the close-coupled hydrogen bond network.

PHYS 313 [787660]: AEI: In the language of mathematics: A physical chemist's research retrospective

Christine V. Hampton, -, PO Box 170, Okemos, MI 48805, champton@mailaps.org

Abstract

Within a truly egalitarian, scientific community, one can imagine the existence of a single mode of communication that connects many, diverse fields. Such a comprehensive language does exist within the tools of mathematics. I will present a retrospective of my past research interests and experiences from the perspective of my personal philosophy and the mathematics that describes the science. The methods presented, represent research into environmental, analytical, and nuclear science. Some examples that may be included are: investigations into nuclear cross sections using classical kinematics of heavy-ion, fusion-evaporation reactions; α -ray signal enhancement techniques using the Fast Fourier Transform; a chromatographic technique for compound elution profiling and various mass spectrometric methods.

PHYS 314 [752904]: Molecular dynamic simulations of tetra n-butyl ammonium chloride and water at varying concentrations and temperatures

Raeanne L Napoleon, Department of the Sciences in Philadelphia, Department of Chemistry, 600 South 43rd Street, Philadelphia, PA 19104, Fax: 215-596-8543, rn0460@uisp.edu, **Rodney J. Wigent**, Chemistry and Biochemistry Department, University of the Sciences in Philadelphia, and **Preston B. Moore**, Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia

Abstract

Computer simulations were performed on the clathrate forming salt tetra-n-butyl ammonium chloride (TBAC) and water using Molecular Dynamics (MD). These simulations comprised of the organic electrolyte were carried out at 298 kelvin and 333 kelvin over varying TBAC molar concentrations (0.21 M - 2.85 M) in the solvent, water. TBAC exhibits anomalous activity and osmotic coefficients, which has a dependence on concentration. This is the first systematic study, that we are aware of, which investigates clathrate formation of TBAC. After initial equilibration, the systems were simulated for 20 nanoseconds from which structural and dynamical properties were analyzed. The structural analysis from this investigation demonstrates how clathrates are formed (by minimizing the free energy). These results have implications to biological system, the petroleum industry as well as a use as an energy storage system. The investigation of TBAC in water was to explore the electrolyte solutions and determine the different molecular contributions. An understanding of these solutions on an atomic level should be capable of being generalized to a broad class of electrolyte solutions.

PHYS 315 [787654]: AEI: Nonadditive ab initio interaction potentials in simulations of condensed phases

Robert Bukowski and Krzysztof Szalewicz, Department of Physics and Astronomy, University of Delaware, 307 Sharp Lab, Newark, DE 19716, Fax: 302-831-1637, bukowski@udel.edu

Abstract

Predictive power of first-principles simulations of clusters, condensed phases, or biomolecular systems crucially depends on the quality of potentials describing the intermolecular interactions. Such description has to account for a variety of physical effects, including the long-range dispersion (missing in the popular Car-Parrinello approach) and nonadditive forces. These accuracy requirements can be met if the total interaction energy is expanded in terms of the two-body, three-body, and possibly higher nonadditive terms, each modeled using a relevant ab initio method. Since higher nonadditive effects are very difficult to model accurately, success of such many-body expansion relies on its convergence properties, investigated in this work. The poster will present efficient methods of ab initio modeling of two-body and three-body interactions along with applications of the resulting potentials in simulations of bulk phases and phase equilibria of water, argon, and carbon dioxide. The results strongly suggest that saturation of nonadditive effects occurs already at the three-body level. This opens up possibilities of accurate first-principles simulations of complex phenomena, requiring large system sizes, and in all thermodynamic regimes.

PHYS 316 [752545]: Estimation of dinitrogen oxide solubility in polar solvents

Stefan Perisanu, Laboratory of General Chemistry, Polytechnic University of Bucharest, 1 Polizu str, Bucharest 78126, Romania, Fax: 40-21-3111796, s_perisanu@chim.upb.ro

Abstract

An estimation method proposed before [1], for the solubility of non-polar gases, whose molecule contains polar bonds (like carbon dioxide), in polar solvents, is extended to dinitrogen oxide - a slightly polar molecule. The method is based only on pure component properties - solubility parameters, molar volume, fugacity, dielectric constant, polarizability and electronic quadrupole moment. The parameter values were taken from literature or calculated by means of solubility

data of the same gas in non-polar solvents. The solubility of N₂O in 12 polar solvents, for which experimental data are available, was calculated, with a mean relative error of 23 %, comparable or better than that of other solubility estimations, even for non-polar systems.

[1] St. Perisanu, «Estimation of CO₂ Solubilities in Polar Solvents», *J. Solution Chem.*, 19, 183-192(2001).

PHYS 317 [752068]: Application of the nuclear-electronic orbital (NEO) method to hydrogen transfer reactions: Importance of electron-proton correlation

Michael Pak, Chet Swalina, and Sharon Hammes-Schiffer, Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, mvp11@psu.edu

Abstract

We have developed the nuclear-electronic orbital (NEO) method for including nuclear quantum effects in electronic structure calculations. In the NEO approach, specified nuclei are treated quantum mechanically on the same level as the electrons, and the nuclear-electronic wavefunctions are calculated using molecular orbital methods. For hydrogen transfer reactions, the transferring hydrogen nuclei, as well as all electrons, are treated quantum mechanically to include nuclear quantum effects such as zero point energy and hydrogen tunneling. Typically the nuclear wavefunction corresponding to the transferring hydrogen is delocalized between the donor and acceptor at the transition state. We investigate this phenomenon in model hydrogen transfer systems using NEO-HF (Hartree-Fock), NEO-CI (configuration interaction), state-averaged NEO-MCSCF (multiconfigurational self-consistent-field), and NEO-MP2 (second-order perturbation theory). Our results indicate that significant amounts of dynamical electron-proton correlation are necessary to describe delocalized nuclear wavefunctions. We also demonstrate analytically that the importance of electron-proton correlation is due to the attractive electron-proton interaction.

PHYS 318 [764634]: Density functional study of organic open-shell triradical 5-dehydro-1,3-quinodimethane

Tunna Baruah¹, Rajendra R. Zope², Mark R. Pederson¹, and Brett I Dunlap². (1) Center for Computational Materials Science, Code 6390, Naval Research Laboratory, Washington, DC 20375-0001, pederson@dave.nrl.navy.mil, (2) Theoretical Chemistry Section, Code 6189, Naval Research Laboratory

Abstract

We present a density functional theory (DFT) based study of the electronic, magnetic and vibrational properties of 5-dehydro-1,3-quinodimethane which is a triradical. Our calculations are carried out using the NRLMOL code that uses an optimized gaussian basis set and a numerical mesh for accurate integration. We present the electron affinities, vibrational frequencies, infrared and Raman spectra of the triradical. The triradical contains three unpaired electrons. We calculate the exchange parameters with the 'broken symmetry' method and obtained energies of different spin manifolds from a mixed DFT/wavefunction approach. This method couples the density functional approach to a many-electron picture by exact diagonalization of a DFT-parametrized exchange hamiltonian. It yields a doublet ground state and a quartet first excited state in agreement with the coupled cluster calculation by Krylov et al.

[L.V. Slipchenko, T. E. Munsch, P. G. Wenthold, and A. I. Krylov, *Angew. Chem. Int. Ed.* 43, pp. 742 (2004)].

PHYS 319 [766878]: Ab initio studies of cyclo(L-proline-L-proline) and theoretical calculation of the UV-CD Spectrum

Kristine L. Carlson, Mark R. Hoffmann, and Kathryn A. Thomasson, Department of Chemistry, University of North Dakota, Grand Forks, ND, ND 58202-9024, kristine.carlson@und.nodak.edu

Abstract

MP2 and DFT geometry optimizations were performed on the cyclic dipeptide cyclo(L-proline-L-proline) starting from crystal structure data. Three stable conformations were identified as energy minima by all methods but assignment of relative energy varied between the methods. The $f_{\pi} \rightarrow f_{\pi}^*$ transition feature of the UV circular dichroic (CD) spectrum was predicted for each minimized structure using the dipole interaction model. The UV-CD predictions were compared with published experimental CD spectra (Bowman, R. L.; Kellerman, M.; Johnson, Jr., W. C. *Biopolymers*. 1983, 22, 1045-1070).

PHYS 320 [749546]: Quantum Monte Carlo study of nucleic acid base properties

Glake A Hill Jr., Department of Chemistry, Computational Center for Molecular Structure and Interactions, Jackson State University, P.O. Box 17910, J. R. Lynch St., Jackson, MS 39217, Fax: 601-979-7823, glakeh@ccmsi.us, Alexander C. Kollias, Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, Lester Group, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Jerzy Leszczynski, Chemistry, Jackson State University, and William A. Lester Jr., Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California at Berkeley, and Chemical Sciences Division, Lawrence Berkeley National Laboratory

Abstract

Damage to human deoxyribose nucleic acid (DNA) by exogenous factors has been the subject of a number of studies, both theoretical and experimental. High-energy radiation (X and gamma rays) interacts with cellular components and can cause significant changes in the structure of deoxyribonucleic acid (DNA). Because DNA is the major component within the cell, damage to this molecule causes major protein deformation, functional dysfunction, and ultimately cellular death. This process becomes manifest in ailments of the central nervous system, the kidneys, and other vital organs. Cancer is also a major consequence of prolonged radiation exposure. Fast electrons produce ionization and excitation throughout nucleic acid bases. These excited states, which result from promotion of an electron to an excited molecular orbital, can cause significant chemical change. Some states dissociate into radicals leading to strand breaks. Ab initio methods are uniquely suited to study these changes. However, the results of these methods are often qualitative when compared to experimental results. Quantum Monte Carlo (QMC) methods have the capability for higher accuracy than other ab initio methods for large systems. In this talk, we will present the results of QMC calculations of ionization potentials and electron affinities of four canonical nucleic acid bases. The computed quantities will be compared to other theoretical and experimental results.

PHYS 321 [757030]: A new quantum expression for the thermal rate constant

Dmitry M. Medvedev, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Bldg. 200, Argonne, IL 60439, Fax: 630-252-9292, dmedvedev@anl.gov, and Stephen K. Gray, Chemistry Division, Argonne National Laboratory, Argonne, IL

Abstract

We give a new quantum expression for the thermal rate constant based on the ideas of Miller, Schwartz, and Tromp. It simplifies the imaginary time propagation, making it easier to compute reaction rates for a range of temperatures. The method is illustrated with an application to the 3-dimensional D + H₂ exchange reaction.

PHYS 322 [765126]: Direct (Monte Carlo) simulation of chemical reaction systems: Studies of gas phase detonations

James B. Anderson, Lyle N. Long, and Patrick D. O'Connor, Department of Chemistry, Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, Fax: 814-865-3314, jba@psu.edu

Abstract

We have extended Bird's direct simulation Monte Carlo (DSMC) method to treat several complex gas-phase reaction systems. Most interesting of these are gas-phase detonations for which the method produces the full details of coupled gas-dynamic and reaction effects as well as temperature, velocity, density, pressure, and species profiles. For a slow reaction we find the reaction and shock regions are well separated and the detonation wave proceeds at the forward speed of sound in the burned gas as predicted by the Chapman-Jouguet and Zeldovich-von Neumann-Doering theories. For a very fast reaction the reaction and shock waves overlap, the assumptions required for the C-J and ZND theories are no longer valid, the von Neumann spike is reduced, and the detonation velocity exceeds that predicted by the C-J and ZND theories to produce an ultrafast detonation.

PHYS 323 [764682]: Performance of post Hartree-Fock, density functional theory and quantum Monte Carlo methods for the electronic structure of 3d-block transition metals

John A.W. Harkless and Ainsley Gibson, Department of Chemistry, Howard University, Washington, DC 20059, jharkless@howard.edu

Abstract

There are few quantum chemical methods that have been successfully applied to the electronic structure of metallic systems. Fewer still have been applied to transition metals, and none have proven completely universal in their predictive power, as measured by consistent, accurate treatment of an arbitrarily chosen metallic system. As a first step in fully investigating the relative performance of high-accuracy ab initio techniques, the study presented here considers the ionization potentials (IP) and electron affinities (EA) of 3d block transition metals. The IP and EA values are estimated using MP2, CCSD, CCSD(T), CISD, MRCI, and multiple ab initio and parameterized density functionals. The most novel aspect of the study is the additional use of

both all-electron and effective core potential variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (DMC) to estimate IP and EA values. The estimates from all these calculations will be compared to available experimental data. Additional commentary will be offered on the recovery of correlation energy as well as the relative performance of ECP-DMC relative to DMC, in the context of the possible expansion of these calculations to more complex metallic systems.

PHYS 324 [762803]: Accurately solving the electronic Schrödinger equation of small atoms and molecules using the explicitly correlated (r12-) multi-reference averaged coupled-pair functional (MR-ACPF)

Robert J. Gdanitz, Department of Physics, North Carolina A&T State University, Martena Hall, Greensboro, NC 27411, gdanitz@ncat.edu, and **Wim Cardoen**, Department of Chemistry, University of Utah

Abstract

The recently proposed r12-MR-CI method, which includes terms that are linear in the interelectronic distances (r12) in the ansatz for the wavefunction—in combination with MR-ACPF—allows for systematically solving the electronic Schrödinger equation to accuracies, which cannot be obtained with present day (traditional) CI methods and computers, without the aid of extrapolations. To demonstrate the high efficiency of this method, it has been applied to the computation of: i) the potential energy curve of N₂; ii) the ground-state energies of first-row atomic ions; iii) their electron affinities; and iv) the dispersion interaction within dimers of He, Be, and Ne [for a recent review, see: *Recent Res. Devel. Quantum Chem.*, 3, (2002) 245–276]. At the time being, we work on the computation of the potential energy surface of the important elementary reaction $F + H_2 \rightarrow HF + H$. In this Paper, we give an outline of the method, demonstrate the outstanding accuracy that can be obtained, and present some new results.

PHYS 325 [746783]: *Ab initio* investigation of XeI and XeI⁻

Gerald J. Hoffman, Chemistry Department, Edinboro University of Pennsylvania, Cooper Hall, 230 Scotland Road, Edinboro, PA 16444, Fax: 814-732-2593, ghoffman@edinboro.edu

Abstract

Calculations on XeI and XeI⁻ were performed at the level of coupled clusters including single, double and noniterative triple excited configurations [CCSD(T)], and of the multireference averaged coupled-pair functional (MR-ACPF) technique. The basis sets used for these calculations were the Stuttgart basis sets with relativistic effective core potentials (ECPs) including potentials for spin-orbit coupling. The MR-ACPF calculations on XeI yield potentials for six states: the three "covalent" spin-orbit split that correlated to separated neutral atoms, and the three "ionic" states that correlate to the separated ions Xe⁺ and I⁻. Including results for XeI⁻ allows comparison of calculated potentials for these species with experimental results of photoelectron spectroscopy of XeI⁻ as well as molecular beam and fluorescence data for XeI.

PHYS 326 [764307]: A fast semiempirical DivCon/Charmm QM/MM approach for biomolecules

Kenneth M. Merz Jr. and **Xiaodong Zhang**, Department of Chemistry, The Pennsylvania State

University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-8403,
merz@psu.edu, zhangxd@merz.chem.psu.edu

Abstract

The QM/MM method has proved to be a very effective method to calculate the electronic structure and reaction pathways in biochemical system (e.g. enzyme-catalyzed reactions). The known QM/MM method includes ab initio QM/MM method, semi-empirical ab initio methods like SCCDFTB and traditional semi-empirical methods like AM1 and PM3. However, they are very computationally expensive if one wants to study a large QM regions. Because of this, we developed a new QM/MM approach based on the density matrix divide-and-conquer(D&C) method. Our results indicate that (1) the calculation time for every SCF cycle is nearly linear with respect to the number of atoms in the QM region. (2) When the number of QM atom is beyond 150, the D&C method is much faster than standard QM/MM methods.

PHYS 328 [764991]: An ab initio study of low-energy electron scattering by NO

Zhiyong Zhang, Chemical Sciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Rd., MS50F-1624, Berkeley, CA 94720, zyzhang@lbl.gov

Abstract

We present an ab initio study of low-energy (0-2.5 eV) electron impact of NO molecule. The low-energy scattering cross sections are dominated by shape resonance contributions associated with the 3^{Σ^-} , 1^{Δ} and 1^{Σ^+} of NO^- . Resonance parameters are obtained from fixed-nuclei complex-Kohn calculations. We also shown that by using analytical continuation from the nuclear configurations where the anion is electronically bound to the region where the anion is autoionizing, we can obtain accurate scattering parameters from sophisticated bound state electronic structure calculations like the coupled cluster and other highly correlated methods. This allows us to study many electron-molecule resonance scattering problems where part of the anion potential curve is electronically bound using accurate bound state electronic structure methods. The local complex potential model was used to calculate vibrational excitation cross sections. Our results are found to be in excellent agreement with recently measured values.

PHYS 327 [748577]: AEI: New approach to *ab initio* molecular dynamics using atom-centered basis functions

John M. Herbert and Martin Head-Gordon, Department of Chemistry, University of California, Berkeley, CA 94720-1460, Fax: 510-643-1255, herbert@bastille.cchem.berkeley.edu

Abstract

We describe a novel extended Lagrangian method for performing *ab initio* molecular dynamics simulations. Whereas other reformulations of the Car-Parrinello technique for use with atom-centered Gaussian basis functions utilize the one-electron density matrix elements as dynamical variables for the electronic degrees of freedom, we instead parametrize the density matrix using an auxiliary set of variables that induce "curvy steps" along the manifold of acceptable density matrices. Rigorously, a curvy step is (up to a specified precision) an idempotency-preserving unitary transformation of the density matrix. By properly constraining the electronic variables, curvy steps facilitate use of a longer time step for integrating the equations of motion, reducing

or eliminating the need to "purify" nonphysical density matrices. The cost of our algorithm scales linearly with the size of the system, and has been implemented within the Q-Chem electronic structure software package. Illustrative applications will be presented.

PHYS 329 [769093]: A theoretical and experimental investigation of the rate determining step for nitrosamide thermolyses

C.F. Rodriguez¹, Chad Vallee¹, Edson V Perez², Martin Brantley¹, and Ron W. Darbeau². (1) Dept. of Chemistry, McNeese State University, Lake Charles, LA 70609-0455, Crodriqu@mail.mcneese.edu, (2) Department of Chemistry, McNeese State University

Abstract

A mechanistic framework was recently postulated by Darbeau et al. J. Org. Chem. 2001, 66, 5027, where the transition state structure for the rate determining step (RDS) is a high energy, strained, 4 membered ring of the oxadiazetyl family. Model calculations using density functional theory at the B3LYP/6-311++G(d,p) and B3LYP/6-31++G(d,p) level were used to probe the potential energy hypersurface for this reaction and, thereby, to provide insight into the RDS in N-nitrosoamide thermolyses. The molecules investigated were ONN(X)CO(Y) where X=Y=H; X=F, Y=H; X=CH₃, Y=F; and X=C₆H₅CH₂, Y=t-Butyl. Calculations were done using Gaussian98 and include zero-point vibrational energies, thermal corrections and entropies. On the potential energy hypersurface five critical points were found: two transition structures and three minima. The critical points were characterized by harmonic vibrational frequencies and the surface verified by intrinsic reaction coordinate calculations. At the B3LYP/6-311++G(d,p) level for X=Y=H; X=CH₃, Y=F ; X=F, Y=H; the activation energies are 29.1, 24.0 and 21.4 kcal/mol, respectively. While at the B3LYP/6-31++G(d,p) level the activation energy for the thermal rearrangement of N-benzyl-N-nitrosopivalamide is about 15 kcal/mol. The calculated results are consistent with experimental activation energies. These calculations also allow us to investigate the structural and electronic effects which dominate the reaction mechanism.

PHYS 330 [765682]: Calculated vibrational circular dichroism of nucleic acid oligomers utilizing DeVoe polarizability theory making use of DFT derived input parameters

Steven D. Ferber, Department of Chemistry, Howard University, 525 College Street, N.W, Washington, DC 20059, Fax: 202-806-4232, sferber@howard.edu

Abstract

The Vibrational Circular Dichroism (VCD) of Nucleic Acids is a sensitive function of their conformation. DeVoe's classical polarizability theory allows the calculation of polymer absorption and circular dichroism spectra in any frequency range. Following the approach of Tinoco & Cech, Moore obtained calculations of nucleotide & nucleoside absorption and CD spectra in the near UV region. This was found useful in estimating monomer parameters for use in polymer CD and absorption calculations. Moore and Self developed and published calculations extending into the IR region with this theory for the first time. Here we present calculated absorption and CD spectra in the infra-red (vibrational) region for nucleic acid oligomers. These calculations improve upon the earlier attempts which utilized data and normal coordinates estimated from only partial analysis of the molecule. The input values for the DeVoe

theory parameters are found from density functional theory calculations of the nucleotide monomers using the GAUSSIAN '98 program to obtain the local equilibrium structure and vibrational normal coordinates. These more complete polarizability parameters include ALL contributions to specific vibrational normal modes (absorption frequencies) for the entire nucleotide structure (base, sugar and phosphate backbone) which therefore model the spectra more accurately. Calculated Spectral Intensities will be presented.

PHYS 331 [764690]: A theoretical study of the benzene excimer using time-dependent density functional theory (TDDFT)

Jay C. Amicangelo, School of Science, Penn State Erie, The Behrend College, 5191 Station Road, Erie, PA 16563, jca11@psu.edu

Abstract

A theoretical characterization of the potential energy surface of the singlet excimer of benzene has been performed using time-dependent density functional theory (TDDFT). The B3LYP and the BPW91 functionals were combined with the 6-31+G* basis set to first optimize the ground-state geometry of the benzene monomer, and then to compute the singlet excitation energies of the benzene dimer, using the optimized monomer geometries. The potential energy surface of the lowest singlet excimer state was characterized by computations along three basic intermolecular coordinates: (i) translation of two parallel monomers along the centroid axis, (ii) in-plane rotation of two monomers at a fixed distance, and (iii) in-plane translation of two monomers along the long and short monomer axes. The calculations at both levels of theory predict that the benzene excimer is bound in its lowest excite singlet state with a minimum at 3.15 Å and binding energies that compare favorably to the experimental binding energy. The calculations also predict that in-plane rotation and in-plane translational at the minimum distance destabilizes the excimer, suggesting that the minimum energy conformation of the benzene excimer is the parallel D_{6h} structure. The transition energy for the D_{6h} excimer structure at the minimum distance was also calculated at both levels of theory and found to be in reasonable agreement to the experimental transition energy. Overall, this study suggests that TDDFT methods can be used to characterize the energetics of aromatic excimers with reasonable accuracy.

PHYS 332 [765699]: A generalization of Kimball-Overhauser approach to finite inhomogeneous systems

Sergey A. Varganov, Chemistry Department, Iowa State University, 201 Spedding Hall, Ames, IA 50011, sergej@si.fi.ameslab.gov, and Mark S. Gordon, Department of Chemistry/Scalable Computing Laboratory, Iowa State University & Ames Laboratory

Abstract

The Kimball-Overhauser approach, initially developed for the treatment of a homogeneous electron gas, is generalized for solving the electron correlation problem in atoms and molecules. The method is based on the representation of the many body electron problem as a sum of effective two-electron problems. The effective two-electron functional and pair distribution functions are optimized in self-consistent manner. The connection of this approach to density matrix functional theory and wave function methods is discussed.

PHYS 333 [763577]: Can the cost of high accuracy theoretical pKa calculations be reduced?

Brian F. Yates and Alison M. Magill, School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Australia, Brian.Yates@utas.edu.au

Abstract

The landmark paper by Liptak and Shields¹ outlined a sophisticated quantum chemistry technique for highly accurate calculation of pKa values. This protocol uses the complete basis set (CBS-QB3) method in conjunction with the conductor-like polarised continuum (CPCM) solvation model. We have applied the method to predict the absolute and relative pKa values for a series of N-heterocyclic carbenes in water, dimethylsulfoxide and acetonitrile. Remarkably good agreement between the calculated and experimental pKa values was obtained for the two available experimental numbers, confirming that this state-of-the-art theoretical approach can be used to calculate highly accurate pKa values without fitting to experimental data. Recently we have applied the method to a C₁₉H₂₀N₂ compound which represents possibly the largest system yet studied by the Liptak-Shields method. These benchmark calculations allow us to assess whether lower levels of theory can be used with any degree of reliability to obtain accurate pKa values.

1 Liptak, M. D.; Shields, G. C. J. Am. Chem. Soc. 2001, 123, 7314-7319.

PHYS 334 [754746]: A theoretical study of potential energy surfaces in the photodissociation of carbonic dibromide

Peng Zhang and Keiji Morokuma, Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 30322, pzhang@euch4e.chem.emory.edu

Abstract

Complete active space self-consistent field (CASSCF) and multi-reference single and double excitation configuration interaction (MRSDCI) calculations have been carried out on the potential energy surfaces of carbonic dibromide to study the photodissociation dynamics starting from the first singlet electronically excited state. Both internal conversion and intersystem crossing channels, which could bring the excited carbonic dibromide back onto the ground state surface and lead to dissociation on the ground state, have been identified with planar C_s, twisted C_s and C₁ symmetries. However, from the energetic viewpoint, none of these possible reaction channels is energetically favorable. Direct dynamics calculations indicate that the energy difference between S₁ and T₁ states is always quite small, suggesting that the cumulated transition probability between S₁ and T₁ states could be prominent. Therefore, the reaction mechanism could be that the molecule goes through two intersystem crossing (S₁?T₁?S₀) channels and finally jumps onto the ground state surface, where it dissociates to the molecular products.

PHYS 335 [765561]: A time-dependent Hartree-Fock approach for studying the electronic optical response of molecules in intense fields

H. Bernhard Schlegel¹, Xiaosong Li¹, Stanley M Smith¹, Alexei N Markevitch², Dmitri A

Romanov³, and Robert J Levis². (1) Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202, Fax: 313-577-8822, hbs@chem.wayne.edu, (2) Department of Chemistry, Center for Advanced Photonics Research, Temple University, (3) Department of Physics, Center for Advanced Photonics Research, Temple University

Abstract

In high intensity oscillating electric fields, where a perturbative approach is no longer valid, we have used time-dependent Hartree-Fock (TDHF) theory to simulate the response of the electron density. We have developed a unitary transform approach combined with the modified midpoint method to provide a stable and efficient means of integrating the non-linear TDHF equations for the electronic density using a gaussian basis set. For H₂, the density follows the field adiabatically at $3.5 \cdot 10^{14}$ W/cm² and 760 nm, but shows increasing nonadiabatic behavior at higher intensities. The TDHF results are nearly indistinguishable from calculations using the full time-dependent Schrödinger equation. Simulations of N₂ in the same fields show even greater complexity. This approach is used to study the response of polyenes and polyacenes to intense laser fields.

PHYS 336 [764465]: Ab initio and empirical model simulation studies of "neat" liquid

Yves A. Mantz¹, Helene Gerard², Radu Iftimie³, Glenn Martyna¹, and Bin Chen⁴. (1) Physical Science Division, IBM Research, TJ Watson Research Center, PO Box 218, Yorktown Heights, NY 10598, Fax: 914-945-4506, yamantz@cmm.upenn.edu, (2) Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, (3) Department of Chemistry, New York University, (4) Department of Chemistry, Louisiana State University

Abstract

The structure of water, and how it is affected by the presence of solute, is of long-standing interest but is generating intense new scrutiny based on recent experimental studies [Phys. Rev. Lett. **90**, 075502 (2003), Nature **416**, 829 (2002)]. In this presentation, the temperature dependence of the structure predicted by a variety of theoretical methods is compared, including the first Car-Parrinello *ab initio* MD study. In addition, the *cis-trans* isomerization of a simple peptidic fragment, *N*-methylacetamide [CH₃-C(O)-N(H)-CH₃], is examined via umbrella sampling *ab initio* and classical MD [YA Mantz et al., J. Am. Chem. Soc. **126**, 4080 (2004)]. A new interpretation of the C(O)-N bond restructuring in terms of maximally localized Wannier function centers and ELF isosurfaces is presented. Additionally, a full analysis of the solvation shell including the orientational structure is given, complementing our studies of the "neat" liquid and offering data for comparison to anticipated new experiments.

PHYS 337 [746310]: Ab initio molecular orbital study of the silsesquioxanes

Takako Kudo, Department of Fundamental Studies, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Japan, Fax: +81-277-40-1026, tkudo@sci.gunma-u.ac.jp, and **Mark S. Gordon**, Scalable Computing Laboratory, Ames Laboratory-Iowa State University, 201 Spedding Hall, Iowa State University, Ames, IA 50011, Fax: 515-294-5402, mark@si.fi.ameslab.gov

Abstract

Polyhedral oligomeric silsesquioxanes (POSS) and related compounds (e.g., zeolites and metal-substituted POSS) have attracted considerable experimental and theoretical interest for many years because of their wide variety of practical uses. Although there have been many studies of their structures and properties, very little is known about the mechanism(s) by which they form. In continuation of our previous studies, we would like to explore the whole mechanism for the synthesis of silsesquioxanes by ab initio molecular orbital calculations. The process is expected to be so complicated and have many possible steps to arrive at the final products. Therefore, we focus on the synthetic process of T8 ((HSiO_{1.5})₈) that is considered as quite stable and one of the most popular POSS and examine the potential energy surfaces of the various condensation reactions.

PHYS 338 [765289]: Ab initio studies of F(2P), Cl(2P) and Br(2P)-HF Van der Waals complexes

Malgorzata M. Szczesniak¹, Grzegorz Chalasinski², and Jacek Klos¹. (1) Department of Chemistry, Oakland University, Rochester, MI 48309, Fax: 248-370-2321, maria@ouchem.chem.oakland.edu, test@email.com, (2) Faculty of Chemistry, University of Warsaw

Abstract

Study of Van der Waals interaction between open-shell halogen atoms and closed shell polar hydrogen halides molecules is of a great importance for reactivity of such systems. These complexes exist in the entrance and exit channels of the heavy-light-heavy hydrogen-exchange processes. Recently, there is a great deal of interest in the helium droplet spectroscopy in these complexes. The adiabatic and diabatic potential energy surfaces for F(2P)-HF, Cl(2P)-HF and Br(2P)-HF are studied at the RCCSD(T) and MRCI levels of ab initio theories. The effect of spin-orbit (SO) coupling in these complexes is very important and cannot be neglected if one needs to perform dynamical calculations. SO coupling changes the anisotropy and well depths of Van der Waals minima thus influencing energetics and dynamics. Ab initio results are compared to the recent works of Hutson and Meuwly where they present semi-empirical results for some of these complexes.

PHYS 339 [754034]: AEI: Ab-initio study of excited electronic states of the C₃H₃ radical

Milena Shahu and Charles D. Pibel, Department of Chemistry, American University, 4400 Massachusetts Ave. N.W, Washington, DC 20016-8014, Fax: 202-885-1752, mshahu@american.edu

Abstract

The propargyl radical is an important molecule in combustion processes and it is proposed that two propargyl molecules can form benzene or phenyl radicals directly, which lead to the formation of polycyclic aromatic compounds: the major precursor to soot. This radical is also thought to be important in the low temperature chemistry of extraterrestrial planetary atmospheres. In this study we present ab initio calculations carried out on the first few doublet electronic states of the propargyl radical (and other C₃H₃ isomers) using the Complete Active Space Self Consistent

Field (CASSCF) as well as Configuration Interaction-Singles (CIS) methods. The vertical and adiabatic excitation energies will be reported and compared to the experimental data available. The dynamics of the excited electronic states of this radical will be discussed.

PHYS 340 [747625]: Ab initio studies of the interaction of oxygen with perfect and defective graphite surfaces

Natasa Mateljevic and John C. Tully, Department of Chemistry, Yale University, PO Box 208107, New Haven, CT 06520, Fax: 203-432-6144, natasa.mateljevic@yale.edu

Abstract

In low Earth orbit (LEO), at 300 km altitude, the faint atmosphere interacts with satellite materials leading to the degradation of these hydrocarbon materials. O(3P), the predominant species in LEO, collides with 5eV of kinetic energy with these materials at orbital velocity. We study the interaction of O and graphite, as a model for the satellite surface. As part of the theoretical effort, we performed our first-principles calculations using VASP (Vienna Ab initio Simulation Package) and Gaussian 3.0 development version. The main goal is to investigate the interaction of atomic oxygen with perfect and defective graphite surfaces. We varied oxygen coverage, position, and orientation. Preliminary results show that the bridge site is more stable than the on top site, as the binding site for oxygen. Reactions of 5eV oxygen with a clean and perfect graphite surface tend to be very endothermic, but exothermicity increases with oxygen coverage. Reactions of O atoms at defects are exothermic to remove a C atom and form CO(g) and CO₂(g), where oxygen can substitute for one or more carbons in the graphite sheet plane.

PHYS 341 [766839]: Ab initio studies on the acidities of carbon acids, I: the cyano substituted 1,3-cyclopentadienes

Lin Chen¹, Bradley Burcar¹, and Richard EDWIN Brown². (1) Dept. of Chemistry, Michigan Technological University, Houghton, MI 49931, rebrown@mtu.edu, (2) Department of Chemistry, Michigan Technological University

Abstract

Carbon acids, where the acidic hydrogen is attached to a carbon atom are traditionally considered to be very weak acids. For example, the pK_a of 1,3-cyclopentadiene is 15. However upon substitution, the resonance and inductance effects can drastically change this perception by effecting the electronic structure of both the acid and its conjugate base. The cyano-substituted 1,3-cyclopentadienes are a case in point with some analogues having been determined to possess K_a values that are several orders of magnitude larger than some of the common acids like HCl. Strong carbon acids are of interest since there is a need for strong acids that are soluble in organic solvents and are a source of weakly coordinating anions. This work presents the results of high level ab initio predictions of these acidities in both the gas phase and aqueous phase as well as a study of the structural and electronic effects that drives these acidities. Calculations were performed at the AM1, Hartree Fock, MP2 and DFT levels of theory using a variety of basis sets from the 6-31+G(d) to the aug-cc-pVTZ sets. Initial results show that there is a very strong correlation between the gas phase acidities and the solvent phase acidities. In all cases, the enthalpic term dominates the variation in the acidities of these acids.

PHYS 342 [764515]: Application of time-dependent quantum mechanics to electron transport in molecular junctions

Natalie Carroll, Chemistry Department, Drexel University, Philadelphia, PA 19104, nrc22@drexel.edu, and **Karl Sohlberg**, Department of Chemistry, Drexel University

Abstract

To date, the great majority of theoretical treatments of electron transport in molecular junctions have been of the time independent variety. Time dependence, however, is critical to such properties as switching speeds in binary computer components and alternating current devices. We present the application of time-dependent methods to study electron transport across a molecular junction, modeled as a single molecule sandwiched between two clusters of close packed metal atoms. The time dependence of electron transport is investigated by initially localizing an electron on the donor electrode cluster and following the time development of the corresponding non-stationary wavefunction. We demonstrate that the time dependent treatment of electron transport predicts physically intuitive results while providing insights not available from time-independent methods.

PHYS 343 [750590]: Atomic charges for classical simulations of polar systems

Hendrik Heinz, Materials Directorate, Branch of Polymers, Airforce Research Laboratory, 2977 Hobson Way, Wpaafb, OH OH-45433, Fax: (937) 6464068, hendrik.heinz@wright.edu, and **Ulrich W. Suter**, Department of Materials, ETH

Abstract

Polarity often determines structure and reactivity. This reflects in atomic charges in classical simulations, which are a prime factor in force fields for polar systems due to long range and energetic impact. Modern experimental methods yield accurate atomic charges (± 0.1 e) well-suited for simulations, while ab-initio methods often entail uncertainty. We introduce a novel semiempirical concept for chemical bonding based on both covalent and ionic contributions, represented by the atomization energies and the ionization energies/electron affinities of the elements. The relationship to compounds is established with an extended Born model. Evaluation of the basic energy quantities in relation to available reference compounds yields very good atomic charges. Our theory is in principle exact while contributions of localized bonding are not included in charge equilibrations based on electronegativity equalization. Force fields for several minerals based on our charge assignment lead to as low as ~ 0.3 % deviations in geometry from published crystal structures.

PHYS 344 [744374]: Molecular dynamics simulation of polymer structure using an implicit solvent quality technique

Thomas W. Scott, Kinetic Simulations Inc, 527 Upper Way, Wharton, NJ 07885, twscott@molydyn.com

Abstract

Molecular dynamics simulation of hydrocarbon polymers is used to explore a recent implicit solvent quality technique. The technique calls for multiplying the dispersion energy in the force field by a factor β . This factor starts in vacuum at $\beta = 1$ and then decreases to $\beta = 0$ as solvent

screening increases. This term takes into account the fact that dispersion interactions between any pair of atoms in the polymer depend on the medium in which the polymer exists. In testing this model, we studied how changes in β alter three types of structural distribution functions. The structural distributions for small β values reflect expanded coils appropriate for hydrocarbon polymers in good solvents at high dilution. The shapes of the distributions are compared to recent theory based on scaling forms. It is found that the scaling forms used to fit our data agree with the theoretical forms reported for excluded volume chains.

PHYS 345 [754835]: Correlation energies in the high density limit

Takeyce K. Whittingham, Department of Chemistry, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, Fax: 732-445-5312, takeyce@rutchem.rutgers.edu, and Kieron Burke, Department of Chemistry and Chemical Biology, Rutgers

Abstract

The high density limit of the correlation energy of ions was studied using accurate data for large nuclear charge ions. Increasing the nuclear charge is like scaling the electronic density, the difference being that scaling in this way results in changes in the density. Expressions for the expansion of the correlation energy, electronic density, and correlation potential were derived and expansion coefficients determined for select isoelectronic series. This method can be used to assess the accuracy of functionals in this limit as we show for a few popular correlation functionals.

PHYS 346 [752198]: Analytic gradients for the EOM-SF-CCSD and EOM-EE-CCSD methods: Theory and applications

Tao Wang, Sergey V. Levchenko, and Anna I. Krylov, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, taowang@usc.edu

Abstract

Using a Lagrangian formulation, the analytic gradient of the energy is derived and implemented in Q-Chem for the equation-of-motion coupled-cluster singles and doubles (EOMCCSD) model for excitation energies (EOM-EE-CCSD) and in the spin-flip (EOM-SF-CCSD) variant. Application to the geometry optimization of diradical and triradical are present. In particular, the effect of substitution on the ground state multiplet and excitation energies in diradical and triradical is discussed.

PHYS 347 [755378]: Capture, re-dissociation, and vibrational deactivation in the $\text{OH}(v) + \text{NO}_2 \leftrightarrow \text{HONO}_2^* \rightarrow \text{OH}(v') + \text{NO}_2$ reaction system

Yong Liu, Department of Atmospheric, oceanic, and Space Sciences, University of Michigan, Ann Arbor, MI 48109, Fax: 734-936-0503, liuyz@umich.edu, John R. Barker, Department of Atmospheric, Oceanic, and Space Sciences, Department of Chemistry, University of Michigan, and Lawrence L. Lohr, Department of Chemistry, University of Michigan

Abstract

Quasi-classical trajectory calculations were used to determine rate constants in the temperature range 300 K to 2000 K for interaction of $\text{OH}(v)$ with NO_2 . An analytic potential energy surface

was developed from experimental geometries and vibrational frequencies, combined with *ab initio* quantum chemical calculations. The results show that the capture rate constant, which can be identified with the recombination reaction rate constant at the high pressure limit (k_∞), does not depend on vibrational state of OH(v) and is only weakly dependent on temperature. The re-dissociation rate of the highly vibrationally excited HONO₂* is strongly dependent on both the initial OH(v) vibrational state and the temperature. The calculated distribution of final OH(v') vibrational states shows that OH(v) is efficiently deactivated and that the vibrational deactivation rate constant can be used as a surrogate for k_∞ , to a reasonable degree of accuracy.

PHYS 348 [766950]: Numerical simulations of 2-D NMR spectra and MR images by parallel computation

Prasad S. Lakkaraju¹, Motohiro Mizuno¹, and Warren S. Warren². (1) Dept. of Chemistry, Princeton University, Princeton, NJ 08544, plakkara@princeton.edu, (2) Department of Chemistry, Princeton University

Abstract

This poster presents numerical simulations of two-dimensional NMR spectra of solutions in inhomogeneous magnetic fields involving inter-molecular zero and multiple quantum coherences as well as spectra of liquids under magic-angle spinning conditions. Two distinct types of simulations will be shown. (a) Simulations of two-dimensional spectra in inhomogeneous magnetic fields including samples of biological tissue. For solution phase studies, samples containing two chemically distinct species (uncoupled, for example water and acetone) with a phantom sample grid size of 64x64x64 will be presented. These calculations are expected to reveal the intricate effects of dipolar demagnetizing fields on the multiple quantum coherences and lay a firm theoretical background for more complicated simulations involving spin-spin coupling. (b) For studies of liquid NMR spectrum using techniques of solid NMR, effect of magic-angle spinning and multiple-pulse for dipolar recoupling on the spectrum will be presented. Two-dimensional spectra of intermolecular double quantum coherence using these techniques will be shown.

PHYS 349 [764695]: Data-driven approximations in electronic structure theory

Benjamin G Janesko, Department of Chemistry, University of Pittsburgh, 219 Parkmann Av, Pittsburgh, PA 15260, Fax: 412-383-9646, bjanesko@andrew.cmu.edu, and David Yaron, Department of Chemistry, Carnegie Mellon University

Abstract

Ab initio electronic structure methods give accurate results for small systems, but do not scale well to large systems. However, chemical insight tells us that molecular functional groups will behave approximately the same way in all molecules, large or small. This phenomenon of "molecular similarity" is exploited in semiempirical electronic structure methods, which can treat large systems by incorporating a (relatively small) number of atom- or functional-group-specific parameters that are fitted to reproduce experimental data. We propose that high-level calculations on small molecules provide a source of parameterization data that is much richer than that obtained from experiment. In principle, we can select an interesting functional group, generate a large amount of ab initio data on the group in various small-molecule environments,

and "mine" this data to build a sophisticated model for the group's behavior in large environments. We are exploring two implementations of this idea: a relatively simple data-mining treatment of core polarization in effective core potentials, and a pair correlation density predictor that acts as a functional-group-specific DFT functional.

PHYS 350 [765527]: Condensed phase relaxation dynamics: Non-adiabatic mixed quantum/classical molecular dynamics simulations of photo-excited sodide (Na^-)

C. Jay Smallwood¹, Michael J. Bedard-Hearn¹, Ross E. Larsen², and Benjamin J. Schwartz¹. (1) Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles Young Drive East, Los Angeles, CA 90095-1569, cjs@chem.ucla.edu, (2) Department of Chemistry, University of California, Los Angeles

Abstract

We present a series of non-adiabatic mixed quantum/classical molecular dynamics simulations of electron photo-detachment from sodide (Na^-) in model solvents. Due to the fact that the solute has only electronic degrees of freedom, this system is ideal for studying the influence of the solvent in condensed phase charge-transfer reactions. In our calculations, a single valence electron is treated quantum mechanically while the sodium core and the solvent are treated classically. This work will focus on the influence of electronic symmetry and the role of the molecular nature of the solvent on excited-state relaxation dynamics. We will compare to previous ultra-fast experiments and analyze the specific solvent dynamics that drive the excited-state relaxation. Additionally, each solvent requires a physically accurate pseudopotential. We present a novel methodology that is sufficiently computationally efficient to avoid some approximations that have been necessary in the past. Comparisons between other solvent pseudopotentials will be made.

PHYS 351 [754687]: Controlling the dynamics of molecular systems

Florence J. Lin, Department of Mathematics, University of Southern California, 3620 Vermont Avenue, KAP 108, Los Angeles, CA 90089-2532, Fax: 213-740-2424, fjlin@math.usc.edu

Abstract

This paper uses classical mechanics to treat two laser experiments involving diatomic molecules as control systems. In the first scenario, an oriented state of a diatomic molecule is accessible via a local potential energy maximum. In a second scenario, a dissociated state of a diatomic molecule is accessible via a centrifugal potential energy barrier. These are steps toward further studies of the coherent control of quantum-mechanical molecular systems.

PHYS 352 [753561]: Density matrix renormalization group with localized orbitals

Dominika Zgid and Marcel Nooijen, Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada, Fax: 519-746-0435, zgid@uwaterloo.ca

Abstract

In quantum chemistry the quest for a general multi-reference method is still of high importance. It has been shown that DMRG is suitable to incorporate non-dynamic correlation. We are developing a DMRG method for multi-reference problems in large active spaces. DMRG has been particularly successful in applications to 1-D model systems, that are characterized by localized orbitals and sparse Hamiltonian matrix elements. We can capitalize on these aspects also in applications to molecules by using localized orbitals. The localized scheme also allows to treat parts of molecules as domains, which can be improved separately. We discuss the size-consistency of the method with localized orbitals. Since the convergence of the method depends on the 1-D ordering of the orbitals, we compare previously used ordering criteria with our new ordering criterion based on the localization. We also investigate how the sparsity of the Hamiltonian matrix in a localized basis can be exploited in DMRG.

PHYS 353 [754852]: Dissociation of hydrogen fluoride in HF(H₂O)₇

Jer Lai Kuo and Michael L. Klein, Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania, 231 S. 34th St., Philadelphia, PA 19104-6323, jkuo@vitae.cmm.upenn.edu

Abstract

We have previously demonstrated that H-bond arrangement has a significant influence on the energetics, structure and chemistry of water clusters [J.-L. Kuo, C. V. Ciobanu, I. Shavitt, L. Ojamae, and S. J. Singer *J. Chem. Phys.*, 118: 3583 (2003)]. In this work, the effect of H-bond orientation on the dissociation of hydrogen fluoride with 7 water molecules is studied by means of graph theory and high level ab initio methods. It is found that cubic structures of HF(H₂O)₇ are more stable than structures of other topologies reported in the literature. Electronic calculations on all possible H-bond orientations of cubic HF(H₂O)₇ show that ionized structures are energetically more favorable than non-ionized ones. This is an indication that 7 water molecules might be capable of ionizing hydrogen fluoride.

PHYS 354 [763593]: Calculations of intermolecular interaction energies using a perturbational approach based on density-functional theory

Eugeniya Tchoukova, Department of Physics, University of Delaware, Newark, DE 19716, etchouko@physics.udel.edu, Alston J. Misquitta, Department of Chemistry, University of Cambridge, and Krzysztof Szalewicz, Department of Physics and Astronomy, University of Delaware

Abstract

Until recently it has not been possible to accurately predict intermolecular interaction potentials for larger monomers (containing more than about ten atoms) due to computer resource requirements of electronic structure methods adequate for calculations. Recently, a new method has been proposed [1,2] which applies symmetry-adapted perturbation theory (SAPT) but utilizes density-functional theory (DFT) description of monomers. The SAPT(DFT) method is very efficient and has the potential of predicting interaction energies for much larger systems than possible so far. Such application requires solving several technical difficulties connected with large-scale calculations. Progress in this direction will be reported as well as results of calculations for monomers containing about ten atoms.

[1] A.J. Misquitta and K. Szalewicz, Chem. Phys. Lett. 357, 301 (2002). [2] A.J. Misquitta, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 91, 033201 (2003).

PHYS 355 [755336]: Domain wall motion study of ferroelectric crystals using the bond-valence model

Young Han Shin, Valentino R. Cooper, Ilya Grinberg, and Andrew M. Rappe, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104, yhshin@sas.upenn.edu

Abstract

Ferroelectric oxides (solids possessing switchable spontaneous electric dipoles) are extremely useful as nonvolatile memory storage materials. The speed at which polar domains can be reversed is a critical characteristic for future development of these materials. With current computational abilities, it is not feasible to study polarization reversal of ferroelectric crystals using a fully quantum-mechanical approach.

Therefore, we present a classical potential model (bond-valence model) for performing molecular dynamics simulations on ferroelectric oxides. This potential is parameterized from the first-principles DFT calculations, using a functional form based on Brown's Rules of Valence, a widely-used crystal chemistry approach. In our model, these rules for the interactions between atoms are used to construct a potential to represent the ionic and covalent bonding in these materials. The observation of antiparallel domains and the switching kinetics related to the domain-wall motion will be presented.

PHYS 356 [755697]: Can accurate properties of methane clathrates be obtained from molecular simulations using *ab initio* force fields?

Omololu Akin-Ojo and Krzysztof Szalewicz, Department of Physics and Astronomy, University of Delaware, Newark, DE 19711, Fax: 302-831-1637, prayerz@Udel.edu

Abstract

Direct experimental measurement of the hydrate (clathrate) phase of methane is difficult, leading to a limited amount of available data. Also, most of the data are of low accuracy. This is an area in which molecular simulations can fill the gap. We attempt to calculate bulk properties of methane clathrates via molecular dynamics and Monte Carlo simulations using *ab initio* force fields developed by us. These accurate two-body force fields for CH₄-H₂O interactions were obtained using *ab initio* quantum chemistry methods namely, the supermolecular method at the CCSD(T) level of theory and the symmetry adapted perturbation theory (SAPT). The force fields were first tested in the calculation of the cross second virial coefficient B₁₂(T) for the dimer.

PHYS 357 [763398]: Dynamics study of unimolecular decomposition

Chris Stopera, Dave Thweatt, and Michael Page, Department of Chemistry, North Dakota State University, Fargo, ND 58105, Fax: 701-231-8831, Christopher.Stopera@ndsu.nodak.edu

Abstract

Understanding the dynamics of reactions is of fundamental importance in physical chemistry;

however, this task can be experimentally difficult, especially when the reactants of key steps in a reaction cannot be isolated. In such cases, ab initio methods are a promising option. Starting with the reaction path hamiltonian of Miller, Handy, and Adams, we derived a quantum/classical approach to describing the dynamics of unimolecular reactions. This method was then applied to HF elimination from fluoroethane, and HCl elimination from chloroethane, HONO elimination from methylene nitramine.

PHYS 358 [751665]: Molecular dynamics calculation of absolute binding free energy: Aromatic ligands bind to a nonpolar Cavity of T4 Lysozyme

Yuqing Deng and Benoit Roux, Biochemistry Department, Weill Medical College of Cornell University, 1300 York Avenue, New York, NY 10021

Abstract

We describe a staged simulation protocol for absolute binding free energy calculation using molecular dynamics. To increase sampling efficiency, the binding free energy is calculated by introduction of a ligand in the binding pocket with translational and rotational constraints. The effect of the constraints is removed by gradual removal of the constraints in separate simulations. The constrained ligand is introduced in three stages according to the interaction activated: repulsion, dispersion and electrostatic interaction. The separate of repulsion and dispersion for the Lennard-Jones potential is implemented with WCA (Weeks, Chandler, Andersen) scheme. The introduction of repulsion itself is further split to stages with an additional shift parameter introduced in the WCA repulsive potential. The simulation system comprises a ligand and a sphere of protein atoms around it. The effect of the rest of the system is accounted for by a generalized solvent boundary condition (GSBP). We calculated the binding free energies of some aromatic ligands in the nonpolar cavity of T4 lysozyme L99A mutant. For binders, (benzene, toluene) of this cavity, the calculated free energy agree with the experiment values excellently. Furthermore, our calculation is capable of identifying a decoy molecule, phenol.

PHYS 359 [754165]: Effect of excited angular momentum states upon the isomerization dynamics of DCN

Rudolph C. Mayrhofer, Department of Physical Science, Kutztown University, Kutztown, PA 19530, mayrhofer@kutztown.edu

Abstract

A classical mechanical study on the isomerization dynamics of DCN to CND will be presented. The role of highly excited angular momentum states in enhancing this the process is investigated. Classical trajectories along with FFT are used to assess the transfer of energy between the various degrees of freedom. The effect of K , the projection of the total angular momentum along the body fixed axis a , is examined to investigate its influence on the isomerization process. Results with zero total angular momentum ($J=0$) will also be presented. These results include using Poincare surface of section plots in conjunction with FFT to assess whether the dynamics is regular or chaotic. Since the role of the CN coordinate in the isomerization process is minimal, this coordinate is held fixed for all calculations.

PHYS 360 [764821]: Combining variation and diffusion calculations in quantum Monte Carlo

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

Abstract

A modified diffusion Quantum Monte Carlo (DQMC) method is used to calculate corrections to variational wavefunctions and their energies. The corrected functions and energies are equivalent to those of fixed-node quantum Monte Carlo calculations, but the statistical errors associated with diffusion are reduced because they occur only in the corrections. The combination of methods is particularly useful in reducing computation requirements for large systems and in exploiting correlated sampling to predict weak molecular interactions.

PHYS 361 [745844]: Effective fragment potential method: From molecules to clusters to the bulk

Heather Netzloff and Mark S. Gordon, Department of Chemistry, Iowa State University, 201 Spedding Hall, Ames, IA 50011, heather@si.fi.ameslab.gov

Abstract

Modeling environmental effects, especially those in the condensed phase, is a growing area of computational quantum chemistry. The ultimate goal is to develop a method that would give accurate and reliable predictions across the full range of molecules to clusters to bulk. A trade-off exists between the use of highly sophisticated, ab initio methods for accuracy and the computational demands of such an endeavor. The Effective Fragment Potential (EFP) method has been developed with these goals in mind. The EFP method reproduces fully quantum structures and energies very well. In order to test the ability of the EFP method to predict bulk properties, an EFP molecular dynamics (MD) code has been implemented within the GAMESS program. As the EFP model is improved from HF to DFT to MP2, the predicted radial distribution functions (RDF) for water become increasingly accurate. Since the cluster trends suggest that each EFP level of theory accurately reproduces relative energies and structures from the corresponding QM method, it is likely that the MD results reflect the abilities of the corresponding levels of theory to reproduce the RDF, one of the simplest bulk properties, without the cost of performing the full QM calculations.

PHYS 362 [750138]: Effects of proton donor-acceptor vibrational motion on proton-coupled electron transfer in solution and proteins

Alexander V Soudackov, Elizabeth R Hatcher, and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, souda@chem.psu.edu

Abstract

Proton-coupled electron transfer (PCET) reactions play a vital role in many important chemical and biological processes. Our group has developed a multistate continuum theory for PCET reactions. The solute is described with a multistate valence bond model, the solvent is

represented as a dielectric continuum, and the active electrons and transferring protons are treated quantum mechanically. We have extended this theory to include the effects of the proton donor-acceptor vibrational motion. This motion significantly influences the PCET reaction rates by modulating the proton transfer distance and thereby the overlap between the reactant and product hydrogen vibrational wavefunctions. We present several theoretical approaches to treat this motion in the framework of the multistate continuum theory. Nonadiabatic rate expressions are presented for the classical and fully quantum treatments of the proton donor-acceptor mode. Dynamical effects on the reaction rates are also discussed. The theoretical results are illustrated on a model system for PCET in solution.

PHYS 363 [772076]: Experimental and computational studies of water – glassy polymer network interactions

Hua Zhang, Department of Chemical Engineering, Polytechnic University, 6 Metrotech Center, Brooklyn, NY 11201, Fax: 718-260-3125, hzhang02@utopia.poly.edu, and Jovan Mijovic, Department of Chemical and Biological Sciences and Engineering, Polytechnic University

Abstract

The molecular-level interaction between water and glassy polymer network is studied with the combined use of Dielectric Relaxation Spectroscopy (DRS), Near Infrared (NIR) and molecular dynamics (MD) simulations. DRS study shows that the majority of water molecules form hydrogen bonds (HBs) with the polymer network. The deconvolution of the NIR spectra yields three spectroscopically distinguishable forms of water, with zero, one and two hydrogen atoms participating in hydrogen bonding. MD simulation shows that 1) absorbed water destroys some HBs originally present in the dry network; 2) absorbed water rotates anisotropically: the vector μ , which coincides with the direction of the water dipole moment, rotates more slowly than the other two vectors, which are perpendicular to vector μ and each other; HBs between network hydroxyl hydrogen and water oxygen are the origin of the slowdown; and 3) water's translation process combines oscillation with occasional jumps from one site to another.

PHYS 364 [747623]: Detailed balance and equilibrium in mixed quantum-classical dynamics

Priya V Parandekar, Department of Chemistry, Yale University, PO box 208107, New Haven, CT 06520, Fax: 203-432-6144, priya.parandekar@yale.edu, and John C. Tully, Dept. of Chemistry, Yale University

Abstract

Mixed quantum-classical dynamical methods- namely mean field (Ehrenfest) and surface hopping- are approximate methods which can be applied to study systems involving one or few quantum degrees of freedom and many classical degrees of freedom- for example, proton or electron transfer reactions. The short term dynamics predicted by these methods is frequently in good agreement with full quantum dynamics. However, in these methods, on a longer timescale, the system does not attain the correct equilibrium state. We demonstrate that the Ehrenfest method will approach infinite temperature at long times, whereas certain variations of surface hopping approach the correct equilibrium (quantum and classical) distributions. Thus, the surface hopping algorithm (or variations) may solve the problem of achieving detailed balance and

approaching the correct equilibrium state on a longer timescale, while retaining realistic dynamics on a shorter timescale.

PHYS 365 [764523]: Molecular dynamics simulations of the two-way junction hairpin ribozyme

Maria M. Rhodes¹, Kamila Reblova², Jiří Šponer², and Nils G. Walter¹. (1) Department of Chemistry, University of Michigan, 930 N. University, Ann Arbor, MI 48109-1055, mmmrhodes@umich.edu, (2) National Centre for Biomolecular Research

Abstract

The hairpin ribozyme is in many ways a model system for the folding behavior of RNAs. During the reaction pathway, the ribozyme must both fold reversibly (i.e., dock) into the active structure and undock after cleavage to release the products. Knowing the mechanics of the ribozyme's undocking behavior will both be relevant to the reaction pathway and provide added detail on how nucleotides play critical roles in maintaining the active structure. We have performed molecular dynamics simulations on the two-way junction hairpin ribozyme, starting from a fully docked conformation, as well as on three single-site mutants that have been experimentally found to exhibit altered (un)docking rate constants due to disruption of at least one interdomain interaction. All simulations were equilibrated and run under the Parm99 force field of AMBER-6.0. A detailed comparative analysis of the RNA structural dynamics and of the water and cation interactions will be presented.

PHYS 366 [765721]: First-principles studies of structures and phase transitions of platinum dioxides

Shuping Zhuo, School of Chemical Engineering, Shandong University of Technology, Zibo 255049, China, sz36@drexel.edu, and Karl Sohlberg, Department of Chemistry, Drexel University

Abstract

Platinum dioxides are used as catalysts, and in optical, electrochemical and other technological applications. We report first principles DFT calculations of the structures and dynamics of three phases of PtO₂. First-principles-based thermodynamic calculations are employed to determine the relative stabilities of the phases. First-principles-based kinetics calculations are used to study the phase transformations. The results reveal that there are three nearly energy degenerate polymorphs of PtO₂. The *f*^{''}- (CaCl₂-type) structure is the most stable phase, while the *f*^{'''}- (rutile) structure represents an unstable fixed point (saddle point) on the potential energy surface, or is just barely bound. The *f*^Ñ- (CdI₂-type) structure is a true metastable phase, but since the barrier to conversion from CdI₂- to CaCl₂-type PtO₂ is very high, once the CdI₂-type has formed, it will decay very slowly to the CaCl₂-type structure. These calculations reconcile seemingly contradictory findings and answer several longstanding fundamental questions about the platinum dioxides.

PHYS 367 [752859]: Group III atomic wires on Si(100)-(2x1) reconstructed surfaces

Deborah D. Zorn and Mark S. Gordon, Chemistry Department and Ames Laboratory USDOE, Iowa State University, 201 Spedding Hall, Ames, IA 50011, deb@si.fi.ameslab.gov

Abstract

Group III atomic wires on Si(100)-(2x1) reconstructed surfaces. Atomic wires have been grown in the laboratory by depositing group III metals onto a Si(100)-(2x1) reconstructed surface. The metals form rows parallel to the silicon dimers. In order to correctly model the reactive part of the silicon surface and to also include the bulk properties of the lattice the embedded cluster, QM/MM (hybrid quantum mechanics/molecular mechanics) method, SIMOMM was used. Ab Initio calculations have been performed on Al atoms on silicon clusters. Natural orbital occupation numbers show that Si(100) reconstructed surfaces display diradical character so a multi reference method is needed. A multi-configuration self consistent field (MCSCF) calculation with a 6-31G(d) basis set and effective core potentials was used to optimize geometries. Hessians were calculated to characterize stationary points and improved treatment of dynamic electron correlation was obtained using multi-reference second order perturbation theory (MRMP2) single point energy calculations.

PHYS 368 [751045]: Heat capacity of gas phase Ag₂

Michael L. Biolsi¹, **Louis Biolsi**¹, and Paul M. Holland². (1) MEAD Technologies, 712 Oak Knoll Road, Rolla, MO 65401, michael@biolsi.com, (2) Thorleaf Research, Inc

Abstract

The silver dimer, Ag₂, is an important diatomic molecule since it is the smallest bridge molecule between molecular properties and the properties of silver clusters. Silver clusters of a certain size may serve as a prototype for solid surface studies and silver surfaces have important catalytic properties. We report calculations of the heat capacity of Ag₂, including contributions from several low lying bound electronic states of the molecule, from low temperatures to 5000K. The results are calculated two ways; by using the partition function approach to thermodynamic properties and by relating the heat capacity to second virial coefficients and their derivatives. The results obtained using the two methods are compared with a discussion of some possible reasons for the differences.

PHYS 369 [765746]: Efficient real-space configuration interaction method for calculating ground and excited state multi-electron and spin dynamics in the condensed phase

Ross E. Larsen, Department of Chemistry, University of California, Los Angeles, 607 Charles E. Young Dr. East, Los Angeles, CA 90095, and Benjamin J. Schwartz, Department of Chemistry and Biochemistry, University of California, Los Angeles

Abstract

We introduce a method for calculating the electronic properties of multi-electron objects immersed in disordered, condensed-phase systems. The method invokes two new computational techniques to make configuration interaction (CI)-based molecular dynamics practical. The first technique allows the accurate evaluation of CI Coulomb and exchange integrals using a novel, highly efficient real-space quadrature for the six-dimensional integrations. The second

computational technique makes use of the fact that only a small subset of single-electron configurations contributes to the two-electron wavefunctions at any given instant, which allows us to perform the CI calculation using a periodically updated subset of "important" configurations. Thus, this method allows electronic states to be computed with full multireference CI for every time step of a mixed quantum/classical molecular dynamics trajectory, including spin dynamics.

PHYS 370 [752052]: Including nuclear quantum effects directly into the calculation of NMR shielding and spin-spin coupling

Chet Swalina, Michael Pak, and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, chet@chem.psu.edu

Abstract

We have recently developed the nuclear-electronic orbital (NEO) method for including nuclear quantum effects in electronic structure calculations. In the NEO approach, specified nuclei are treated quantum mechanically on the same level as the electrons, and the nuclear-electronic wavefunctions are calculated using molecular orbital methods. Here we discuss the extension of the NEO approach to calculate magnetic properties such as NMR shielding and spin-spin coupling. The ab initio calculation of such properties has reached a level of accuracy that now requires consideration of vibrational corrections to computed values. In principle, these types of corrections are inherent in NEO calculations. Additionally, new shielding/deshielding effects associated with the quantum nature of protons involved in hydrogen bonding may become apparent in NEO-NMR shielding calculations.

PHYS 371 [747465]: Inclusion of dispersion effect in the MP2 based effective fragment potential method (EFP1)

Jie Song and Mark S. Gordon, Chemistry Department and Ames Laboratory USDOE, Iowa State University, 201 Spedding Hall, Ames, IA 50011, Fax: 515-294-5204, jie@si.fi.ameslab.gov

Abstract

The Effective Fragment Potential Method (EFP1) is a discrete method for solvation effects, which was originally developed using the Hartree-Fock (HF) level of theory and later extended with density functional theory (DFT). The DFT based EFP model illustrates the necessity of including electron correlation at the short range, but the long range correlation is absent. In the newly developed MP2 based EFP model, electrostatic, polarization, and exchange/charge transfer effects are calculated in a manner similar to the DFT and HF based method. The dispersion effect, which mainly accounts for long-range electron correlation, has been added as the fourth energy contribution. The dispersion term, combined with the second-order correction for exchange repulsion/charge transfer, is fitted by an expansion in R^{-n} ($n=6$ and 8) multiplied by a damping term. It is implemented for both ab initio-fragment and fragment-fragment interactions. Inclusion of the dispersion should generate more accurate potentials. Initial test results show that MP2 based EFP is able to reproduce MP2 results at very low computational costs.

PHYS 372 [754274]: Inclusion of dispersion into DFT by optimization of analytic pseudopotentials

O. Anatole von Lilienfeld-Toal¹, Ivano Tavernelli¹, Ursula Rothlisberger¹, and Daniel Sebastiani². (1) Institut of Chemical Sciences and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland, anatole.vonlilienfeld@epfl.ch, (2) Max-Planck-Institut fuer Polymerforschung

Abstract

In plane wave based electronic structure calculations the interactions between core and valence electrons are in general represented by effective core potentials. These pseudopotentials are usually constructed such that the shape of the atomic valence orbitals outside a certain core radius is reproduced correctly with respect to an atomistic all-electron calculation. As a new method we propose to tune additional parameters in the pseudopotentials in order to reproduce molecular properties from arbitrarily accurate reference calculations. We demonstrate the validity of our approach by including dispersion interactions into DFT via the optimization of additionally added pseudopotential parameters. Without increasing the computational cost our scheme allows to conduct first principle DFT based molecular dynamics of large molecular systems taking dispersion forces into account.

PHYS 373 [764685]: Excited-state density functionals?

Rene Gaudoin, Department of Chemistry & Chem. Biology, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, rene@dft.rutgers.edu

Abstract

There exist ordinary excited-state densities that arise from more than one external local one-body potential. This is due to a qualitatively different energy-density relationship from that of the ground state and is related to positive eigenvalues in the non-local susceptibility for excited states. Problems with the generalization of the density functional methodology to excited states are discussed.

PHYS 374 [752623]: Interfacial characterization of n-octanol and 3-octanol using molecular dynamic (MD) simulations

Preston B. Moore, Department of Chemistry & Blochemistry, University of the Sciences in Philadelphia, 600 South 43rd Street, Philadelphia, PA 19104, Fax: 215-596-8543, p.moore@usip.edu, and Raeanne L Napoleon, Department of the Sciences in Philadelphia, Department of Chemistry

Abstract

Molecular Dynamic (MD) computer simulations of interfacial n-octanol and 3-octanol were investigated at 298 Kelvin. The octanols were simulated at a water interface at a vapor interface and also in the bulk. These octanol-water systems were initially placed randomly into a box and were equilibrated using constant pressure techniques to minimize bias. After equilibration in which an interface formed, the octanol-water systems were simulated for 20 nanoseconds from which structural and dynamical properties were analyzed. The analysis consisted of the comparison of the surface structures with that of the experimental results. Our results supports

the idea of order interface only 1-2 molecular layers deep before bulk properties are reached. Our simulations of the orientational dynamics suggest frustration at the surface. The octanols form a hydrogen bonded network with the water ordering the surface molecules, creating a hydrophilic/hydrophobic layering.

PHYS 375 [766900]: Explicit solvent TDDFT simulations of anomalous Stokes shift in substituted [2.2] paracyclophane

Artem Masunov¹, Sergei Tretiak¹, Janice W. Hong², and Guillermo C. Bazan³. (1) Theoretical Division, Los Alamos National Laboratory, MS B268, Los Alamos, NM 87545, amasunov@t12.lanl.gov, (2) Department of Chemistry, University of California, Santa Barbara, (3) Department of Chemistry and Biochemistry, UC Santa Barbara

Abstract

The [2.2] paracyclophane (pCp) core provides a basis for the examination of interchromophore electron coupling. Chromophores built upon this pCp core are unique in that besides excitation typical to one chromophore unit, they display excitations that correspond to through-space charge transfer from one unit to another. Recently a water-soluble, pCp-based chromophore octa(tetrakisbutylammonium)4,7,12,15-tetra-(3',5'-bisbutoxysulfonate)-styryl[2.2]paracyclophane had been experimentally studied and its emission spectrum was compared to a hydrophobic analog in nonpolar solution. In this contribution we investigate the reasons for unusually strong solvatochromic shift and increase in fluorescence lifetime upon increased solvent polarity. Our TD-B3LYP calculations confirm that solvatochromic shift in absorption spectrum is negligible. To simulate the emission spectrum, we optimized the molecular geometry of the excited states were at CIS level of theory and found that long-lived "phane" state is less polar than "chromophore" state, and thus its stabilization can not be described with polarizable continuum solvation models. In order to alleviate this shortcoming, we extended quantum cluster equilibrium model to describe the explicit solvation in the excited state. We found that in one of the most stable configurations two chromophore units are linked together by H-bonding water molecules. This leads to dihedral twist which disrupts pi-conjugation chain and destabilizes short-lived state, while long-lived state remains almost unaffected.

PHYS 376 [755796]: Extensions of the molecular dynamics with quantum transitions approach for proton transfer in solution

Soo Young Kim, Department of Chemistry, The Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University

Abstract
Nuclear quantum effects such as tunneling, energy quantization, and zero point energy play an important role in proton transfer reactions. Since a fully quantum mechanical treatment of condensed phase systems is not practical, mixed quantum/classical methods have been used to simulate proton transfer reactions in solution. The molecular dynamics with quantum transitions (MDQT) method incorporates nonadiabatic transitions among the vibrational states. We have extended the MDQT method to treat both the hydrogen and the donor-acceptor vibrational motions quantum mechanically. Here we present the application of this approach to a model system representing intramolecular proton transfer within a phenol-amine complex in liquid methyl chloride. In addition, we explore the fundamental effects of dissipation through the

application of the MDQT method to a symmetric double well system coupled to a dissipative bath. The calculated rates for this model system are compared to the exact quantum dynamical rates.

PHYS 377 [749465]: Isotope effects with the nuclear-electronic orbital approach

Andres Reyes and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, Fax: 8148653314, reyes@chem.psu.edu

Abstract

The nuclear-electronic orbital (NEO) approach was previously developed in our group to incorporate nuclear quantum effects in electronic structure calculations. In this approach, specified hydrogen nuclei are treated quantum mechanically on the same level as the electrons. We have extended the NEO approach to treat bosons as well as fermions quantum mechanically. This extension enables the calculation of deuterium kinetic isotope effects. We have successfully implemented this approach at the NEO-HF (Hartree-Fock), NEO-CI (configuration interaction) and NEO-MCSCF (multiconfigurational self-consistent-field) levels. Applications of this approach to small molecules will be presented. In addition, the calculation of tunnel splittings for systems involving hydrogen transfer will be discussed.

PHYS 378 [747621]: AEI: Kinetic Monte Carlo model for graphite slabs exposed in low-Earth orbit

K. Lance Kelly and John C. Tully, Dept. of Chemistry, Yale University, PO Box 208107, New Haven, CT 06520-8107, Fax: 203-432-6144

Abstract

At 300 km altitude, i.e. low Earth orbit (LEO), the faint atmosphere interacts with satellites and space vehicles, leading to the rapid degradation of hydrocarbon materials. At orbital velocity, O (3P) (the predominant species in LEO) collides with 5 eV of kinetic energy. We are part of a theory/experiment collaboration studying O + graphite as a test surface. Described here is a "top down" approach--modeling macroscopic surface morphologies (such as pitting, roughness) with a code we developed for the removal of carbon atoms. This kinetic Monte Carlo method efficiently simulates micron-sized slabs (38M surface atoms). Results qualitatively match the observed temperature dependence of roughness and pitting, and they also suggest the existence of an important interlayer reaction mechanism.

PHYS 379 [755789]: Thermochemical and kinetic analysis on decomposition and oxidation of sulfur hydrocarbons

Fei Jin, **Joseph W. Bozzelli**, Li Zhu, and Jongwoo Lee, Chemistry, New Jersey Institute of Technology, University Heights, Newark, NJ 07102

Abstract

Thermochemical and kinetic properties on decomposition and oxidation of di-ethylsulfides, CH₃SCH₃ and CH₃SH and radicals corresponding to loss of H atom are analyzed to understand the stability, reaction paths and kinetics of sulfur hydrocarbons (sulfides) in the atmosphere and in combustion processes. Density functional (B3LYP/6-311G(d,p)) and complete basis set

extrapolation (CBS-QB3) computational methods are utilized. Entropy and heat capacities $C_p(T)$ are determined using geometric parameters and vibration frequencies obtained at B3LYP/6-311G(d,p) level of calculation. Carbon based sulfur radicals are found to react with oxygen by mechanisms that are similar to that of normal hydrocarbons. Sulfur based radical reactions with oxygen form very shallow wells, only a few kcal-mol⁻¹, and rapidly dissociate back to reactants. Barriers and kinetics are also reported for a number of retro-ene reactions.

PHYS 380 [754774]: Vibrational couplings in peptide oligomers examined by ab initio calculations and multidimensional infrared spectral measurements

Jianping Wang¹, Chong Fang¹, Yungsam Kim¹, Paul, H Axelsen², and Robin, M Hochstrasser¹.

(1) Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, PA 19104, wang4@sas.upenn.edu, (2) Departments of Pharmacology, Biochemistry and Biophysics, and Medicine, the Johnson Foundation for Molecular Biophysics, University of Pennsylvania

Abstract

Inter and intramolecular vibrational anharmonic coupling constants are potentially useful in determining molecular structures in condensed phases. The through space and through bond vibrational couplings between amide-I modes of selected secondary structure templates (including the α -, 3_{10} - and P_{II} - helices, and the β -sheets) were evaluated by using ab initio DFT calculations on model peptides, and by using the transition charge interactions including charge fluxes. Simulations based on Hamiltonian matrix diagonalization of both one- and two-exciton states of the amide-I modes incorporating these couplings, yield intrinsic features of the 1D and 2D IR spectra of these model peptides. The results were compared with the 1D and 2D IR measurements of the isotopically substituted peptide oligomers that are available, from which the vibrational couplings were determined by examining the transition energy separations and intensities in 1D IR and the profiles of cross peaks in 2D IR. For the α -helix, the sign and magnitude of the calculated couplings for up to four consecutive amide units were in reasonable agreement with values derived experimentally. For the antiparallel β -sheets, the ¹³C-enhancement in the 1D IR spectra was reproduced by incorporating both interstrand and intrastrand coupling to ¹²C modes. These results confirm the delocalization nature of the peptide amide-I vibrations, and contribute to the understanding of the variety of peptide local structures.

PHYS 381 [755104]: Modeling a pure fluid using lattice fluid theory

Steven G. Arturo and Dana E. Knox, Department of Chemical Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102-1982, sga5892@njit.edu

Abstract

A fluid model based on lattice statistics is proposed. A Gibbs ensemble is created using the canonical ensemble proposed by Knox et al. (J. Sol. Chem., 1984). Lattice vacancies are included, allowing for system density to vary with temperature and pressure. If the random distribution of holes is described using Flory statistics, the model reduces to the Sanchez-Lacombe equation of state (J. Phys. Chem., 1976) and is similar to the model proposed by Taimoori and Panayiotou (Fluid Phase Equil., 2001). This work explores using Guggenheim statistics to describe the random distribution of holes. Given a lattice size volume, the molecular

volume, interaction energy, and number of interaction sites are fit to the critical point of the pure fluid. Physical trends are seen in these quantities, and pure fluid volumetric data using these parameters is presented.

PHYS 382 [755412]: Vibrational energy relaxation of liquid oxygen or liquid nitrogen from a semiclassical molecular dynamics

Being J. Ka¹, Qiang Shi², and Eitan Geva². (1) Department of Chemistry, University of Michigan, 930 N. University, Ann Arbor, MI 48109-1055, being@umich.edu, (2) Department of Chemistry, University of Michigan

Abstract

Vibrational energy relaxation rate constants for neat oxygen molecules in liquid were calculated from Local harmonic approximation of Linearized semiclassical representation (LHA-LSC). The results at various temperatures through 60K to 90K provide similar order of magnitude of rate constants as experimental data, which would not be directly obtainable from corresponding classical molecular dynamics without ad hoc quantum correction factors. The current results justify that our LHA-LSC theory can be extended to broader temperature range of liquid. Vibrational energy relaxation of liquid nitrogen from LSC-IVR is also compared to that of liquid oxygen at the same temperature, 77K.

PHYS 383 [766868]: Modeling mechanical molecular nanodevices

Xiange Zheng¹, Rebecca Orndorff¹, and Karl Sohlberg². (1) Dept. of Chemistry, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104-2875, xiangezheng@yahoo.com, (2) Department of Chemistry, Drexel University

Abstract

The modeling of molecular “nanodevices” is a formidable computational problem. Some of the simplest known examples are based on switchable rotaxanes consisting of ca. 200 atoms. Typically, the switching mechanism involves multiple charge or electronic states of the system, demanding a true quantum electronic structure description. An efficient modeling procedure will be presented. The theoretical foundation of the procedure is the concept that sampling a potential energy surface at points near local minima produces a conformational density of states (CDOS), which at most, varies linearly from the true CDOS. A propagation-of-errors proof for this foundation will be presented, as well as a numerical test. Finally, the procedure will be demonstrated for a [3]rotaxane. Statistical analysis of the structure-energy profile shows that prox- co-conformations (adjacent rings) are favored over dist- ones (separated rings), in agreement with experimental observations. Further analysis reveals that co-conformational preference correlates to backbone coiling.

PHYS 384 [762295]: Molecular dynamics simulations of laser ablation

Patrick F. Conforti¹, Yaroslava G. Yingling², and Barbara J. Garrison². (1) Department of Chemistry, The Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, pat@chem.psu.edu, (2) Department of Chemistry, Penn State University

Abstract

The interaction of lasers with organic materials, or laser ablation, has shown to be important in such applications as laser surgery, mass spectroscopy, microfabrication on surfaces, and pulsed laser deposition of organic films and coatings. Even though the development of applications has been numerous, the intricacy of the processes involved in laser ablation, which include laser excitation of absorbing molecules, material degradation, and ejection of material, impede a complete analytical description. The dependence of material ejection on laser pulse duration, the fluence and wavelength of light, laser spot size, and initial temperature of the substrate material has shown to be important. In addition several imaging methods have been used to study the dynamics of material ejection and ablation plume expansion. Our group has employed a molecular dynamics (MD) simulation approach to understand a complete microscopic picture of the processes involved in the laser ablation.¹ The advantage of the MD studies is that only details of the microscopic interactions need to be specified with the limitation being the time and scale of the simulation. We present the results of our study on the dependence of material ejection mechanism on laser fluence and laser pulse duration in the thermal confinement regime of ultraviolet laser ablation. The simulations also show the differentiations in the ablation plume composition and the ablation threshold value.²

References: 1. Zhigilei, L. V.; Leveugle, E.; Garrison, B. J.; Yingling, Y. G.; Zeifman, M. I. Chem. Rev. 2003 103, 321-347. 2. Yingling, Y. G.; Conforti, P. F.; Garrison, B. J.; Appl. Phys. A, in press.

PHYS 385 [763567]: Implementation and performance of the modified Becke-Roussel exchange-correlation functional

Artur F. Izmaylov, Sergey N. Maximoff, and Gustavo E Scuseria, Department of Chemistry, Rice University, Houston, TX 77005, arthuri@rice.edu

Abstract

Becke's meta-GGA exchange-correlation functional [A. D. Becke and M. R. Roussel, Phys.Rev. B 39, 3761 (1989); A. D. Becke, J. Chem. Phys. 88, 1053 (1988)] is based on appealing physical ideas but suffers from numerical instabilities that hinder its self-consistent implementation within the Kohn-Sham scheme. We present a modification of the Becke-Roussel model that circumvents numerical problems and surpasses in accuracy the original approximation. The revised functional has excellent convergence properties and performance, as demonstrated by computing enthalpies of formation, ionization potentials, electron and proton affinities, vibrational frequencies, NMR shielding tensors, and spin-spin coupling constants for a test set of molecules.

PHYS 386 [764697]: Nitrous oxide formation in UV photolysis of O₃/O₂/N₂ mixtures: A useful testbed for the reaction dynamics involving electronically excited species

Sheo S. Prasad, Creative Research Enterprises, 6354 Camino del Lago, Pleasanton, CA 94566, Fax: 925-426-9417, ssp@CreativeResearch.org

Abstract

Understanding how simple gas phase reactions occur on excited electronic state surfaces is one of the major challenges facing the fields of reaction dynamics and kinetics. Formation of the N_2O in UV photolysis of $O_3/O_2/N_2$ is one of the useful testbeds for that challenge, since N_2O formation from N_2 and either O_3 or O_2 or O_3 in ground state is either spin forbidden or highly endothermic. The talk will explain how the cumulative evidence from various experiments suggest N_2O formation from excited singlet and triplet O_3 . With the present understanding of the chemical reaction mechanism, it is difficult to comprehend how rapidly dissociating molecules may drive a reaction. However, it is equally difficult to ignore the messages of the new experimental developments (including the NO_x formation from O_2 B-triplet sigma). These call for more laboratory experiments and quantum chemistry studies of the reaction dynamics of dissociating species.

PHYS 387 [748524]: Nonorthogonal configuration interaction treatment of density localization in a model hydrogen tunneling system

Jonathan H Skone, Michael Pak, and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, jhs204@psu.edu

Abstract

Recently the nuclear-electronic orbital (NEO) method was developed in our group to treat specified nuclei on the same level as electrons in molecular orbital calculations. For hydrogen tunneling systems, the exact ground state nuclear-electronic wavefunction has bilobal, delocalized character. Within the NEO framework, two nuclear basis function centers are used to represent the tunneling hydrogen nucleus. The single configurational nature of the NEO-HF (Hartree-Fock) nuclear-electronic wavefunction leads to a ground state solution in which the nuclear density is localized on one of the two centers. We have developed a nonorthogonal NEO-CI (configuration interaction) method to avoid the non-physical NEO-HF solution. In this approach, the total wavefunction is represented as a linear combination of two nonorthogonal NEO-HF localized wavefunctions. Analysis of this two-configuration nonorthogonal NEO-CI approach will be presented for a model hydrogen tunneling system.

PHYS 388 [754146]: Physics behind conformance of microscopic dielectric response of dipolar solvents to macroscopic continuum model

Edward L. Mertz, NICHD, National Institutes of Health, 9000 Rockville Pike, B.9, Rm. 1E125, Bethesda, MD 20892, mertze@mail.nih.gov

Abstract

Two contradicting dielectric concepts existed during last decades: seemingly more rigorous non-local theory relating dielectric response to spatial structure of solvent at molecular scale and the macroscopic dielectric continuum model assuming absence of such structure. These concepts were analyzed against dielectric response energies of dipolar solvents measured for molecular solutes with negligible non-dielectric contributions from specific solute-solvent interactions. For the analyzed solutes, the macroscopic assumption of structureless solvent is strongly violated. Nevertheless, the data conform to the macroscopic model surprisingly well, while existing non-

local models accounting for solvent structure fail qualitatively. This paradox can be resolved by a mean-field model based on symmetry properties of dipole-dipole correlator. The model predicts that response of a wide class of dielectrics to charges located outside the dielectric (or inside solute cavity) may conform to the macroscopic theory despite non-negligible spatial structure of the dielectric.

PHYS 389 [746784]: Proton-coupled electron transfer in soybean lipoxygenase
Elizabeth R Hatcher, Alexander V Soudackov, and Sharon Hammes-Schiffer, Department of Chemistry, Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802, erh119@psu.edu

Abstract

We present an investigation of the proton-coupled electron transfer reaction catalyzed by soybean lipoxygenase-1. This reaction is studied with a multistate continuum theory that represents the transferring hydrogen nucleus as a quantum mechanical wavefunction. Both classical and quantum mechanical treatments of the proton donor-acceptor vibrational motion are presented. The temperature dependence of the calculated rates and kinetic isotope effects is in agreement with experimental data. The weak temperature dependence of the rates is due to the small free energy barrier arising from a balance between the reorganization energy and the reaction free energy. The unusually high deuterium kinetic isotope effect of 81 is due to the small overlap of the reactant and product proton vibrational wavefunctions. The proton donor-acceptor vibrational motion plays a vital role in decreasing the dominant donor-acceptor distance relative to its equilibrium value to facilitate the proton-coupled electron transfer reaction.

PHYS 390 [752594]: Qualitative and quantitative investigation of aqueous insolubility using crystal packing simulations

Laura A. Deschenes, Pharmaceutical Sciences, Pfizer Global R&D, Michigan Labs, 2800 Plymouth Rd, Ann Arbor, MI 48105, Fax: 734-622-3609, laura.deschenes@pfizer.com, Michael A. Walters, Pfizer Global Research and Development-Ann Arbor, and Howard Y. Ando, Ann Arbor Laboratories, Pfizer Inc., Pfizer Global Research & Development

Abstract

The prediction and prevention of aqueous insolubility has been a problem of interest to the pharmaceutical community for many years. Insolubility arises from either an unfavorable interaction between solvent and solute or a too favorable solid phase interaction between solute and solute. A number of well- models (ClogP being the best known) are used to predict an unfavorable interaction between solvent and solute, but have failed to account for strong solid state interactions between solute molecules. This study presents a Monte-Carlo based method for simulating crystal packing structures using the Accelrys Cerius2 polymorph predictor suite. The simulated structures provide valuable qualitative information about the interactions that hold molecules together. Furthermore, a calculation of cohesive energy based on the simulated packing structure gives a single quantitative parameter that encompasses all the interactions taking place in the crystal. Simulated cohesive energy gives a measure of the barrier to dissolution posed by the crystalline attractions, and is shown to be a good predictor of insolubility across a class of structurally related molecules.

PHYS 391 [766960]: Reaction paths, kinetics and thermochemical properties on reaction of methylthiol (CH₃SH) and dimethylsulfide (CH₃SCH₃) radicals with O₂

Fei Jin, Li Zhu, and **Joseph W. Bozzelli**, Chemistry, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, lxz6816@njit.edu

Abstract

Thermochemical properties and reaction pathways for the association of O₂ with C•H₂SH, CH₃S•, and CH₃SC•H₂ radicals are analyzed. CBS-QB3 and density Hf,298, S298, and Cp(T)Δfunctional methods are utilized to estimate for reactants C•H₂SH, CH₃S•, and CH₃SC•H₂, intermediate radicals C(OO•)H₂SH, CH₃SOO•, CH₃OSO•, CH₃SCH₂OO•, C•H₂SCH₂OOH and transition states. Isodesmic working reactions are applied to evaluate enthalpies of formation. Intramolecular rotation potentials are calculated at the B3LYP/6-311G(d,p) level and used to determine contributions to entropy and heat capacities. Reaction paths involve intramolecular hydrogen atom transfer to the peroxy radical, peroxy radical addition to the sulfur, dissociation and further reaction of the H atom transfer isomers. Kinetics parameters are evaluated using chemical activation analysis and unimolecular dissociation of the stabilized adducts.

PHYS 392 [751109]: Linear scaling multi-proton MSEVB algorithms

Feng Wang, The Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, UT 84112, seymour@hec.utah.edu, and Gregory A. Voth, Department of Chemistry & Henry Eyring Center for Theoretical Chemistry, University of Utah

Abstract

A novel iterative approach based on Multi-State Empirical Valence Bond (MS-EVB) model is described. This approach allows the dynamics of proton transport to be described efficiently and accurately in a Molecular Dynamics simulation. The computational cost of this new iterative approach scales linearly with respect to the number of protons in the simulation cell. Test simulations were carried out in water solution and on NafionTM membranes. Very insightful results were obtained from these simulations.

PHYS 393 [751845]: Relaxation of rotationally hot CN in liquid argon

Guohua Tao and Richard M. Stratt, Department of Chemistry, Brown University, 324 Brook Street, Providence, RI 02912, Guohua_Tao@brown.edu

Abstract

Recent experiments have shown that highly excited rotational states survive for long times in liquids, offering us an unprecedented microscopic view of the rotational relaxation process. We have studied this process with classical molecular dynamics simulations of the relaxation of the highly rotationally excited CN radical in liquid Argon. The relaxation we observed is quite long, about 10 ps, with a strikingly bimodal distribution of rotational states. One of interesting results is that CN shows a strong orientational coherence resembling a free gas phase rotator for about 2

ps. Surprisingly, the relaxation rates for molecular reorientation and rotational energy are very different at short times.

PHYS 394 [754726]: MAME: Minimal Atomic Multipole Expansion of molecular fields

Eugene V. Tsiper, Center for Computational Material Science, George Mason University and Naval Research Laboratory, NRL Code 6390, 4555 Overlook Ave. S/W, Washington, DC 20375, and Kieron Burke, Department of Chemistry and Chemical Biology, Rutgers

Abstract

Careful choice of atomic multipoles based on the Lewis structure reproduces molecular fields everywhere beyond molecular volume and eliminates redundancies inherent in the distributed multipole analysis. Resulting atomic charges conform to chemical intuition, are unique, rotationally-invariant and free of sampling errors. They also recover the total charge, dipole and quadrupole moments of the molecule.

Accurate polarization energies result when MAME is coupled with distributed polarizabilities. Hydrogen bonding and other features of well-studied water pair potential are reproduced to fine detail, with parameters based almost entirely on experimental data for a single water molecule.

The minimal set of multipoles normally consists of a charge on each heavy atom, a dipole moment on every hydrogen, and a few higher multipoles to describe lone pairs. The hydrogen is best described by a dipole placed at the proton and directed along the bond because its sole electron participates in the bond and is not centered at the proton.

PHYS 396 [754438]: Simulation study of space charge patterns to trap dipoles in photoconductive film

Choongkeun Lee¹, Nam Soo Lee¹, Mino Yang¹, and Nakjoong Kim². (1) Department of Chemistry, Chungbuk National University, Cheongju 361-763, South Korea, cckbug@hanmail.net, (2) Department of Chemistry, Hanyang University

Abstract

Formation of the space charge field in photoconductive film has been extensively studied in experimental and theoretical fields. Baessler and Novikov had established theoretical works using models about photoconductivity in molecularly doped polymers, i.e., Gaussian disorder model(GDM) and correlated disorder model(CDM). Schieldkraut exploited the phenomena of space charge generation using numerical method. We have employed the disorder models to obtain a correlation between the physical properties of trap molecules and the space charge generation by Monte Carlo simulation method. Simulation study shows that the trap depth is strongly dependent on the dipole moment of trap molecules, and plays a significant role on the space charge generation, mainly due to the charge redistribution or the charge recombination process in the photoconductive film. The detailed correlations between the physical properties of trap molecules and the space charge generation will be presented.

PHYS 397 [751766]: Solvent effects in the reaction of peroxyxynitrite and carbon dioxide

Mariano C. Gonzalez Lebrero and Dario A. Estrin, Department of Chemistry, University of Buenos Aires, Ciudad Universitaria, Pabellon II, Buenos Aires C1428EHA, Argentina, Fax: 541145763341, nano@pepa.q1.fcen.uba.ar

Abstract

Peroxyxynitrite is formed in vivo by the reaction of NO with the anion superoxide. CO₂ is one of the main targets of peroxyxynitrite, due to its large physiological concentrations. The reaction yields an adduct, which decomposes in the radicals CO₃ and NO₂. In this work we investigate the environment influence on the formation of this adduct using a QM-MM scheme in which the reactants are treated at the QM DFT level, while the solvent is treated classically using the TIP4P water model. Reaction free energy profiles were obtained using umbrella sampling techniques. We find that the reaction is barrierless in vacuum, but it exhibits a significant barrier in water solution. The barrier is associated to the large degree of charge redistribution of the adduct upon reaction, which affects profoundly the structure of the first solvation shell.



PHYS 398 [755683]: Molecular properties from the auxiliary density: Selected applications of deMon 200X

Alberto Vela, Chemistry, CINVESTAV, Av. I.P.N. 2508; A.P. 14-740, Mexico City 07000, Mexico, Fax: 52 55 50 61 71 13, avela@mail.cinvestav.mx

Abstract

After a brief review of the fundamentals behind the introduction of the auxiliary density to avoid the evaluation of three-center integrals in Kohn-Sham calculations, as it is done in deMon 200X, it will be shown how this approach plus other algorithmic improvements lead to a dramatic reduction of the computational time required to optimize molecular geometries and calculate several molecular properties. To illustrate the differences of using the orbital and the auxiliary density, the following applications will be presented: • Conformational search of several naturally occurring aminoacids with local and GGA exchange-correlation functionals. • Electron density and molecular electrostatic potential of several cyclodextrins. • Electric field generated by several models of carbon nanocones.

PHYS 399 [769053]: Structure and energetics of [B, N, O, H₂]: Quantum mechanics shows multiple minima

Carol A. Deakyne and Aaron K. Corum, Department of Chemistry, University of Missouri - Columbia, Columbia, MO 65211-7600, Fax: 573-882-2754, deakynec@missouri.edu

Abstract

High level quantum chemical calculations have been performed to study [B, N, O, H₂], which is isoelectronically related to the well-known ketene H₂CCO and to [B, C, F, H₂]. Cyclic and acyclic systems with both B–N and B–O connectivities have been examined for the singlet state, and a variety of isomeric forms have been identified. As chemical intuition suggests the most stable structure is H₂NBO. However, thus far, eleven additional minima have been disclosed on the potential energy surface, including classical chain structures, ring structures and hydrogen-bonded structures. AIM and NBO analyses have been carried out to gain an understanding of the bonding in the various isomeric forms of [B, N, O, H₂].

PHYS 400 [755043]: Nearly degenerate excitations in density functional theory

Fan Zhang, Department of Physics and Astronomy, Rutgers, 136 Frelinghuysen Road, Piscataway, NJ 08854, Fax: 732-445-4343, fzhang@physics.rutgers.edu, Neepa T. Maitra, Department of Physics and Astronomy, Hunter College of the City University of New York, Robert J. Cave, Department of Chemistry, Harvey Mudd College, and Kieron Burke, Department of Chemistry and Chemical Biology, Rutgers

Abstract

Excited state properties can be calculated in density functional theory (DFT) via different approaches. Time-dependent DFT (TDDFT) with linear response yields excitations, but only single excitations within the (standard) adiabatic approximation. A frequency-dependent exchange-correlation kernel is needed to capture double excitations. Second-order Goerling-Levy perturbation theory can be applied to both non-degenerate and nearly degenerate excited states. Some excitations are shown to be poorly described to first order (i.e. in exact exchange), no matter how weakly correlated the system is. Results are demonstrated on a simple model and short chain polyenes.