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Eighteenth Annual West Coast Theoretical Chemistry Conference: Book of Abstracts

Berkeley, California
April 9–11, 1997

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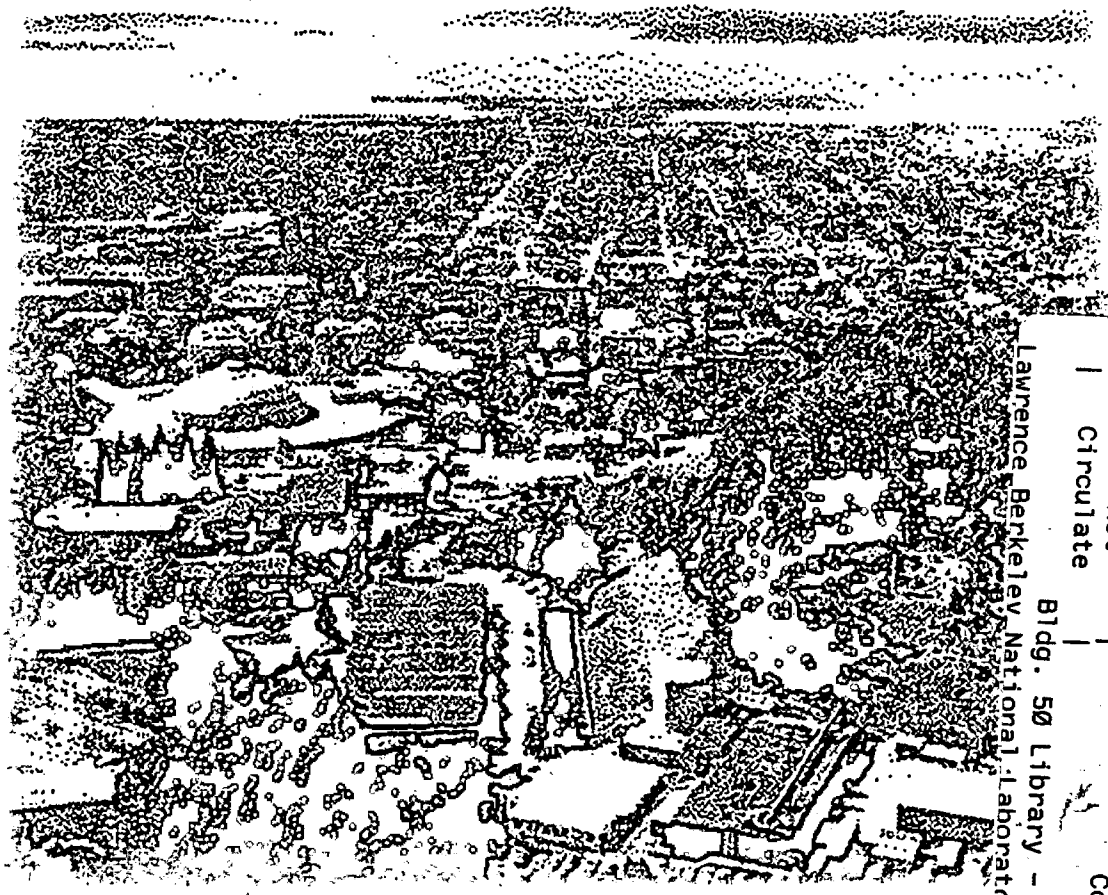

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Eighteenth Annual

West Coast Theoretical Chemistry Conference

Ernest Orlando Lawrence Berkeley National Laboratory April 9–11, 1997

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West Coast Theoretical Chemistry Conference

WEDNESDAY MORNING

Session Honoring the Memory of Bowen Liu

A.D. McLean, *Presiding*

8:30 Registration. Building 50 Auditorium Lobby

9:00 Welcome.

9:15 The Science of Bowen Liu. **H.F. Schaefer III**, University of Georgia, Athens

10:15 Intermission

10:30 Making Molecular Simulations Useful to Computational Chemists. **William C. Swope**, IBM Almaden Research Center

11:30 Application of density functional theory to systems containing metal atoms. **Charles W. Bauschlicher, Jr.**, NASA Ames Research Center

12:30 Lunch

WEDNESDAY AFTERNOON

K.A. Robins, *Presiding*

1:30 New Methodology in the Quasiclassical Simulations of A + BC Reactive Events. **Michael R. Salazar** and Jack Simons

1:50 Energy Transfer Rate for a Two-Dimensional Solute in a Dissipative Medium. **Sabine K. Reese** and Susan C. Tucker

2:10 Semiclassical Initial Value Representation for Electronically Non-Adiabatic Molecular Dynamics. **Xiong Sun** and William H. Miller

2:30 Intermission

2:50 Effects of Protein Dynamics on Biological Electron Transfer. **Iraj Daizadeh** and A.A. Stuchebrukhov

3:10 Semiclassical molecular dynamics simulations of ultrafast photodissociation dynamics associated with the Chappius bands of ozone. **Victor S. Batista**

3:30 Poster Session I

Poster Session I

Building 54, 3:30-5:00

1. Classical Trajectory Simulation Using a C^1 Interpolant to determine the reactive energy Threshold for the Reaction $Al^+ + (H_2; D_2;$ or $HD) \rightarrow (AlH^+ + H; AlD^+ + D;$ or $AlH(D)^+ + D(H))$. **R.L. Bell** and Jack Simons

2. The Affect of Intrinsic Twist on the Structure of Chromatin as Modeled by an Elastic Rod. **Thomas C. Bishop** and John E. Hearst

3. DFT Calculations on the Proton Affinity of H-ZSM-5. **Nick O. Gonzales**, Alexis T. Bell and Arup K. Chakraborty

4. *Ab Initio* Study of the MgO/Water Interface: An Embedded Cluster Model Including Solvent Effects. **Michael A. Johnson**, Eugene V. Stefanovich, and Thanh N. Truong

5. Lattice Sums for Irregularly Shaped Semi-infinite Solids. **Gwon Hee Ko** and William H. Fink

6. Local Electron Correlation Methods for Large Molecules. **Paul E. Maslen** and Martin Head-Gordon

7. New Methods for Ab Initio Excitation Energy Calculations. An Approach for Near Degeneracy Problem of Single Reference Configuration Interaction Method. **Manabu Oumi**, David Maurice and Martin Head-Gordon

8. Ab Initio Analysis of the Geometries, Electronic Structure and Harmonic Frequencies of Nickel Porphyrins. **Mari Carmen Piqueras** and Celeste McMichael Rohlfing

9. Theoretical Study of Reaction Mechanisms and Transition State location Using *Ab Initio* Molecular Orbital Calculations. **Chirine Soubra-Ghaoui** and Thomas A. Albright

10. Semiclassical Methods Applied to Reactive Systems. **Bruce W. Spath** and William H. Miller

11. A General Methodology for Quantum Modeling of Free Energy Profile of Reaction in Solution: An Application to the Menshutkin NH_3 + CH_3Cl Reaction in Water. **Thanh N. Truong**, Thanh-Thai T. Truong and Eugene V. Stefanovich

12. Energy level statistics and classical phase space analysis for torsion-rotation interactions. **James T. Vivian** and John H. Frederick

13. Thermal Rate Constant Calculation Using Flux-Flux Autocorrelation Function: Application to $Cl + H_2 \rightarrow ClH + H$ Reaction. **Haobin Wang**, Ward H. Thompson, and William H. Miller

14. Stabilization of a one-dimensional short-range potential in high intense laser fields. **Danny Barash**, Ann E. Orel, and K.C. Kulander

THURSDAY MORNING

T. N. Truong, *Presiding*

9:00 VRT Spectroscopy of Water with Terahertz Lasers: Towards a Complete Molecular Model of the Liquid. **R.J. Saykally**, University of California, Berkeley

10:00 Intermssion

10:20 Tunneling Currents and Pathways of Electron Transfer in *E. coli* Photolyase. **Margaret S. Cheung** and Alexei A. Stuchebrukhov

10:40 Simulation of Water-Chlorinated Hydrocarbon Interfaces with Many-Body Potentials. **Tsun-Mei Chang** and Liem X. Dang

11:00 Characterization of the Clustering Behaviour of a Supercritical Two-Dimensional Lennard-Jones Fluid. **M.W. Maddox** and S.C. Tucker

11:20 A theoretical approach for modeling reactivity at solid/liquid interfaces: Application to NaCl(100)/water. **Eugene V. Stefanovich** and Thanh N. Truong

11:40 The Photophysics of the Three Lower Lying Singlet States of Pyrazine. **Clemens Woywod**

12:00 Direct Evidence for Modified Solvent Structure Within the Hydration Shell of a Hydrophobic Amino Acid. Teresa Head-Gordon, **Jon M. Sorenson**, Alexander Pertsemlidis and Robert M. Glaeser

12:20 Lunch

THURSDAY AFTERNOON

W.H. Miller, *Presiding*

1:30 Sextuple Zeta Core-valence Correlation Consistent Basis Sets: Benchmark Calculations Near the Complete Basis Set Limit. **Angela K. Wilson** and Thom H. Dunning, Jr.

1:50 Electronic Structure of Large Systems: Linear Scaling in Computation of the One Electron Density Matrix. **Roi Baer** and Martin Head-Gordon

2:10 Ab-Initio Calculations of Electron and Hole Transport in CsI Crystals Doped with Tl and Na. **S.E. Derenzo** and M.J. Weber

2:30 Intermission

2:50 Compact Variational Wavefunctions based on Natural Orbitals. **C. David Sherrill** and H.F. Schaefer

3:10 Linear scaling schemes for self-consistent field and coupled perturbed theories using density matrix-based formulations. **Christian Ochsenfeld** and Martin Head-Gordon

3:30 Poster Session II

Poster Session II

Building 54, 3:30-5:00

1. Theoretical Study of Photodissociation of C_2H Radical. **Goksin Apaydin-Erdogan** and William H. Fink

2. Thermal Rate Calculations of Free Base Porphyrin Tautomerization. **Robert L. Bell** and Thanh N. Truong

3. Investigation of some relativistic approximations. **Thomas Enevoldsen** and Kenneth G. Dyall

4. Improving the Efficiency of Perturbative Monte Carlo Simulations Using QM/MM Potentials. **Tom J. Evans**, Thanh N. Truong and Jack Simons

5. Quantum mechanical pressure-dependent reaction and recombination rates for $O + OH \rightarrow H + O_2$, HO_2. **Timothy C. Germann** and William H. Miller

6. Ultrafast Non-Adiabatic Dynamics in Electronically Excited Polyatomic Systems on "on the fly" Generated PES". **A.I. Krylov**, C.D. Sherrill and M. Head-Gordon

7. A New Quantum Chemistry Method: Polarized Atomic Orbitals. **Michael S. Lee** and Martin Head-Gordon

8. Long-Distance Electron Tunneling in Homogeneous Continuum Model. **EunJoo Lee** and Alexei A. Stuchebrukhov

9. Ab intio Studies of Hydrogen Bonding Effects on the Tyrosyl Radical. **Dianne Meador** and William H. Fink

10. *Ab Initio* Characterization of the Electronically Excited States of Carbonyl Anions. **Kathleen A. Robins** and Chirine S. Ghaoui

11. Thermal Reaction Rates for $OH + O \rightarrow H + O_2$ from Flux Autocorrelation Functions: $J \neq 0$ in the Helicity Conserving Approximation. **David E. Skinner** and William H. Miller

12. Thermal Rate Constants Via Semiclassical Transition State Theory. **Kathy L. Sorge** and William H. Miller

13. A Parallel Implementation of the Classical Generalized Conductor-like Screening Model (GCOSMO), and its Application to Solvation of Macromolecules. **James M. Vollmer**, Eugene V. Stefanovich and Thanh N. Truong

FRIDAY MORNING

T.H. Dunning, Jr. *Presiding*

9:00 Low-energy electron scattering from polyatomic molecules: the role of electron correlation and the interface with quantum chemistry **C. W. McCurdy**, Lawrence Berkeley National Laboratory

10:00 Intermission

10:20 Calculation of ESR *G*-Tensors Based on Gauge Including Atomic Orbitals and Density Functional Theory. **Georg Schreckenbach** and Tom Ziegler

10:40 Linear Coulomb Builds and Diagonalization Free Energy Minimizations. **Christopher A. White** and Martin Head-Gordon

11:00 Using Direct and Cached Integrals in Parallel Quantum Chemistry Algorithms. **Adrian T. Wong**

11:20 Interfacing relativistic and nonrelativistic methods. **Kenneth G. Dyall**

11:40 End Of Conference

The Science of Bowen Liu

Henry F. Schaefer III
Center for Computational Quantum Chemistry
University of Georgia, Athens

Abstract

Bowen Liu must be considered one of the genuine pioneers in the field of computational quantum chemistry. His research, ranging from state-of-the art methods for the evaluation of molecular integrals to multiconfiguration self-consistent field methods to the identification and analysis of the basis set superposition error (BSSE), sets a high standard for future generations. Further, as part of a scientific team including Doug McLean, Megumu Yoshimine, and Paul Bagus, Bowen Liu made IBM San Jose a powerful research center for the study of molecular quantum mechanics.

Making Molecular Simulations Useful To Computational Chemists

William Swope
IBM Almaden Research Center
650 Harry Road
San Jose CA 95120

Abstract

I will provide some memories of Bowen Liu and a discussion of some of his last scientific efforts, which involved, of all things, an attempt to make statistical mechanics techniques useful to the field of computational chemistry.

Several characteristics of statistical mechanical methodologies conspire to make the field much more of a black art than most people care to admit. Among these are statistical sampling errors, the difficulty in knowing when a system is equilibrated, effects due finite system size, and the approximations made to simplify molecular interactions enough to make the calculations possible.

Quantum chemistry methodologies, on the other hand, have evolved to the point that they are reliable, robust and useful to non-experts. In an effort to make statistical mechanical techniques just as accessible, a great deal of effort was spent by Bowen and by the people working with him to remove some of the more mysterious aspects of the black art.

Finally, I will share a number of amusing observations Bowen and I made about the differences between quantum chemists and molecular simulation people. Understanding these differences is an important aspect of effective interdiscipline communication.

Application of density functional theory to systems containing metal atoms

Charles W. Bauschlicher, Jr.
NASA Ames Research Center
Moffett Field, CA 94035

March 24, 1997

Abstract

The accuracy of density functional theory (DFT) for problems involving metal atoms is considered. The DFT results are compared with experiment as well as results obtained using the coupled cluster approach. The comparisons include geometries, frequencies, and bond energies. The systems considered include MO_2, $M(OH)_n^+$, MNO^+, and MCO_2^+. The DFT works well for frequencies and geometries, even in cases with symmetry breaking, however, some examples have been found where the symmetry breaking is quite severe and the DFT methods do not work well. The calculation of bond energies is more difficult and examples of the successes as well as failures of DFT will be given.

New Methodology in the Quasiclassical Simulations of A + BC Reactive Events

Michael R. Salazar and Jack Simons
University of Utah
Salt Lake City, UT 84112

Traditionally, in the study of reactive dynamics on *ab initio* potential energy surfaces (PES) one is forced to fit the PES to an global analytical function (GAF). The dynamics of the system are then propagated on this GAF. The assumption of this technique is that the GAF is representative of the true PES wherever the trajectory may sample. In our experience this technique has turned out to be very difficult and problematic.

Recently, we have developed an alternative methodology that uses the *ab initio* energies and their gradients as the basis for the interpolation of energies and gradients wherever a trajectory may sample. Our methodology subdivides the domain of a PES into simplices; this is known as the tessellation of the PES. For the dynamical evolution of the system the necessary energy and gradients are subsequently interpolated within a tessellated simplex. The interpolant guarantees the continuity of the energy and gradients across the boundary of simplices, and, therefore, one may propagate a particle or a wavefunction on this local tessellated representation of the PES rather than a global functional fit to a PES.

Energy Transfer Rate for a Two-Dimensional Solute in a Dissipative Medium

Sabine K. Reese and Susan C. Tucker
Department of Chemistry, University of California
Davis, CA 95616

Abstract

We present a new formalism for calculating the energy-transfer-limited activated barrier crossing rate of a two-dimensional solute in a dissipative medium. Previous treatments of this problem are limited, in that they are only valid for either the case of strong qz-coupling, for which the dynamics in the solute reactant well are strongly mixed and may be treated by RRKM theory, or for the case of very weak qz-coupling, for which the z-coordinate may be treated as a bath mode and eliminated. Our new theory enables us to treat the intermediate case in which the rate of energy exchange between the reactive and bound state coordinates, q and z, is of the same order as the rate of energy exchange between the solute coordinates and bath. We handle this intermediate case by introducing the curvilinear-reaction-path in qz-space as the single non-cyclic generalized coordinate of the solute. The solute-solvent potential coupling of interest is retained as a result of the curvilinear definition of this coordinate.

Semiclassical Initial Value Representation for Electronically Non-Adiabatic Molecular Dynamics

Xiong Sun and William H. Miller

Department of Chemistry, University of California, Berkeley and

Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA, 94720.

Abstract

The semiclassical initial value representation (SC-IVR), which has recently seen a great deal of interest for treating nuclear dynamics on a single potential energy surface, is generalized to be able to describe electronically non-adiabatic (i.e., multi-surface) processes. The essential idea is a quantization of the classical electron-nuclear Hamiltonian of Meyer and Miller [*J. Chem. Phys.* **70**, 3214 (1979)] within the SC-IVR methodology. Application of the approach to a series of test problems suggested by Tully shows it to provide a good description of electronically non-adiabatic dynamics for a variety of situations.

Effects of Protein Dynamics on Biological Electron Transfer

Iraj Daizadeh and A. A. Stuchebrukhov
Department of Chemistry, University of California
Davis, CA 95616

Abstract

Long-distance electron transfer plays a crucial role in fundamental biological processes such as photosynthesis and mitochondrial respiration. The rate of electron transfer in the conventional semi-classical Marcus theory is proportional to the product of two independent factors. First, the probability that polarization fluctuations that depend exponentially on standard free energy and free energy of reorganization bring donor and acceptor orbitals into (near) degeneracy. This is the so-called transition state for the electron transfer reaction. The second factor is the probability that at the transition state, the quantum particle will tunnel through the protein medium from a particular donor to acceptor orbital. The latter purely quantum probability depends on the separation distance between donor and acceptor and the nature of the biological medium.

We have found a new aspect in long-distance electron transfer reactions in proteins which reveals that the quantum mechanical tunneling process occuring at the transition state involves in an intricate way dynamics of the protein medium. (Daizadeh, I.; Medvedev, F.A.; Stuchebruchov, A.A. *Proc. Natl. Acad. Sci.* Accepted). The coupling of electronic and vibrational degress of freedom (phonons) seem to be of critical importance for the dynamics of electron transfer in proteins. This coupling results in a modification of the conventional Marcus' picture of electron transfer and adds a new element in which the traveling charge is capable of emitting or absorbing vibrational energy from the biological medium. As a result, some biological electron transfer reactions that were previously thought to be in the inverted region may in fact occur in an activationless manner.

Semiclassical molecular dynamics simulations of ultrafast photodissociation dynamics associated with the Chappuis bands of ozone.

Victor S Batista

University of California, Berkeley
Department of Chemistry
Berkeley, CA 94720-1460

We investigate the $^1B_1 -^1 A_2$ state predissociation dynamics of photoexcited O_3 using a semiclassical initial value representation (SC-IVR) method and a model Hamiltonian gained from the quantization of the classical electron-nuclear Hamiltonian of Meyer and Miller [J. Chem. Phys. 70,3214 (1979)]. We explore the capabilities of these techniques as applied to the study of realistic nonadiabatic excited state dynamics dominated by vibronic coupling by comparing with available experimental data from spectroscopic studies of the Chappuis bands of ozone.

Classical Trajectory Simulation Using a C^1 Interpolant to Determine the Reactive Energy Threshold for the Reaction $Al^+ + (H_2; D_2; \text{ or } HD) \text{ ---> } (AlH^+ + H; AlD^+ + D; \text{ or } AlH(D)^+ + D(H))$

R.L. Bell and Jack Simons
Chemistry Department
University of Utah
Salt Lake City, Utah 84112

Abstract:

For the reaction $Al^+ + HD$ ---> $AlD^+ + H$ or $AlH^+ + D$ it was observed by Armentrout and coworkers [1] that the formation of AlD^+ occurs at a considerably lower threshold energy than AlH^+. In this work we have shown that the collinear reaction is an unfavorable means to products. We have introduced a three atom classical Hamiltonian to construct the equations of motion for this system. Our dynamics simulation begins with tessellating the domain of the potential energy surface. Once the domain has been tessellated, the surface is interpolated using the Clough-Tocher Interpolating Polynomial, which provides potential energy values and gradients at any given data point. From this we employ the Adams-Moulton Fourth-Order Predictor-Corrector method to integrate our equations of motion. Our intention is to present trajectory results for the reactions $Al^+ + H_2$ ---> $AlH^+ + H$, $Al^+ + D_2$ ---> $AlD^+ + D$, and $Al^+ + HD$ ---> $AlH(D)^+ + D(H)$, and discuss the results.

1. P. B. Armentrout, *Int. Rev. Phys. Chem.*, **9**, 115 (1990)

The Affect of Intrinsic Twist on the Structure of Chromatin as Modeled by an Elastic Rod

Thomas C. Bishop and John E. Hearst

Department of Chemistry
University of California at Berkeley
Berkeley, CA 94709-1460

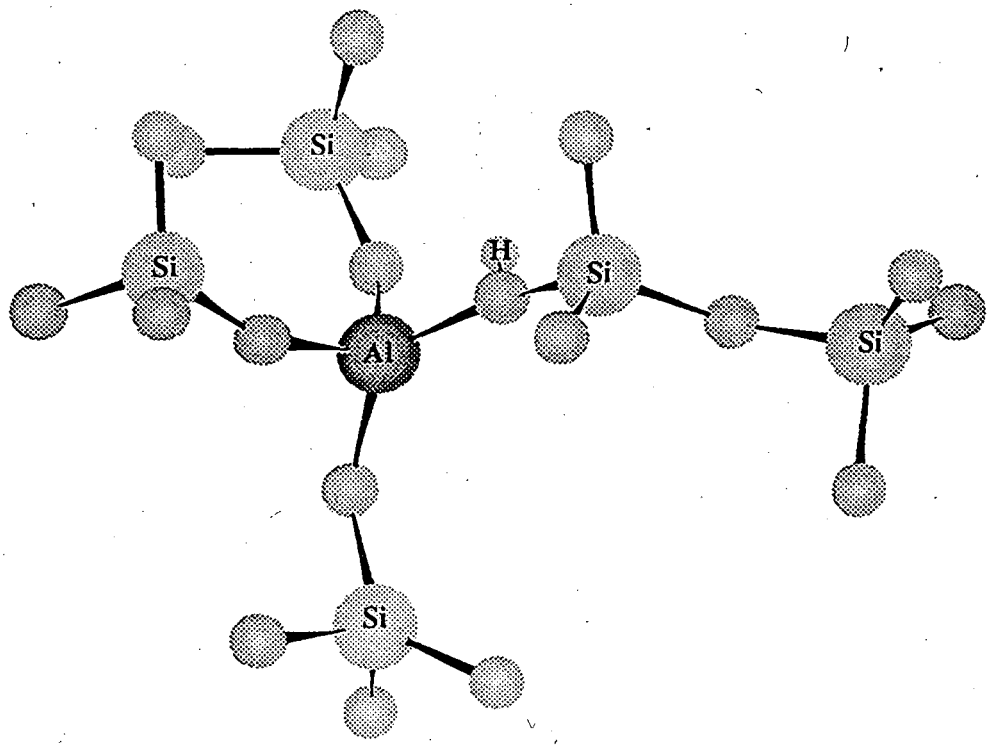
An isotropic elastic rod model is utilized as a continuum model for the structure of chromatin. By introducing a complex force and torque into the mathematical analysis of the elastic rod, the equations of equilibrium are transformed into a non-linear Schrödinger equation. This transformation allows us to obtain closed form solutions for the stationary state conformation of the elastic rod as a function of four parameters. Three parameters are determined by boundary conditions that correspond to the observed conformation of chromatin. The remaining parameter represents the intrinsic twist in the elastic rod, and it is varied to obtain conformations of the elastic rod as a function of twist. Results from this model indicate that if the structure of chromatin is influenced by the elastic properties of DNA then the structure will be strongly dependent on the inherent twist in DNA. This observation has significant implications for biological processes occurring in the cell which alter the twist in DNA. Such processes include transcription and replication.

DFT Calculations on the Proton Affinity of H-ZSM-5

Nick O. Gonzales, Alexis T. Bell, and Arup K. Chakraborty
Lawrence Berkeley Laboratory and Department of Chemical Engineering,
University of California, Berkeley, CA 94720

ABSTRACT

Experiments show that the acidity, and hence proton affinity, of the zeolite H-ZSM-5 is affected by the presence of Al atoms at the next nearest neighbor T site and by the presence of crystal defects. However, the extent to which these factors contribute to changes in the proton affinity are difficult to quantify experimentally, since all experimental methods are based on an average over all types of sites. Our aim was to identify the relative effects of local composition and defect structure on the proton affinity of H-ZSM-5. We found that the proton affinity of the bridging hydroxyl group ranges from 281 to 333 kcal/mol depending on the composition and structure of the model zeolite cluster. Our zeolite cluster is shown below without the oxygens labeled and with the terminating hydrogen atoms deleted for clarity.



Ab Initio Study of the MgO/Water Interface: An Embedded Cluster Model Including Solvent Effects

Michael A. Johnson, Eugene V. Stefanovich, and Thanh N. Truong

University of Utah
Department of Chemistry
Salt Lake City, Utah 84112

Chemistry at the interface between water and metal oxides is important in the field of geochemistry and is central to environmental issues. In the present work, a dielectric continuum representation of bulk water was coupled with an embedded cluster model to study the solvation effects on molecular water adsorption at the MgO(001) surface. In particular, the quantum cluster consists of a molecular water adsorbate and the surface Mg adsorption site, including four oxygen nearest neighbors. Surrounding this region are pseudopotentials and point charges that provide an accurate Madelung field in the quantum region. The structure and binding energy of H_2O at the MgO/water interface are compared with those at the MgO/vacuum interface and also with results from literature.

Lattice Sums for Irregularly Shaped Semi-infinite Solids

Gwon Hee Ko and William H. Fink
Chemistry Department
University of California
Davis, California 95616

The relative energies of one, two and three dimensional Bravais lattice Lennard-Jones particles can be calculated by lattice sums. The expression of lattice sums over Lennard-Jones potentials can be manipulated into a form that converges rapidsly in this case. In principle, one can also apply this summation technique to the evaluation of the coulombic interaction. The method provides an alternative way to calculate the relative energies from the surface and the interior bulk sites of many chemically interesting systems.

Local Electron Correlation Methods for Large Molecules.

Paul E. Maslen, Martin Head-Gordon

Department of Chemistry, University of California, Berkeley, CA USA

Abstract

To reduce the cost of electronic structure calculations, several groups have applied localization constraints to conventional ab-initio and tight binding calculations. Li, Nunes and Vanderbilt experimented with localizing the one particle density matrix P(r;r'); terms connecting distant points r and r' were set to zero. Saebo, Pulay and Meyer introduced local-MP2, whereby occupied orbitals are correlated only with nearby virtual orbitals.

In this poster we present a general framework for introducing local constraints to any *ab-initio* calculation. The key quantity is the metric matrix, which in many cases is equal to a many-particle overlap matrix. The size of the metric matrix can be reduced by applying a local constraint, and this reduces the cost of the calculation. By considering the metric explicitly we have overcome some of the technical difficulties experienced in previous work. The framework can be applied to any ab-initio calculation, for example SCF, MP2 or CCSD.

We have implemented several alternative local constraints for MP2 calculations, and we present results pertaining to their speed and accuracy.

New Methods for Ab Initio Excitation Energy Calculations. An Approach for Near Degeneracy Problem of Single Reference Configuration Interaction Method.

Manabu Oumi, David Maurice and Martin Head-Gordon

Department of Chemistry, University of California, Berkeley, CA 94720

We have formulated and implemented a new theory to approach the problem of CIS (Configuration Interaction Singles) excited states and CIS(D) (CIS with Doubles correction) excitation energy which occurs when CIS results are near degenerate. Since CIS(D) is a non-degenerate perturbation theory for CIS results, when CIS is degenerate it is not formally valid. A CIS state which is close to another state is not as reliable as the other states. We have solved this problem by diagonalizing the whole singles block of the response matrix to second order. This requires an iterative procedure which didn't exist in CIS(D), but the actual iteration doesn't require many cycles when we start with CIS eigenvectors. It means the computation scales as N^5 of the molecular size which is the same as CIS(D), but improved reliability is achieved in cases with near-degeneracies. Several example calculations are presented to illustrate these considerations.

AB INITIO ANALYSIS OF THE GEOMETRIES, ELECTRONIC STRUCTURE AND HARMONIC FREQUENCIES OF NICKEL PORPHYRINS.

Mari Carmen Piqueras and Celeste McMichael Rohlfing
Combustion Chemistry Department
Sandia National Laboratories
Livermore, CA 94551-0969

Ab initio calculations have been performed to understand the geometry, electronic structure, and vibrational frequencies of nickel porphyrin (NiP) and nickel tetra(t-butyl)porphyrin (NiTtBuP) in order to analyze the conformationally-dependent photophysical properties of these systems. Calculations at the Hartree-Fock (HF) and second-order perturbation (MP2) levels have been performed using polarized basis sets. For NiTtBuP the HF calculations have been carried out on the domed, ruffled, and waved conformers. The calculated geometrical parameters and scaled HF frequencies are in very good agreement with crystal structure determinations and observed infrared and resonance Raman data.

Theoretical Study of Reaction Mechanisms and Transition State location Using *Ab Initio* Molecular Orbital Calculations.

Chirine Soubra-Ghaoui, Thomas A. Albright

Chemistry Department

University of Houston, Houston, Texas 77204-5641

Abstract

Ab initio molecular orbital calculations have been used in the studies concerned with organometallic transition metal complexes. The specific area targeted is the determination of ground state and transition state structures involved in intramolecular and intermolecular reaction mechanisms. The systems involved are $H_2Ru(PH_3)_4$ and $H_2Fe(CO)_4$ in the polytopal rearrangement of 18 electron, octahedral metal dihydrides. The reaction of $W(CO)(PhC{\equiv}CPh)_3$ with excess acetylene to form $W(CO)(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)$ has also been studied. DFT calculations have also been performed and the results obtained show strong agreement with experimetal evidence where available.

Semiclassical Methods Applied to Reactive Systems

Bruce W. Spath and William H. Miller

Department of Chemistry, University of California

Berkeley, California 94720

We have applied several semiclassical initial value representation approximations to reactive model problems. Both Filinov smoothing of the primitive semiclassical propagator and the propagator based on the method developed by Herman and Kluk [E. Kluk *et al.*, J. Chem. Phys. **84** , 326 (1986)] have been investigated. Preliminary results for one- and two-dimensional models will be presented.

A General Methodology for Quantum Modeling of Free Energy Profile of Reaction in Solution:

An Application to the Menshutkin NH_3 + CH_3Cl Reaction in Water

Thanh N. Truong*, Thanh-Thai T. Truong and Eugene V. Stefanovich

Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

We present a general methodology for calculating free energy profile of reaction in solution using quantum mechanical methods coupled with the dielectric continuum solvation approach. Particularly, the Generalized Conductor-like Screening Model (GCOSMO) was employed in this study, though any continuum model with existing free energy derivatives could also be used. Free energy profile is defined as the steepest descent path from the transition state to the reactant and product channels on the liquid-phase free energy surface. Application of this methodology to calculate the free energy profile of the Menshutkin NH_3 + CH_3Cl reaction in water is discussed. The efficiency of the GCOSMO method allows characterization of stationary points and determination of reaction paths to be carried out at less than 20% additional computational cost compared to gas-phase calculations. Excellent agreement between the present results and previous QM/MM simulations confirms the accuracy and usefulness of the GCOSMO model.

Energy level statistics and classical phase space analysis for torsion-rotation interactions

James T. Vivian and John H. Frederick
Department of Chemistry and Program in Chemical Physics
Mail Stop 216, University of Nevada, Reno, NV 89557

We present a combined classical-quantum study of the interaction between overall molecular rotation and an internal rotation (torsion) degree of freedom. The correspondence between spectral statistics of eigenvalues from a quantum basis set calculation and the fraction of chaotic phase space from classical trajectory calculations is investigated. The relationship between eigenvalue statistics of quantum systems and the associated classical dynamics is well characterized for two limiting cases: the *regular* case, in which the classical phase space supports only quasiperiodic trajectories, and the *irregular* case, for which the classical phase space is dense with chaotic trajectories. The regular limit typically leads to a Poisson-type distribution of nearest-neighbor level spacings (NNLS) for the eigenvalue distribution in the corresponding quantum problem, while the irregular limit typically reveals a Gaussian-type NNLS distribution. We present an intermediate case: one which exhibits a mixed phase space comprised of both regular and chaotic trajectories. The role of coupling and degeneracy are elucidated for the spectral statistics, and the quantum analog of the transition to chaos is observed.

Poster Abstract: 18-th West Coast Theoretical Chemistry Conference, 9-11 April, 1997, Berkeley, CA.

Thermal Rate Constant Calculation Using Flux-Flux Autocorrelation Function: Application to $Cl + H_2 \rightarrow ClH + H$ Reaction

Haobin Wang, Ward H. Thompson, and William H. Miller

Department of Chemistry, University of California
and Chemical Science Division, Lawrence Berkeley Laboratory
Berkeley, CA 94720-1460

Up to date the most efficient way of evaluating quantum mechanical thermal rate constant for bimolecular reactions *directly* (i.e., avoiding detailed state-to-state scattering calculation) but nevertheless rigorously (i.e., without inherent approximation) is the flux-flux autocorrelation function formalism. This method combines nice features of both time-independent and time-dependent quantum scattering methods and is at least an order of magnitude more efficient than the traditional methods. In this presentation, the flux autocorrelation function method is applied to $Cl + H_2 \rightarrow ClH + H$ reaction in full dimension. Comparisons with previous theoretical results and other approximation methods will be made and the efficiency of the method will be demonstrated.

Title: Stabilization of a one-dimensional short-range potential in high intense laser fields

Danny Barash (graduate student)
Department of Applied Science
UC Davis/Livermore
email: barash@vsattui.llnl.gov

Under the guidance of:

Dr. Ann E. Orel :woodin@tamp.llnl.gov
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Abstract.

Numerical Simulations using grid methods to solve the time-dependent Schrodinger equation predict the creation of atomic stabilization by high intense laser fields. In low fields, as the intensity of a light beam gets higher, the rate of ionization increases. However, for high values of laser frequencies and intensities, a suppression of ionization has been reported for a variety of potentials and laser pulses. Our goal is to study the stabilization structure for a short-range potential in one dimension, using photon frequencies as low as those corresponding to three-photon ionization and high frequency singe-photon excitation as well. Mixing the two regimes might lead to an unpredicted behavior of the stabilization process. In order to carry out our search for stabilization in multi-dimensional parameter space (laser frequency, intensity, pulse shape) we would like to make use of parallelizable algorithms and computational techniques such as non-linear optimization methods.

VRT Spectroscopy of Water Clusters with Terahertz Lasers: Towards an Accurate Molecular Model of the Liquid

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Abstract

Extensive measurements of Vibrational-Rotational-Tunneling (VRT) spectra have been made for various isotopomers of the water dimer, trimer, tetramer, pentamer, and hexamer with the use of tunable CW lasers in the 2-4 THz frequency range. Analyses of the spectra confirm the theoretical predictions of quasiplanar ring structures as the most stable forms of the trimer, tetramer and pentamer. The competition between maximizing the number of hydrogen bonds and minmizing the bond strain causes a structural transition to occur at the hexamer, wherein a 3-D cage structure with 8 hydrogen bonds is observed.[1]

The internal dynamics in all but the dimer are dominated by a low-barrier "flipping" motion, in which water monomers undergo hindered rotation about their H-bond. A second internal motion ("bifurcation") common to all of these clusters exchanges free and bonded hydrogens on a donor monomer. The two motions have very different time scales (10ps and $\approx$ 10ns, respectively in H_2O clusters). The reaction paths for these rearrangements have been characterized by Wales.[2]

These measurements have provided a quantitative characterization of the hydrogen bond cooperativity operating in these clusters. Both the average O-O separation and the average monomer dipole moment exhibit exponential convergence as a function of cluster size to the values measured for ice I_h. These deductions are strongly supported by the Diffusion Quantum Monte Carlo calculations of Gregory and Clary and by *ab initio* calculations.[3,4]

The VRT spectra of the water dimer are currently being fit to a six-dimensional potential energy surface model using the Wigner DVR formalism of Leforestier.[5]. It is expected that this new and highly detailed potential energy surface, along with the quantificaton of three and four-body forces that will proceed from analysis of the VRT data for higher clusters, will facilitate the construction of improved moelcular models for describing liquid water.

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Tunneling Currents and Pathways of Electron Transfer in *E. coli* Photolyase

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Abstract

A theoretical method for the analysis of interatomic tunneling currents for long-range electron tunneling process has been developed recently. The theory is applied for the calculation of tunneling currents and electronic matrix element in *E. coli* Photolyase from a recent experimental work of Heelis and coworkers. The semi-empirical extended Hückel basis set is employed in such calculation. Tunneling counts and pathways of important amino acids selected by pruning procedure reveal a structure of current flow at atomic resolution in the intervening medium between donor Trp^{306} and acceptor FADH in this system.

Simulation of Water-Chlorinated Hydrocarbon Interfaces with Many-Body Potentials

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Classical molecular dynamics simulations are carried out to study the equilibrium properties of pure water, carbon tetrachloride, and the water-carbon tetrachloride interface. In these studies, many-body model potentials were employed, which were developed to accurately describe the structural and thermodynamic properties of the pure liquids and the liquid/vapor interfaces. The structures of the interfaces are examined via the molecular density profiles, radial distribution functions, and molecular orientation analyses. In addition, with the use of the polarizable potential models, we were able to model the electrostatic properties at the interface more realistically. Results of the transport free energies of organic solutes and ions across this interface will also be discussed.

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Characterization of the Clustering Behavior of a Supercritical Two-Dimensional Lennard-Jones Fluid

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A molecular dynamics simulation technique has been used to study a model two-dimensional fluid at several state points, including the supercritical region. Snapshots from these simulations show a visible difference between the structure of the system in the supercritical region, and the structure of the system in the liquid or gas phase regions. The roughly homogeneous nature of the liquid and gas phases is replaced by a distinct clustering of discs in the supercritical region. This well known behavior, which is also apparent in real fluids, is related to the divergence of the fluid compressibility as the critical point is approached. Supercritical solvents have many potential applications, including the accurate control of reactions performed in the supercritical media. However, before meaningful studies of such applications can be undertaken, it is important to fully characterize the clustering behavior of the supercritical fluid.

We present several techniques for the characterization of the clustering behavior in our model fluid. Our methods focus on the local density of the system, the local and long range pair distribution functions, and the sizes and shapes of designated clusters. Characterization results will be presented for our model fluid at several state points.

A theoretical approach for modeling reactivity at solid/liquid interfaces: Application to NaCl(100)/water

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We present a new general methodology capable of modeling chemical reactions at solid/liquid interfaces called CECILIA (Combined Embedded Cluster at the Interface with LIquid Approach). The main idea is to combine the embedded cluster molecular orbital or density functional methods for describing interactions at the surface of a solid with the dielectric continuum approach for modeling a liquid. More details are given on how to apply this methodology to model processes at the ionic solid/water interface. Geometries and adsorption binding energies of H_2O, NaCl, Na^+ and Cl^- at the NaCl(001)/water interface are calculated using this approach and compared with those at the NaCl(001)/vacuum interface.

THE PHOTOPHYSICS OF THE THREE LOWER LYING SINGLET STATES OF PYRAZINE

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The photophysics and photochemistry of the three lower lying singlet states of pyrazine has attracted a great deal of interest among experimental and theoretical chemists during the past two decades. The strong vibronic coupling of the $S_1(1^1B_{3u}(n\pi^*))$- and $S_2(1^1B_{2u}(\pi\pi^*))$-states in pyrazine is considered to be a model for this type of interaction. Another reason is the 'channel three' phenomenon, i.e. the strong quenching of the fluorescence quantum yield upon excitation beyond a certain threshold energy below the onset of the S_2 absorption band.

We will give a brief overview of different approaches to model the ultrafast $S2 \rightarrow S1$ internal conversion process. The old question of the 'true' equilibrium structure of the S_1 state is discussed and a possible mechanism for the 'channel three' phenomenon is suggested.

Direct Evidence for Modified Solvent Structure Within the Hydration Shell of a Hydrophobic Amino Acid

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Abstract

In this study we provide a molecular explanation as to why there is a shift to smaller angle in the main neutron diffraction peak for liquid water for solutions of a hydrophobic amino acid, while the peak remains unperturbed for solutions of a hydrophilic amino acid. We demonstrate that the shift to smaller angle for N-acetyl-leucine-amide is attributable to alterations in the water hydrogen-bonded network that extends roughly two solvation layers from the leucine side chain surface. We evaluate the various contributions to the total scattering with molecular dynamics simulations and show that the water-water correlations are primarily responsible for the observed shift. The altered hydration structure near the leucine side chain is characterized by a distribution of hydrogen bonded ring sizes that are more planar and dominated by pentagons in particular, than those near the glutamine side chain. The different structural organization of water near the hydrophobic solute that gives rise to the inward shift in the main neutron diffraction peak under ambient conditions may also provide insight into the same directional shift of the main diffraction peak for pure liquid water as it is cooled and supercooled.

To be presented at the 18th Annual West Coast Theoretical Chemistry Conference

Sextuple Zeta Core-valence Correlation Consistent Basis Sets: Benchmark Calculations Near the Complete Basis Set Limit

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The family of core-valence correlation consistent polarized basis sets (cc-pCVXZ) has been extended to include the sextuple zeta set (cc-pCV6Z) for the atoms boron through neon. These new sets were developed as first described by Woon and Dunning [J. Chem. Phys. **103**, 4572 (1995)]. Using the core-valence correlation consistent basis sets from double zeta to sextuple zeta quality, we report:

- Energies of the first row atoms, as compared with results from numerical Hartree-Fock calculations and estimates of total non-relativistic, infinte nuclear mass energies by Davidson *et al.*

- Results from both frozen-core and all-electron calculations, including dissociation energies, for first row hydrides from BH to HF.

From the above examples it is clear that the cc-pCV6Z basis set, when coupled with the most advanced electronic structure methods, provides unequaled accuracy in atomic and molecular calculations.

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Electronic Structure of Large Systems: Linear Scaling in Computation of the One Electron Density Matrix

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Abstract

One of the long-standing goals of theoretical quantum chemistry is to determine the electronic structure of extended atomic and molecular systems. The range of applications is enormous, covering but not limited to structure and dynamics of proteins, catalytic surface chemistry, nano-structures and polymers. However, conventional methods of quantum chemistry have had only limited success in addressing these problems, even within the self consistent field approximations. The computational efforts were dominated, until recently, by the time consuming step of constructing the Fock or the KS effective Hamiltonian matrices from a given one-electron density matrix. Traditional quantum-chemical methods of executing this task scale as $O(N^4)$, where N is the number of atoms in the system. Recently, important innovations have enabled to dramatically reduce the computational scaling of this stage down to a O(N) (linear) regime [1],[2]. With these important achievements, the rate limiting step of electronic structure calculations has shifted to the complimentary feat, that of determining the HF or KS density matrices from the effective Hamiltonian. The straightforward procedure is to diagonalize the Fock or KS matrix and take the lowest N_e eigenstates (where N_e is the number of electrons in the system). This routine scales as $O(N^3)$ and is now emerging as the new bottleneck of the computational algorithm for large systems.

We propose a new computational method, scaling linearly with system size, for accomplishing this task. The method consists of directly constructing the density matrix, without recourse to the expensive diagonalization phase. We expand the Fermi-Dirac matrix (FDM) of the effective one electron Hamiltonian by a uniformly convergent series of Chebychev polynomials.

We show that the Chebychev polynomial expansion is not only an efficient numerical device, but can also be used as an outstanding theoretical tool which allows to easily prove some important analytical properties of the density matrix. We provide a general proof that the DM is sparse in R-space, where the spatial width is inversely proportional to the square root of the HOMO-LUMO gap. These properties have been proved by W. Kohn [3] for one dimensional periodic systems but are now shown to hold for a general system in three dimensions.

The assured sparsity of the density matrix, in a R-localized basis representation, allows us to consider linearly scaling algorithms and to directly construct the density matrix out of the effective Hamiltonian, by a finite number P of Hamiltonian operations. We present numerical results comparing our method to traditional diagonalization procedures (which are highly efficient for small systems). We demonstrate that our linear scaling algorithms becomes beneficial for systems having a few hundreds of atoms. Other aspects of the algorithm are also discussed.

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Ab-Initio Calculations of Electron and Hole Transport in CsI Crystals Doped with Tl and Na*

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We describe methods for using a standard molecular orbital program (Gaussian94) to compute energies and electron distributions that describe (1) the electronic structure of excess electrons and holes in the crystal CsI, (2) energy barriers for hole transport, (3) electron and hole trapping near Tl and Na activator atoms, and (4) the excited state of Tl and Na atoms in CsI. To model hole transport, the Schrödinger equation is solved at the Hartree-Fock level for two nearest neighbor I atoms, each caged by eight nearest neighbor Cs atoms and six nearest neighbor I atoms. This cluster of 12 Cs and 12 I atoms is imbedded in a lattice of 2720 point charges to provide an accurate electrostatic potential. The solution for an excess electron describes the electron as spatially diffuse, involving the Rydberg levels of all 24 atoms. The solution for a missing electron describes the hole as located on the two central I atoms, which have each given up 0.5 electrons to form the classic V_k center (I_2^-). When the two I atoms are relaxed, their nuclear separation decreases from 4.57 Å to 3.84 Å and the cluster energy decreases ($\Delta E = -0.27$ eV). When one of the two atoms of the V_k center is moved away from the cluster center along the 1,0,0 axis, the other member is pulled along at first, but then jumps back almost to its normal lattice position as the V_k bond shifts to the outer I atom along the direction of motion. To model the capture of a hole or electron by an activator atom, we use a cluster consisting of a central Cs, Tl, or Na atom plus eight nearest neighbor I atoms and six nearest neighbor Cs atoms in a lattice of 2729 point charges. The results for these 15-atom clusters show: (1) a Tl atom can trap a hole in its vicinity ($\Delta E = -0.20$ eV) but binds an electron more loosely ($\Delta E = -0.08$ eV), (2) after a Tl atom traps a hole, it can then trap an electron ($\Delta E = -3.4$ eV) to form an excited Tl atom in which a Tl valence electron is promoted to the Tl Rydberg levels, (3) a Na atom can trap an electron in its vicinity ($\Delta E = -2.0$ eV) but not a hole ($\Delta E = +0.31$ eV), and (4) after a Na atom traps an electron it can then trap a hole ($\Delta E = -3.1$ eV) to form an excited state in which the eight I atoms collectively provide an electron that is promoted to the Rydberg levels of all 15 atoms in the cluster. These computations take approximately 300 hours of NERSC time. We conclude that it is now possible to perform preliminary calculations of many of the critical processes in activated scintillators. Anticipated advances in computer speed should allow the systematic exploration of many other host/activator combinations to guide the search for useful new scintillators.

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COMPACT VARIATIONAL WAVEFUNCTIONS BASED ON NATURAL ORBITALS

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Single-reference *ab initio* electronic structure methods are not generally applicable across entire potential energy surfaces: they may break down outside the equilibrium geometry region if the Hartree-Fock method cannot provide a qualitatively correct reference solution. Multireference configuration interaction (CI) wavefunctions, on the other hand, are capable of providing very accurate results not only at the equilibrium geometry, but also across a wide range of nuclear configurations. Unfortunately, multireference CI methods are generally difficult to apply because of the need to select the N-electron functions making up the CI space. Some method of automating the reference selection would be highly desirable. One solution is to divide the orbital space into subspaces and to select the N-electron functions according to how many electrons they place in each orbital subspace. This is the procedure of the second-order CI and of the Restricted Active Space CI of Olsen *et al* [1]. Obviously, this scheme requires a hierarchical ordering of the orbitals, and such an ordering is afforded by CI natural orbitals, which exhibit exponentially decreasing occupation numbers. We will present results of CI wavefunctions which incorporate limited triple and quadruple excitations in a method we designate CISD[TQ] [2,3], and we will demonstrate how CISD natural orbitals allow us to further reduce the dimension of the CI space with minimal loss in correlation energy [4].

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Linear scaling schemes for self-consistent field and coupled perturbed theories using density matrix-based formulations

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Density matrix-based formulations of self-consistent field (SCF) methods and coupled perturbed theories open the way to achieve linear scaling of the computational effort with molecular size M. The increasing importance to avoid the $\mathcal{O}(M^3)$ diagonalization step in conventional SCF density update schemes motivates the formulation of density matrix-based SCF (D-SCF) methods aiming for linear scaling. Although it is clear that the important advantage of these methods is their potential for large molecules, it is highly desirable to be even for small molecules strongly competitive to conventional algorithms. Furthermore, we present a reformulation of the coupled perturbed SCF (CPSCF) theory within a fully local density matrix-based scheme (D-CPSCF). The sparsity of the derivative density matrix allows to solve the $\mathcal{O}(N)$ CPSCF equations necessary for the calculation of vibrational frequencies of a molecule scaling only linearly with system size. An efficient implementation of these methods is discussed and a comparison to conventional algorithms is presented.

Theoretical Study of Photodissociation of C_2H Radical

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Abstract

Being one of the most abundant polyatomic species C_2H radical has received much attention both from the experimental[1] and theoretical[2] point of view. The goal of this study is to explore photodissociation pathways of C_2H radical. In order to investigate photodissociation dynamics theoretically, one needs a reasonable analytical potential energy function. In our research we have studied C_2H potential by means of electronic structure theory. ROHF and several levels of correlated electron calculations have been performed with (10s6p) basis set with [5s4p] Dunning contraction[3] for carbon and (9s3p)/[4s3p] basis set[4] for hydrogen with one d polarization function. The calculated results together with the experimental findings have been used to parametrize analytical potential function in the form of many body expansion terms.

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Thermal Rate Calculations of Free Base Porphyrin Tautomerization

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Thermal rate constants based on transition state theory and canonical transition state theory with semiclassical tunneling methods for the cyclic intramolecular exchange of the two interior hydrogens in free base porphyrin are presented. Structures of the reactant and intermediate and transition state structure are given. The transition state and cis isomer are found to be 18.6 and 9.1 kcal/mol above the reactant at the BH&H-LYP/6-31G(d,p). This double proton transfer has been shown by others to proceed via a stepwise mechanism. Quantum effects such as tunneling are examined using the Wigner, Eckart and CVT/ZCT approximations. The thermal rate constants and kinetic isotope effects are calculated and compared to their experimental counterparts, which are based on NMR techinques.

Investigation of some relativistic approximations

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Abstract

The inclusion of relativistic effects in molecular calculations within a sequence of approximations is explored for a number of small systems involving heavy atoms. The methods used are the full 4-component Dirac-Fock method, an atomic 4-spinor expansion method, and a method in which designated atoms are treated nonrelativistically. These three are compared to determine the range of validity and the errors incurred for each level of approximation.

Improving the Efficiency of Perturbative Monte Carlo Simulations Using QM/MM Potentials

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Combined quantum mechanical/molecular mechanical (QM/MM) techniques are useful in studying condensed phase processes where the important region requires a quantum mechanical treatment, while the remaining region can be approximated by molecular mechanics force fields. Molecular dynamics or Monte Carlo simulations using such QM/MM potentials are computationally expensive due to the large number of quantum mechanical calculations required for reasonable statistics. The recent perturbative Monte Carlo (MC) approach provides an effective way of reducing the computational demand of such simulations; instead of performing a full self-consistent field (SCF) calculation with every MC displacement of a solvent molecule, the SCF portion of the simulation is done every n^{th} MC displacement of the classical particles and the energy of the system is updated using perturbation theory, with little loss of accuracy[1]. It is possible to further increase the efficiency of the perturbative MC technique by introducing an error weighting function, which is a function of the distance from the solute region to the selected classical particle. This allows for optimal efficiency by accumulating the same error for many solvent displacements far from the solute, as would be produced due to few displacements of solvent molecules close to the solute. When the accumulated error reaches a predetermined level, the SCF energy is calculated. The results of perturbative MC simulations which include this error weighting procedure will be presented.

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Quantum mechanical pressure-dependent reaction and recombination rates for $O + OH \rightarrow H + O_2$, HO_2

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Abstract

We extend recent flux-flux autocorrelation function methods for the direct computation of thermal reaction rate constants and unimolecular recombination rates to the case where both reaction and recombination are possible. Rather than a single transition state dividing surface, dividing surfaces are placed on both the reactant (r) and product (p) sides of the intermediate collision complex region. The thermal recombination rate expression then involves a flux cross-correlation function $C_{rp}(t)$ in addition to the usual autocorrelation function $C_{rr}(t)$, both of which are computed during a single quantum time propagation. This method is applied to the three-dimensional $O + OH \rightleftharpoons H + O_2$ ($J = 0$) reactions, employing parallel computation due to the necessary large basis (2^{18} grid points) and long propagation times (2–3 ps). Thermal rate constants (in the absence of recombination effects) are presented for $T = 500-2000$ K, using the J-shifting approximation to account for nonzero total angular momentum; good agreement is found with experimental measurements of both forward and reverse rate constants. Collisional recombination by a bath gas is included via the strong collision assumption, and rate constants for the competing $O + OH$ reaction ($H + O_2$) and recombination (HO_2) channels are calculated as a function of collision frequency, i.e., pressure of the bath gas.

Ultrafast Non-Adiabatic Dynamics in Electronically Excited Polyatomic Systems on "on the fly" Generated PES"

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March 18, 1997

Abstract

The purpose of this work is to understand the mechanisms of photodissociation, electronic relaxation, photoinduced isomerization in polyatomic molecules. The theoretical treatment of electronically excited states in polyatomic systems poses a severe problems for theoreticians due to *unique* features of these states, such as *delocalized character of excited states, many-body nature of interactions, and electronic degeneracy.* To solve this problem, we are developing new approach for modeling non-adiabatic dynamics in polyatomic molecules by means of semiclassical Molecular Dynamics with "on the fly" generated *ab initio* PES. This requires reformulation of existing quantum chemical methods to be feasible to dynamical calculations.

We intent to apply our method to study ultrafast internal conversion in hexatriene.

As a first approximation to electronic structure problem we are using extended single-reference approaches such as extended version of CIS (Configurational Interaction Singles) method which includes selected double excitations. In order to treat dynamics with electronic transitions we are using Semiclassical Mean-Field and Surface-Hopping approach. Local gauge for construction continuous individual electronic states is used.

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A New Quantum Chemistry Method: Polarized Atomic Orbitals

One of the goals of *ab initio* calculations is to accurately calculate properties of large molecules. Unfortunately, accurate methods are expensive and sometimes impractical for many large systems. The primary reason for this is that in order to improve the quality of a calculation one must augment the size of the atomic orbital basis set. However, as one increases the size of the basis set the memory scales quadratically $O(N^2)$ and the CPU time scales cubically $O(N^3)$, where N is the number of basis functions. This implies that large molecules can only be analyzed with small, perhaps deficient, basis sets.

We present a new approach which uses a small set of atomic orbitals known as "Polarized Atomic Orbitals" or "PAO's". What is unique about these PAO's is that they are dynamically formed during a quantum chemical calculation. This allows the PAO's to adjust, or polarize, to their molecular surroundings. In practice, the PAO's are formed by optimizing linear combinations of a larger set of atomic orbitals. Simultaneously, in an *ab initio* calculation, the molecular orbitals are optimized as linear combinations of the PAO's.

Results are presented which assess the accuracy of the PAO approximation compared to the conventional Self-Consistent Field (SCF) procedure. When efficiently implemented, the PAO approach can be faster and less memory-intensive than the standard SCF method. The PAO method is expected to become an excellent starting point for fast, accurate methods for large molecules.

Long-Distance Electron Tunneling in Homogenous Continuum Model

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Abstract

We develop a rigorous formulation of a homogeneous dieletric model for long-range tunneling and compare our theoretical results with experimental data for the distance dependence of the tunneling matrix element in Ru-modified azurins and cytochromes. In this model the donor and acceptor metal ions are placed in spherical cavities embedded in a dielectric continuum with unknown effective dielectric constant ϵ. The primary physics of this model is that the tails of donor and acceptor wave functions will penetrate beyond cavity boundaries into the dieletric region. The overlap of the two wave functions determines the strength of the electronic coupling. A rigorous method for the calculation of the tunneling matrix element in such a 3D model given the cavity sizes and dieletric constant is proposed. Analytical solutions for donor and acceptor wave functions were obtained using a special form of perturbation theory.

Ab initio Studies of Hydrogen Bonding Effects on the Tyrosyl Radical

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Abstract

The reactivity of amino acids involved in enzymatic mechanistic steps is often controlled by the orientation of the side chain which can be determined by the factors of localized motion, as well as, local environments, such as inter- and intramolecular bonding interactions. An example of this type of reactivity can be seen in Photosystem II (PS II), a component of the green plant photosynthetic process where water oxidation takes place at an oxygen-evolving complex (OEC) that consists of a tetranuclear Manganese cluster. In this water splitting process the amino acid tyrosine, denoted as Yz, has been shown to play a significant role in the mechanism. Previously, it was thought that Yz was only involved in the electron transfer process between the tetranuclear Mn cluster and the chlorophyll moiety P680, however, it has become evident that tyrosine is involved in the hydrogen atom transfer process as well.

The current mechanistic views are that the redox-active Yz is the sole electron transfer intermediate between the photooxided P+680 chloropyll moiety and the tetranuclear Mn cluster at the heart of the OEC. An ESE-ENDOR study has determined the proximity of the Yz radical to the tetranuclear Mn reaction center may be as close as 4.5 Angstroms, indicating that the Yz radical is directly involved in water oxidation. In the mechanistic scheme proposed by Britt et.al., Yz is oxidized by P+680 , resulting in a tyrosine radical, which is known to be neutral This requires the phenolic proton to be quickly transferred to a proximal base, such as histidine. Then the tyrosine radical is rereduced and reprotonated by the tetranuclear Mn-water complex in either a concerted step or sequential steps.

In this study, ab initio methods are being used to elucidate structural and energy information on the effects of hydrogen bonding to the tyrosine radical. An ammonium ion is used to model this hydrogen bonding. The internal rotational barriers of the phenolic ring of the isolated and hydrogen bonded tyrosine radical is calculated at the MP2/6-31G* level. Hydrogen bonding is observed to decrease the rotational barrier by approximately 1 kcal/mol. By contrast hydrogen bonding is observed to have little to no effect on the isotropic hyperfine parameters of the phenolic ring hydrogens or the beta-methylene hydrogens of the tyrosine radical models used here.

Ab initio Characterization of the Electronically Excited States of Carbonyl Anions

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The determination of electronically excited states for a target group of carbonyl anions, focusing on the simplest prototype HCO^-, will be presented. The zeroth order CIS approach has been used for a qualitative determination of states. Optimized structures, vibrational frequencies and transition energies have been obtained at this level of theory. CASPT2 has also been used for excited state energy determinations on the smallest system, HCO^-. A comparison of theoretical methods coupled with any available experimental evidence will be presented.

Thermal Reaction Rates for $OH + O \rightarrow H + O_2$ from Flux Autocorrelation Functions: $J \neq 0$ in the Helicity Conserving Approximation

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We extend recent work on thermal reaction rates for this reaction to include nonzero total angular momentum via the helicity conserving approximation (HCA). The angular momentum about the body-fixed $O - O$ axis is assumed to be nearly conserved. The thermal reaction rate $k_{J,K}(T)$ is calculated for several (J, K) , each requiring approximately the same effort as a $J = 0$ calculation. The total rate, including all (J, K), is then calculated by interpolation. Comparison is made with other theoretical treatments and experimental results.

Thermal Rate Constants Via Semiclassical Transition State Theory

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Quantum effects such as tunelling are included in transition state theory by multiplying the rate constant by a semiclassical transmission coefficient. These transmission coefficients are expressed as functions of the locally conserved action variables at the transition state[1,2]. This leads to the inclusion of non-separable couplings between the reaction coordinate and the other degrees of freedom. The potential energy is then expanded to quartic terms in the locally conserved action variables, which leads to an anharmonic description of the potential energy surface. The anharmonicity can have a large effect on the calculated rate constant. In an attempt to describe the tunneling through the barrier more accurately, the semiclassical transmission coefficient is replaced by the exact quantum mechanical transmission coefficient for the eckart barrier. This substitution may lead to more accurate rate constants.

The rate constants for the $H_2 + OH \rightarrow H_2O + H$ and $D_2 + OH \rightarrow HOD + D$ reactions are calculated using the quantum mechanical transmission coefficients for the eckart barrier and the semiclassical transmission coefficients. Calculations are performed using both anharmonic and harmonic potential energy surfaces. The results are compared with experimental results and previous theoretical work. The calculated rates constants fall within experimental errors and demonstrate the importance of using an anharmonic potential.

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A Parallel Implementation of the Classical Generalized Conductor-like Screening Model (GCOSMO), and its Application to Solvation of Macromolecules

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The present work is a presentation of the methodology for the parallel implementation of the classical Generalized Conductor-like Screening Model (GCOSMO), a dielectric continuum model for solvation, and the preliminary results of this model. Our hope is to apply this model to the study of solvation effects on macromolecules, and specifically, on the HIV virus.

Low-energy electron scattering from polyatomic molecules: the role of electron correlation and the interface with quantum chemistry

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Abstract

Until ten years ago the principal barrier to the accurate theoretical description of electronic collisions with polyatomic molecules was the problem of scattering by a nonlocal potential which is arbitrarily asymmetric. Recent years have seen the development of numerical techniques capable of solving the potential scattering problem, and applications of accurate methods for treating many-body aspects of collisions of electrons with polyatomic molecules have begun to appear in the literature. We describe the complex Kohn method and the use, in scattering calculations, of methods for treating electronic correlation which are standard in bound-state quantum chemistry. The intimate interface of the scattering calculation with quantum chemistry codes to treat correlation consistently is now the principal theoretical problem in the field. As examples we present the results of ab initio calculations of electronic excitation in polyatomics, an effect caused only by electronic correlation, and on electron scattering from CH_4, SiH_4, and C_2H_6, all of which exhibit Ramsauer-Townsend minima at low impact energies which are also pure correlation effects.

Calculation of ESR *G*-Tensors Based on Gauge Including Atomic Orbitals and Density Functional Theory

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The subject of this contribution is the calculation of the *g*-tensor of electron spin resonance (ESR) spectroscopy from first principle density functional theory [1,2] (DFT). Our implementation is based on the use of "gauge including atomic orbitals" (GIAO) -- a method that is known to be well suited for other magnetic properties [3]. The new ESR program [4] is an extension to our existing DFT-GIAO program for the chemical shift of nuclear magnetic resonance (NMR) spectroscopy [5-8]; we make full use of the conceptual analogy between the g-tensor and the NMR chemical shift in our formulation. The DFT-GIAO program system is based on the DFT code ADF [9].

To the best of our knowledge, there was no previous first principle method available for the calculation of the ESR *g*-tensor that employs DFT. Neither was there any formulation available that is based on the use of GIAO or other distributed-origin schemes. Given the importance of this spectroscopic property and the success of DFT for other magnetic properties, it seemed timely to fill the gap [4].

We shall start the presentation with some of the theory underlying the DFT-GIAO method for the *g*-tensor. This will be followed by a discussion of calculated results, both in comparison to experiment and to previous *ab initio* calculations. The agreement of calculated and experimental *g*-tensors is good for radicals of first row elements; experimental trends are generally well reproduced. The quality of calculated results is worse if the scheme is applied to compounds of heavier elements. Possible reasons for these apparent shortcomings of the method will be discussed. It will be argued that the most important limitation of the method is probably the use of perturbation theory in the treatment of the various spin-orbit operators.

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Linear Coulomb Builds and Diagonalization Free Energy Minimizations

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The size of molecules treatable through the use of conventional ab initio techniques is limited primarily by two bottlenecks. The first concerns the formation of the Coulomb interaction matrix or J matrix. Conventional methods for J matrix formation scale $O(N^2)$ where N is the number of atoms in the system. The second bottleneck concerns the manipulation (multiplication, diagonalization and storage) of large matrices. Matrix multiplication and diagonalization scale $O(N^3)$ with storage scaling $O(N^2)$. By removing these bottlenecks, one dramatically increases the size of molecules treatable by ab initio techniques.

We will present new linear scaling O(N) methods for the removal of the Coulomb and diagonalization bottlenecks. The Continuous Fast Multipole Method (CFMM) is a linear scaling method for J matrix formation. Calculations on real molecules and models systems give an indication of the crossover between the CFMM and conventional methods. We also introduce a recently developed method for the replacement of diagonalization within conventional self consistent field calculations. This method replaces diagonalization with an unconstrained minimization of the energy with respect to the one particle density matrix. By combining these methods, we can construct a fully linear procedure for the ab inito treatment of large molecules.

Using Direct and Cached Integrals in Parallel Quantum Chemistry Algorithms

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Abstract

The management of integrals is major factor in the design of parallel quantum chemistry algorithms. On massively parallel platforms, the primary emphasis has been on direct algorithms due to the high aggregate processor speed relative to disk access. This talk presents some recent parallel direct algorithms for the Fock matrix construction and four index transformation that incorporate caching in memory and on disk. The unification of the two strategies permits the most efficient utilization of resources for a given parallel platform.

Interfacing relativistic and nonrelativistic methods

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Abstract

It is well-known that relativistic effects must be included in calculations on molecules containing heavy atoms, and that these are to a reasonable extent localized on the atoms. However, because the cost of full 4-component Dirac-Fock calculations for molecules is high, approximations are needed. A method is presented for inclusion of relativistic effects on the heavy atoms while treating the rest of the molecule nonrelativistically, in all-electron calculations. The method involves a systematic and controllable sequence of approximations from the full 4-component methods, and enables a cost-effective treatment of large molecules with a few heavy atoms.

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