

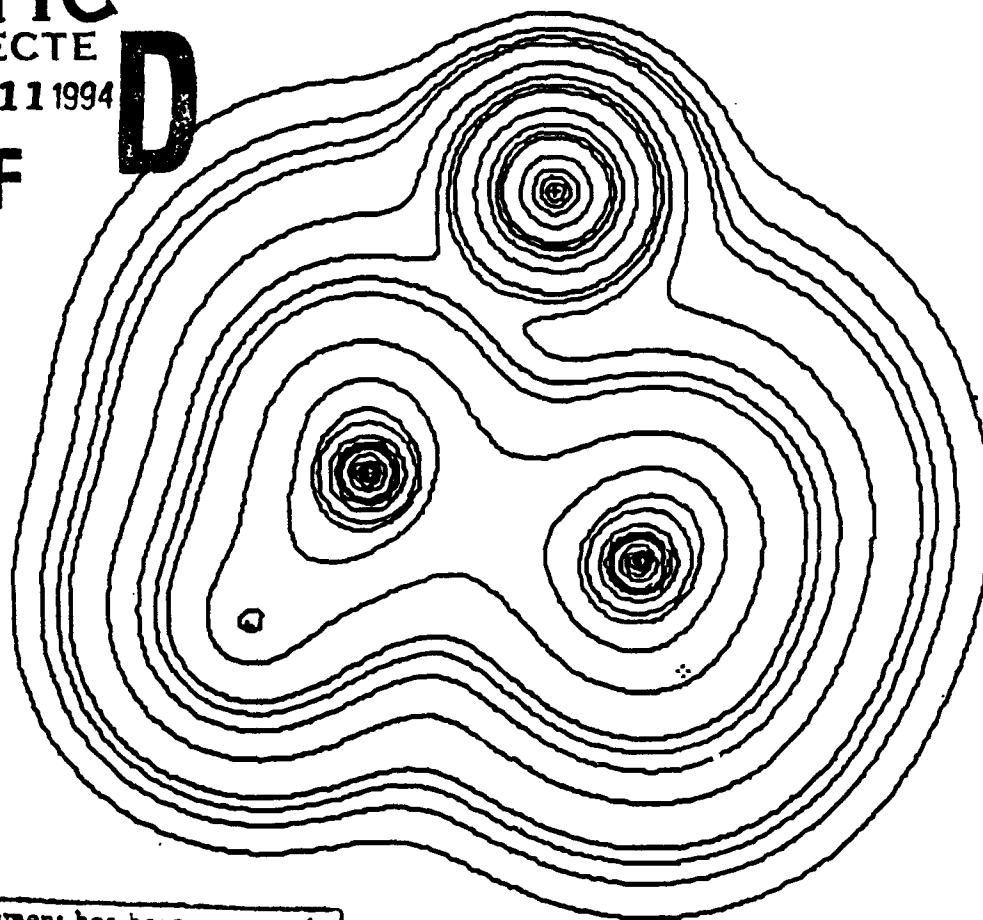
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# 14th Annual West Coast Theoretical Chemistry/Statistical Mechanics Conference

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June 17-19, 1993  
UCLA

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**The 14th Annual West Coast Theoretical Chemistry/Statistical Mechanics Conference  
Honors Howard Reiss**

We are very pleased to have this opportunity to honor our special friend **HOWARD REISS** on the occasion of his 70th birthday. He has inspired us for decades with his constant supply of novel ideas, his generosity of spirit, and his irrepressible interest in just about all aspects of physical science. We are especially gratified -- although not at all surprised -- that Howard is continuing in his "retirement" to teach our undergraduates and to train (us and) our research students via his shining example of how the art of science can best be practised. His half-century of original contributions to the full gamut of physical chemistry, from the Manhattan Project in the 1940's, Bell Labs in the '50's, the North American Rockwell Science Center (Founding Director) in the '60's and UCLA for the past twenty-five years, is a truly impressive testament to his fertile mind and expansive energy. To give us a little of the flavor of this unique life in science, we have asked him to speak at our Conference Banquet about some key highlights and favorite recollections. We look forward to these remarks of Howard's, and even more so to many more years of inspiration and encouragement from his ongoing work. **HAPPY BIRTHDAY HOWARD, AND THANK YOU!**

## West Coast Statistical Mechanics/Theoretical Chemistry Conference

### Thursday, 17 June (UCLA Faculty Center, California Room)

9:00 am–Noon      Registration: California Room  
Noon–2:30 pm      Lunch (*Sequoia Room*)/ Poster Session I (California Room Patio)

#### **Session I**      (*California Room*)

**Chair:** Professor Emily Carter, University of California, Los Angeles

2:30–3:30      Professor Paul Madden, Oxford University  
3:30–3:50      Dr. Michael Colvin, Sandia National Laboratory  
3:50–4:10      Dr. Rajiv Berry, IBM Almaden  
4:10–4:30      *Coffee Break*  
4:30–4:50      Cheryl Weakliem, University of California, Los Angeles  
4:50–5:10      Scott Auerbach, University of California, Berkeley  
5:10–5:30      Dr. Piotr Piecuch, University of Arizona  
5:30–5:50      Dr. John Barker, IBM Almaden

### Friday, 18 June (UCLA Faculty Center, California Room)

8:00–9:00 am      *Refreshments*

#### **Session II**      (*California Room*)

**Chair:** Professor Bill Gelbart, University of California, Los Angeles

9:00–10:00      Professor Stanley Williams, University of California, Los Angeles  
10:00–10:20      Dr. Jeffrey Krause, University of California, San Diego  
10:20–10:40      Dr. Philippe Maitre, NASA–Ames  
10:40–11:00      *Coffee Break*  
11:00–11:20      Dr. Carey Bagdassarian, University of Chicago  
11:20–11:40      Todd J. Martinez, University of California, Los Angeles  
11:40–Noon      Dr. John Nicholas, Pacific Northwest Laboratories  
Noon–12:20      Dr. Alexander Boldyrev, University of Utah  
12:20–2:30 pm      Lunch (*Sequoia Room*)/Poster Session II (California Room Patio)

#### **Session III**      (*California Room*)

**Chair:** Professor Chi Mak, University of Southern California

2:30–2:50      Professor John Wheeler, University of California, San Diego  
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3:10–3:30      Dr. Vladimir Mandelshtam, University of Southern California  
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5:10–5:30      Dr. David Smith, Pacific Northwest Laboratories  
5:30–5:50      Dr. Andrea Liu, University of California, Santa Barbara

7:00

#### **Banquet** (*Sequoia Room*)

After-dinner speaker: Professor Howard Reiss, University of California, Los Angeles

**Saturday, 19 June (UCLA Faculty Center, California Room)**

**8:00-9:00 am      *Refreshments***

***Session IV      (California Room)***

***Chair: Professor Bob Cave, Harvey Mudd College***

9:00-10:00      Professor Eric Heller, University of Washington  
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4:50-5:10      Mark Sharlow, University of California, Los Angeles  
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5:30-5:50      Richard Muller, California Institute of Technology

# 14th Annual West Coast Theoretical Chemistry/Statistical Mechanics Conference

June 17-19, 1993

## Organizing Committee

Emily A. Carter, UCLA

William M. Gelbart, UCLA

Daniel D. Konowalow, AF Phillips Lab Propulsion Directorate

Marcy E. Rosenkrantz, AF Phillips Lab Propulsion Directorate

The Organizing Committee for the 14th Annual West Coast Theoretical Chemistry/Statistical Mechanics Conference wishes to thank the following sponsors for their generous support:

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5:10-5:30	Dr. Grant Smith, Pacific Northwest Laboratories
5:30-5:50	Richard Muller, California Institute of Technology
7:00	<i>Banquet (Sequoia Room)</i>
	After-dinner speaker: Professor Howard Reiss, University of California, Los Angeles

## West Coast Theoretical Chemistry/Statistical Mechanics Conference

### Poster Session Schedule

**NOTE:** Please set up your posters before the morning session and take them down immediately after the afternoon session on the day of your poster session.

#### *Poster Session I, Thursday, June 17, Noon-2:30 pm (California Room Patio)*

Dr. Douglas Beck, University of Washington  
Dr. Paul Weakliem, University of California, Santa Barbara  
Dr. Pawel M. Kozlowski, University of Arizona  
Miguel Angel Sepulveda, University of Washington  
Erik Bierwagon, California Institute of Technology  
Dr. Ito Chao, University of California, Los Angeles  
Dr. Roberta P. Saxon, SRI International  
D. C. Benn, University of California, Los Angeles  
Professor Douglas Henderson, University of Iztapalapa, Mexico  
Kirsten Eurenus, University of California, Los Angeles  
Dr. Hans Horn, IBM Almaden  
Dr. Paul Rejto, University of California, Berkeley  
Professor Robert J. Cave, Harvey Mudd College  
Douglas A. Gibson, University of California, Los Angeles  
Dr. Siddarth Dasgupta, California Institute of Technology  
Dr. Marcy Rosenkrantz, Edwards AFB, California  
Dr. Stephen P. Walch, NASA-Ames  
Dr. Sergio Maluendes, Molecular Research Institute  
Dr. Bruce Garrett, Pacific Northwest Laboratories  
Dr. Michael Ellerby, University of California, Los Angeles  
John Cullen, California Institute of Technology  
Nathan Oyler, University of Arizona  
Willard Brown, University of California; Berkeley  
Dr. Liem Dang, Pacific Northwest Laboratories

#### *Poster Session II, Friday, June 18, 12:20 - 2:30 pm (California Room Patio)*

Rigoberto Hernandez, University of California, Berkeley  
Dr. Tsun-Mei Chang, University of California, Los Angeles  
Nick Gonzales, University of Utah  
Professor J. Vince Ortiz, University of New Mexico  
David Maurice, University of California, Berkeley  
John Eksterowicz, University of California, Los Angeles  
Dr. Byron H. Lengsfeld III, Lawrence Livermore Laboratory  
Dr. Kerstin Andersson, IBM Almaden



3:10-3:30	Dr. Vladimir Mandelshtam, University of Southern California
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## Molecular Dynamics from First Principles - Metals, Colloids, Ionic Melts.....

P. A. Madden  
Physical Chemistry Laboratory  
Oxford University  
South Parks Road, Oxford OX1 3QZ, U.K.

Computer simulations of molecular systems are based upon the representation of the intermolecular interactions as sums of atom-atom (or site-site) potentials. The underlying idea is that no major readjustment of the electron density takes place as the molecules move. However, for any classes of material this idea is not applicable and a description of the total potential energy at a more fundamental level must be applied.

The *ab-initio* molecular dynamics method of Car and Parrinello [*Phys. Rev. Lett.*, **55**, 2471 (1985)] was introduced to permit the simulation of systems with "itinerant" electrons, such as covalent semiconductors, where the electrons move in a non-trivial way as the ions move and thereby change the effective interionic interactions. Examining the way in which such simulations behave when applied to problems in which chemical bonds are broken and formed provides insight into the way the method works [*Molecular Physics*, **70**, 921 (1990)]. The situation of itinerant electrons is not the only physical problem in which the effective interactions between the particles of interest are influenced by an intervening medium which responds to the nuclear motion. In charged colloidal suspensions the "ionic atmosphere" plays a similar role. It will be shown how the C-P method can be adapted to permit an *ab-initio* treatment of the structure of colloidal suspensions [*JCP*, **98**, 3275 (1993)]. Similarly in ionic systems, many-body polarization and dispersion forces can be built into the model and parameterized in a well quantified way [*J. Phys. Condens. Mat.*, **5**, 2687 (1993)].

The basic ideas behind such simulations will be reviewed and a selection of applications described.

# Potential Function for Polyfluorinated Ethers.

**R. L. Berry, R. J. Waltman, and J. Pacansky.**

*IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.*

**Abstract:** The derivation of an accurate potential function for simulating fluorinated ether polymers was achieved by fits to *ab initio* data for small model compounds calculated at the 6-31G\* level. The *ab initio* data utilized consisted of the energies, gradients and Hessian not only for the equilibrium and transition states but also for the distorted geometries expected during the course of the simulation. The potential function closely reproduces the conformation dependant variations in energy and structure as computed by *ab initio* and the vibrational frequencies observed in the infrared spectra.

## A PHYSICALLY CONSISTENT THEORY OF HOMOGENEOUS VAPOR-PHASE NUCLEATION

Cheryl Li Weakliem and Howard Reiss

Department of Chemistry and Biochemistry  
University of California  
Los Angeles, CA 90024

Classical nucleation theory, although developed approximately 60 years ago, is still predominantly used today since it accurately predicts the critical supersaturation (supersaturation for onset conditions) for homogeneous nucleation in single component vapors for a wide variety of substances. However, the rates predicted by this macroscopic theory differ from experimental rates by many orders of magnitude. This seemingly paradoxical situation arises from the exceedingly sharp and nonlinear dependence of the nucleation rate on the supersaturation such that a considerable error in the rate can be tolerated without altering the predicted supersaturation.

More recent theories of nucleation have tried to improve upon the classical theory of nucleation by replacing its ad hoc liquid drop model of clusters with ones which are more physically consistent. We have developed a microscopic cluster model which allows fluctuations in the cluster density. In addition, due to the molecular nature of the cluster definition, the equilibrium distribution of clusters is rigorously derived and can be used in conjunction with detailed balance to obtain reverse rate constants required in the rate theory.

The strict molecular nature of our cluster model can be sacrificed to develop a modified liquid drop model which, although macroscopic in nature, still retains the physical properties of the molecular cluster, most notably its allowance of density fluctuations. Good agreement between this macroscopic theory and simulations using the microscopic cluster definition is obtained for both the internal Helmholtz free energies and the radial density profiles of the clusters. The rate theory developed with the modified liquid drop model gives results which agree with classical theory with respect to its predictions of the dependence of the nucleation rate on supersaturation, but differs in its predictions of the temperature dependence. The disagreement on temperature dependence follows the same trend found when comparing experimental results to classical theory.

## 3D Reaction Probabilities by Power Series Expansion of the Lippmann-Schwinger Equation

Scott M. Auerbach, Claude Leforestier<sup>†</sup> and William H. Miller

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

The use of optical potentials in reactive scattering allows one to eliminate some<sup>1,2</sup> or all<sup>3</sup> asymptotic state information, directly yielding averaged reaction probabilities. This facilitates the use of relatively small spatial grids focused in the strong interaction region. We use a new optical potential technique<sup>2</sup> to compute initial-state-selected reaction probabilities. This requires construction of the scattering wavefunction, which is achieved with the Lippmann-Schwinger equation with absorbing boundary conditions (ABC). The computationally intensive aspect of this approach is the solution of a complex system of linear equations. We propose a new iterative technique<sup>4</sup> for solving the linear system which is fast, accurate and avoids the need to store the Hamiltonian matrix.

We represent the ABC wavefunction as the Fourier transform of the appropriate time-dependent wavefunction. The time evolution is performed very accurately with a Newton polynomial expansion of the propagator,<sup>5</sup> which allows the time-dependent expansion coefficients to be Fourier transformed exactly. As such, the complex linear system can be solved essentially *exactly*, with minimal storage requirements.

We illustrate the new method with quantum scattering calculations on the three dimensional ( $J=0$ )  $D+H_2(vj) \rightarrow DH+H$  reaction, yielding initial-state-selected reaction probabilities over a range of energies and initial rovibrational states. Excellent agreement is found with previous calculations which obtain the full  $S$ -matrix. We find that, with respect to the grid size, the use of optical potentials allow small grids in the product regions of the potential energy surface, as has been found previously.<sup>1-4</sup> In addition, the power series expansion of the ABC wavefunction is found to be stable and accurate in all cases. This appears to be an attractive framework for solving the four atom reactive scattering problem.

<sup>†</sup>On sabbatical leave from Laboratoire de Chimie Théorique, Université de Paris-Sud.

<sup>1</sup>D. Neuhauser and M. Baer, J. Chem. Phys. **91**, 4651 (1989).

<sup>2</sup>W. H. Thompson and W. H. Miller, Chem. Phys. Lett., in press.

<sup>3</sup>T. Seideman and W. H. Miller, J. Chem. Phys. **96**, 4412 (1992).

<sup>4</sup>S. M. Auerbach and W. H. Miller, J. Chem. Phys. **98**, 0000 (1993).

<sup>5</sup>M. Berman, R. Kosloff, and H. Tal-Ezer, J. Phys. A **25**, 1283 (1992).

# **A State-Selective Multi-Reference Coupled-Cluster Method Employing the Single-Reference Formalism: Theory, Implementation and a Test Case Study**

Piotr Piecuch and Ludwik Adamowicz

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

A new state-selective multi-reference (MR) coupled-cluster (CC) method exploiting the single-reference (SR) particle-hole formalism, which we have introduced in our recent paper [P. Piecuch, N. Oliphant, and L. Adamowicz, *J. Chem. Phys.* **98**, XXX (1993)], is reviewed. Hierarchy of approximate schemes, with the MRCCSD approach (MRCC approach truncated at double excitations from the reference determinants) representing the most important one, is defined, and the complete set of equations describing MRCCSD formalism is presented. Our state-selective MRCCSD theory emerges through a suitable selection of the most essential cluster components appearing in the full SRCCSDTQ method (SRCC method truncated at quadruple excitations), when the latter is applied to quasidegenerate states. The size extensivity of the resulting correlation energies is achieved by employing a SRCC-like ansatz for the multi-determinantal wave function. The MRCCSD formalism has been implemented and the results of pilot calculations for the minimum basis set model composed of eight hydrogen atoms in various geometrical arrangements, which enables a continuous transition between degenerate and nondegenerate regimes, are presented. Comparison is made with the results of SRCC (CCD, CCSD, CCSDT and CCSDTQ) and Hilbert-space MRCCD calculations, as well as with the MR configuration interaction (CI) data (with and without Davidson-type corrections) and the exact correlation energies obtained using the full CI method. The possibility of the recursive intermediate factorization [S.A. Kucharski and R.J. Bartlett, *Theor. Chim. Acta* **80**, 387 (1991)] of our approach, leading to an efficient computer algorithm, as well as the possibility to describe excited states, such as the open-shell singlets, are discussed.

## **SURFACE TENSION AND ATOMIC INTERACTIONS IN SIMPLE LIQUIDS: ARGON, KRYPTON AND XENON**

**J. A. Barker, IBM Almaden Research Center K35/801,  
650 Harry Road, San Jose CA95012-6099.**

Accurate Monte Carlo calculations of the surface tension of liquid argon, krypton and xenon near their triple points are described. Reliable pair potential functions are used and calculations are made both with and without the Axilrod-Teller-Muto three-body interaction. A novel perturbation method is used for the calculations with three-body interactions. In this method the three-body interaction is approximated in the first instance by a sum of pair potentials having the same scaling with change of density. Then only the relatively small difference between this approximating function and the actual three-body potential has to be treated by thermodynamic perturbation theory.

Pair potentials alone give values of surface tension which are larger than the experimental values by 19% for argon and by 35% for xenon. When the three-body interaction is included the calculated results are within 2.2% of the experimental values for argon, krypton and xenon. Correction for long-wavelength displacements of the surface not included in the Monte Carlo simulation is made using a theoretical result due to Weeks. This reduces the calculated surface tension by up to 4%, and therefore cannot be neglected in accurate calculations.

It is known that either the pair potentials of Barker and coworkers or those of Aziz and Slamann give good agreement with experimental bulk properties of condensed phases of argon, krypton and xenon if the ATM three-body interaction is included, but not if it is omitted. Similar results are found for solid neon at zero temperature. The present results show that the prescription, "accurate pair potential plus ATM three-body interaction", is an excellent model for the surface properties of the rare gases, as it is for the bulk properties in solid, liquid and gaseous states. This was suggested strongly by earlier approximate calculations but has not previously been demonstrated by accurate calculations for surface tension.

It is also known that inclusion of the three-body exchange-repulsion non-additive term calculated by first-order perturbation theory by Bulski and Chalasinski destroys the good agreement with experiment for bulk thermodynamic properties. This is found to be true for the surface tension as well.



## **Friday, 18 June 1993**

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***(California Room)***

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<b>Noon-12:20</b>	<b>Dr. Alexander Boldyrev, University of Utah</b>
<b>12:20-2:30</b>	<b><i>Lunch (Sequoia Room)/ Poster Session II (California Room Patio)</i></b>

# The Relationship between Growth Kinetics and Surface Morphology: Quantitative Analysis of Scanning Probe Topographs

R. Stanley Williams  
Department of Chemistry and Biochemistry  
UCLA  
Los Angeles, CA 90024-1569

The particular processes that influence the growth and evolution of a solid obviously have a major influence on the morphology of the surface. The nature of these processes can often be determined from a qualitative analysis of images of the surfaces long after the major events that formed them occurred. Examples are the photographs of many of the moons in our solar system that have been used to determine the mechanisms that dominated the formation and aging of the moons. In modern technological applications, the morphology of a surface can be as important as its atomic geometry or composition. Thus, it is important to understand the relationship between the kinetic mechanisms of etching and deposition and the morphology of the resulting surfaces to be able to optimize growth conditions. To this end, a brief overview of several kinetic theories of surface evolution and growth developed by Herring in 1950 and later followed by Kardar, Parisi and Zhang (KPZ), Wolf and Villain (WV), and Lai and Das Sarma (LD) in the '80's and '90's will be presented. Given the mathematical forms of the mechanism-morphology relationships, one is then tempted to see if it is possible to uniquely determine the growth mechanism of an etched substrate or deposited film by the quantitative analysis of surface topographs such as those obtained with scanning tunneling microscopy (STM) and atomic force microscopy (AFM). This talk will focus on recent attempts to experimentally measure kinetically relevant parameters and determine mechanistic details of surfaces prepared by ion bombardment etching, oxygen atom etching (both laboratory and space shuttle experiments), molecular beam epitaxy, and chemical vapor deposition. Images of the surfaces of all these systems share remarkable qualitative similarities, but the quantitative differences contain the kinetic details that technologists would like to be able to control.

# Optimal Control of Wave Packet Dynamics

Jeffrey L. Krause, Robert M. Whitnell, YiJing Yan and Kent R. Wilson

*Department of Chemistry 0339  
University of California, San Diego  
La Jolla, CA 92093*

We employ a recently developed formalism<sup>1</sup> to predict the electric fields that optimally control the dynamics of wave packet evolution on an excited potential energy surface. The method begins by choosing a target distribution in phase (position/momentum) space. The objective, then, is to find the field that excites a wave packet that has the best overlap with the target at a specified final time. This is accomplished by diagonalizing a symmetrized molecular response function, which depends only on properties of the molecule and the target. The eigenvectors of this function are the optimal fields, and the eigenvalues are the target yields. The eigenvector corresponding to the maximum eigenvalue is the globally optimal field.

We present results for a "molecular reflectron" in which a narrow wave packet is focused in the bound region of the  $I_2$  excited state potential with an incoming momentum, and a "molecular cannon," in which a narrow wave packet is focused in the continuum with an outgoing momentum. The optimal fields are simple, and can be well fit Gaussian pulses containing linear and quadratic chirps. Furthermore, the fields are robust with respect to variations in the parameters of the Gaussian fits. We show how finite temperature and molecular rotation affect the results. Finally, we discuss how the focused wave packets can be detected in experiments, such as those underway in the Wilson group.

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<sup>1</sup> Y. J. Yan, R. E. Gillilan, R. M. Whitnell, K. R. Wilson and S. Mukamel, *J. Phys. Chem.* **97**, 2320 (1993).

Binding energy of  $H_2$  in  $H_2-ML^+$  and  $H_2-M(H_2)_n^+$ ,  $n=1-5$ , with  $M = V, Co$  and  $Cu$ .

Philippe Maitre, Harry Partridge and Charles W. Bauschlicher, Jr.  
NASA Ames Research Center  
Moffett Field, CA 94035

Recently, Kemper *et al.* measured the successive binding energies of  $H_2$  to  $Co^+$  and  $V^+$  and found very different behavior for the evolution of the  $H_2$  binding energy, especially when the sixth ligand is added. They also measured the effect of the nature of the ligand  $LCH_4$  and  $H_2O$  on the binding energy of  $H_2$  in  $CoL^+-H_2$ .

We report our theoretical contribution to the understanding of the cooperative ligand effects to the structural parameters and binding energy for the vanadium, cobalt and copper cations. One of the goals of this work was to check the reliability of single reference based correlation treatment for such systems. A systematic geometry optimization of the complexes show the ability of the UMP2 method to reproduce the topology of the potential energy surface. Nevertheless, a good comparison with the experimental results can be achieved only with a higher level of correlation treatment. The main difficulty reside in the description of the donation of the metal to  $H_2$ , especially when a  $\pi$  donor is also coordinated to the metal.

Dynamics of Crystal Growth from Spherical Geometries—Some Initial Ideas  
Carey K. Bagdassarian and David W. Oxtoby

Phase-field equations have been used successfully to describe dynamics of phase transitions. Essentially, they comprise the simplest kinetic equations which guarantee the decrease of free energy with time. Though they cannot model the appearance of the new phase, they are used to capture the growth dynamics of an already inhomogeneous system. We are interested in understanding the liquid-to-crystal phase-transition dynamics from an incipient solid with spherical profile. The solid is described by a single order-parameter with the global free energy written in the square-gradient approximation of Cahn-Hilliard. The homogeneous free energy is modelled with a double parabola which allows for a largely analytic treatment. For example, the stationary critical nucleus profile is easily obtained, and we seek expressions for growth away from perturbations around it. Connections are made to classical nucleation theory.

Abstract for poster to be presented at West Coast Theoretical Chemistry Conference, UCLA, Los Angeles, CA, June 17, 1993

**PSEUDOSPECTRAL SECOND- AND THIRD-ORDER  
MØLLER-PLESSET PERTURBATION THEORY**

Todd J. Martinez and Emily A. Carter

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University of California, Los Angeles  
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We use the Hylleras-variational principle to solve for the second- and third-order Møller-Plesset (MP2 and MP3) energies using pseudospectral techniques. The method scales as  $n^2N^3$  for MP2 and  $n^3N^3$  for MP3, where  $n$  is the number of occupied orbitals and  $N$  is the number of basis functions. Thus, a factor of  $N/n$  is saved for MP2 (relative to the partial integral transform required spectrally) and a factor of  $n$  is saved for MP3. The usual pseudospectral reduction in scaling is not possible in MP2 because of the necessity of explicitly forming some of the 4-index integrals. The equations have been programmed in the atomic orbital basis, permitting the effective use of cutoffs for the time-consuming portions of the calculation. We present results detailing the accuracy of the pseudospectral approximation for several molecules, as well as preliminary timing information.

## **MD Simulation of Shape-Selective Separation in Zeolite Molecular Sieves: Butane and Isobutane in Silicalite**

**John B. Nicholas, Robert J. Harrison, Rik J. Littlefield,  
Lennox Iton, and Anthony C. Hess**

Shape-selectivity is key to the separation of hydrocarbon mixtures by zeolite molecular sieves. This fundamental aspect of zeolite chemistry is vital to the petroleum industry for the production of high-octane gasoline. Theoretical simulation of zeolite-adsorbate systems gives us insight into the factors that control shape-selectivity and the ways we can modify zeolite molecular sieves to enhance their separation behavior.

We have simulated the diffusion of butane and isobutane in the molecular sieve silicalite using molecular mechanics and molecular dynamics (MD) techniques. The studies involve ensembles of 108 adsorbate molecules in a 3x3x3 arrangement of silicalite unit cells. The total system contains 9288 atoms in a volume of 60x60x45 Å. We have included all possible atom-atom interactions in the force field calculations. The adsorbate molecules have complete flexibility while the silicalite is held rigid. We will present the results of one nanosecond long trajectories for two different concentrations of each adsorbate; the longest and largest simulations of these types of systems ever performed. The results show that isobutane diffuses significantly slower than butane; diffusion constants are  $7.5 \times 10^{-6}$  and  $1.5 \times 10^{-7}$  cm<sup>2</sup>/sec respectively. This rather large difference in the diffusion constant demonstrates the shape-selective nature of zeolitic diffusion; the isomers have the same mass, but the branched isomer diffuses much slower. We will also present results for similar simulations in which the zeolite lattice is also given complete flexibility. The inclusion of the dynamics of the lattice increases the rates of diffusion for both molecules by a factor of 3. We also find the occupancy of the two isomers within the silicalite channels is significantly different. The butane molecules prefer to reside in the smaller channels in the zeolites that afford the most favorable van der Waals interactions with the zeolite. The more bulky isobutane molecules spend most of their time in the intersections between channel segments.

## BEYOND ONE GLOBAL MINIMUM APPROXIMATION

A. I. Boldyrev

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Utah 84112, USA

In structural chemistry it is assumed that in studying the structure of molecule in the gas phase experimental structural parameters (bond lengths and valence and dihedral angles) are applicable to isolated molecules. However, in terms of a strict quantum description this is not true. According to the main postulate of the quantum mechanics, an isolated molecule can exist only in stationary states and in such states the molecular's nuclear density function is delocalized with respect to all absolute minima (the number of which for polyatomic molecules containing several identical nuclei is high; e.g., the benzene molecule  $C_6H_6$  has 43, 200 global minima). However, this conclusion is not supported by experience gained in studying the structure of molecule through various physical experimental techniques. According to the latter, the nuclear density function is nevertheless localized in one minimum, and the molecule's structure and properties can be described in terms of quasi-rigid one-minimum models such as "rigid rotator - harmonic oscillator" or "semirigid rotator - anharmonic oscillator" model

It is therefore important to identify the conditions in which we can use the localized description of molecules and retain the classical structural models, and those in which a change to a delocalized description is necessary. An understanding of the reasons for the delocalization of the nuclear density function of the molecule and of the physical phenomena which can lead to delocalization of this function is also important. It is interesting to establish how the delocalization - localization transition of the nuclear density function takes place, and how this transition is reflected in the properties of the molecules.

The aim of the present work is to discuss these problems in the term of the simplest  $A_3B$  and  $LMX_4$  flexible molecular systems. It has been shown that a delocalization mechanism consisting of the destruction of phase coherence arising from quickly varying random changes of the tunnel splitting parameter  $\gamma$ , can occur under the influence of collisions with other molecules. If the temperature of the molecular gas  $T$  is higher than the critical temperature  $T_0$  (for double minimum surface,  $T_0 = \hbar\gamma/k$ ) then the nuclear density function is localized in one minimum, and if  $T < T_0$  than the nuclear density function is delocalized throughout all absolute minima. Normally, the value of  $T_0$  is extremely small and even for the flexible  $NH_3$  molecule  $T_0 = 0.5^\circ K$ . It should be noted that a molecule whose nuclear density function is localized in one minimum is not in a stationary state and over some finite period of time  $t_0$  (this is the life time of the classical structure of a molecule) it will pass into another state with the nuclear density function localized in another minimum.

With these tools we can define the difference between quasi-rigid and non-rigid molecules. If the barriers separating the minima are sufficiently high, then the tunnel splittings are low and the localized state life time is large, and one global minimum models applicable. If the barriers separating the minima are low, than flexible multim minima models (which takes into account all accessible minima) should be used to describe rovibrational levels.



## **Friday, 18 June 1993**

### ***Session III***

***(California Room)***

***Chair: Professor Chi Mak, University of Southern California***

<b>2:30-2:50</b>	<b>Professor John Wheeler, University of California, San Diego</b>
<b>2:50-3:10</b>	<b>Christine Wu, University of California, Los Angeles</b>
<b>3:10-3:30</b>	<b>Dr. Vladimir Mandelshtam, University of Southern California</b>
<b>3:30-3:50</b>	<b>Dr. Jan Michael Rost, University of Washington</b>
<b>3:50-4:10</b>	<b>Kian-Tat Lim, California Institute of Technology</b>
<b>4:10-4:30</b>	<b><i>Coffee Break</i></b>
<b>4:30-4:50</b>	<b>Dr. Doug McLean, IBM Almaden</b>
<b>4:50-5:10</b>	<b>Dr. Xiao Cheng Zeng, University of California, Los Angeles</b>
<b>5:10-5:30</b>	<b>Dr. David Smith, Pacific Northwest Laboratories</b>
<b>5:30-5:50</b>	<b>Dr. Andrea Liu, University of California, Santa Barbara</b>

## Critical Fluctuations in Polymerizing Solutions

John C. Wheeler  
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University of California, San Diego  
La Jolla, CA 92093-0340 U.S.A.

Equilibrium polymerization in a solvent of "living" polymers, such as poly  $\alpha$ -methyl styrene, and of giant polymeric micelles exhibits nonclassical critical singularities governed by the heat capacity singularity of the underlying  $n \rightarrow 0$  vector model. Concentration fluctuations in these solutions, are predicted to exhibit particularly visible effects. Even in the absence of any interaction favoring separation of monomer and solvent, a dramatic enhancement of the concentration fluctuations is predicted above those given by mean field theory (Flory theory) due to the *critical fluctuations* inherent in the polymerization transition itself. The predicted behavior explains recent neutron scattering results on polymerization of poly- $\alpha$ -methyl styrene and suggests improvements in experimental conditions that would lead to the observation of even more interesting behavior. It is also in accord with recent measurements of scattering from solutions forming giant polymeric micelles.

Abstract for a talk to be presented at West Coast Theoretical Chemistry Conference, UCLA, Los Angeles, CA, June 18, 1993

## **H<sub>2</sub> DESORPTION AND H ADATOM DIFFUSION ON Si(100)-2x1**

Christine J. Wu, Irina V. Ionova and Emily A. Carter  
Department of Chemistry and Biochemistry, University of California  
Los Angeles, CA 90024-1569

We present a theoretical study of hydrogen diffusion and desorption on the Si(100)-2x1 surface using both ab initio electronic structure calculations and classical Monte Carlo simulations. Two previously proposed hydrogen  $\beta_1$ -desorption mechanisms were examined via ab initio calculations and were both found to give a higher activation barrier than the experimental values. Therefore, we propose a new desorption mechanism, in which H<sub>2</sub> desorbs via a dihydride species on isolated defects and the desorption rate is strongly influenced by surface diffusion. In order to obtain hydrogen surface diffusion constants, we developed an ab initio-derived silicon-hydrogen potential, from which the diffusion constants were then obtained by classical transition state theory Monte Carlo simulations for temperatures in the range where hydrogen desorption occurs.

## **A new stabilization approach to the scattering problem.**

V.A.Mandelstam and H.S.Taylor  
Chemistry Department  
University of Southern California

A new conceptually simple and computationally economic method of evaluating the spectral density of a scattering Hamiltonian is presented. The spectral density can be then used to compute the density of resonance states, photoabsorption cross section, microcanonical rate constant etc. The method uses only the eigenfunctions and real eigenvalues of the system in a series of finite enclosures. Traditional scattering solutions are avoided, as are dilatation analytic, imaging and absorbing potential techniques.

## **Molecular Dynamics Simulations on Million-Atom Systems**

**Kian-Tat Lim and William A. Goddard, III**

*Materials and Molecular Simulation Center  
California Institute of Technology  
Pasadena, CA 91125*

With the advent of parallel supercomputers and new algorithms such as the Cell Multipole Method (CMM), very large scale molecular dynamics (MD) simulations can now be performed in reasonable time frames. These calculations can provide accurate information on structure and properties of systems such as polymers and viruses that previously was unobtainable without significant approximations and simplifications. This talk will describe the methods used to perform MD on molecular systems as large as 1.15 million atoms. Results and timings from computations on a block of polytetrafluoroethylene (PTFE) and on large starburst dendrimers, performed on a Kendall Square Research KSR-1 parallel supercomputer, will be presented.

## Progress Report on the ARCHEM Open Interface for Computational Chemistry.

Doug McLean  
IBM Almaden Research Laboratory  
650 Harry Road, San Jose 95120-6099

June 18, 1993

### Abstract

At last year's WCTC Meeting, I introduced IBM Almaden's ARCHEM project to establish a machine independent public standardized open interface for computational chemistry. Since then the project has advanced through the full time efforts of the speaker and his colleagues Charles Gillan and Eric Replogle. I will review our progress and outline the ARCHEM implementation that we will make freely available to computational chemistry research groups by the end of this year.

ARCHEM's goal is to provide two levels of independence. First, for program developers to be able to develop machine independent program modules with no knowledge of programming details in other modules. Second, to provide computational scientists with a script language that allows them to run experiments using scripts and program modules that are machine independent.

This talk is supplemented by Eric Replogle's poster at tomorrow's poster session (see his abstract), where in addition to detailed information about ARCHEM there will be documentation available.

**SOME CONSEQUENCES OF THE  $\alpha$ - $\beta$  BIFURCATION OF RELAXATIONS IN  
SUPERCOOLED LIQUIDS**

**Xiao-Cheng Zeng, Daniel Kivelson &**

**Department of Chemistry and Biochemistry, University of California, Los Angeles, Ca 90024,  
and Gilles Tarjus,**

**Laboratoire de Physique Theorique des Liquides, Universite Pierre et Marie Curie,  
4 Place Jussieu, 75252 Paris, Cedex 05, France**

A simple model of relaxation in supercooled liquids is developed in which torques, stresses, and forces are all assumed to relax with the same two characteristic relaxation times, both increasing with decreasing  $T$ , one as an Arrhenius function, the other more rapidly, possibly as a Vogel-Fulcher function. Most of the reported experimental data on supercooled liquids composed of simple molecules can be explained semi-quantitatively by means of this model without the introduction of any criticality other than that possibly implied by the Vogel-fulcher or closely related expression. Limited theoretical justification for the model will also be presented.

+ Supported in part by the NSF and the C.N.R.S.

# Molecular dynamics computer simulations of water and aqueous solutions using a polarizable water model

David E. Smith and Liem X. Dang  
Molecular Science Research Center  
Pacific Northwest Laboratory\*  
Richland, WA 99352

## Abstract

Classical molecular dynamics computer simulations have been used to investigate several properties of aqueous solutions modeled with both polarizable and nonpolarizable water. The dielectric properties of the polarizable water model of Dang [J. Chem. Phys. 97, 2659 (1992)] have been calculated and found to be in qualitative agreement with experiment. The model has been used to determine ion-water structures, potentials of mean force, and ionic association dynamics for aqueous sodium-chloride solutions. The ion-water interaction potentials were constructed through fitting to both experimental gas-phase binding enthalpies for small ion-water clusters and to the solvation enthalpies and structural properties of ionic solutions. The results in polarizable water have been compared with results from similar calculations using nonpolarizable water. The dependence on water polarizability is found to be modest yet measurable, as expected for simple 1-1 electrolyte solutions.

\* The Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.



Abstract Submitted  
for the 1993 West Coast  
Theoretical Chemistry/Statistical Mechanics  
Conference

**Phase Behavior of Semiflexible Diblock Copolymers.\***

C. SINGH, A. J. LIU, G. H. FREDRICKSON; *Dept. of Chemical and Nuclear Engineering, UC Santa Barbara*. A diblock copolymer is a polymer made of two chemically bonded sequences, or blocks, each made of different monomers. At high temperatures, diblock copolymers mix, but at lower temperatures, they tend to phase separate into microphases, characterized by alternating regions rich in each block. Although the nature of this order-disorder transition has been well-studied for flexible diblocks, the thermodynamics of semiflexible diblocks has received only recent attention. We have developed a theoretical framework for the phase behavior near the order-disorder transition of diblock copolymers of arbitrary flexibility. Our approach is based on a free energy functional calculated from a microscopic model of rods connected by free joints. The free energy depends only on a small set of parameters: the Flory chi parameter and Maier-Saupe parameter, which measure the strength of isotropic and anisotropic interactions, respectively, and the bending rigidities and molecular weights of each block. Given these, we have explored the effect of differences in flexibility between the two blocks, as well as the effect of increased stiffness of the diblock as a whole, on the phase behavior.

\*Supported by NSF grant DMR-9100033.

## **Saturday, 19 June 1993**

### ***Session IV (California Room)***

***Chair: Professor Bob Cave, Harvey Mudd College***

<b>9:00-10:00</b>	<b>Professor Eric Heller, University of Washington</b>
<b>10:00-10:20</b>	<b>Dr. Rony Granek, University of California, Los Angeles</b>
<b>10:20-10:40</b>	<b>Professor Bernie Kirtman, University of California, Santa Barbara</b>
<b>10:40-11:00</b>	<b><i>Coffee Break</i></b>
<b>11:00-11:20</b>	<b>Professor Craig Martens, University of California, Irvine</b>
<b>11:20-11:40</b>	<b>Dr. Karl-Heinz Pfeifer, IBM</b>
<b>11:40-Noon</b>	<b>Professor Brian Moore, Eastern Washington University</b>
<b>Noon-12:20</b>	<b>Larry Carter, University of California, Los Angeles</b>
<b>12:20-2:30</b>	<b><i>Lunch (Sequoia Room)/Poster Session III (California Room Patio)</i></b>

**New Developments in Semiclassical Approximations: Dynamics,  
Spectroscopy, and Chaos\***

**Eric Heller**

**University of Washington**

The connection between quantum dynamics and classical mechanics is much closer than was believed just a year ago. Complete molecular spectra can be recreated solely by running classical trajectories. This is true even if the dynamics is chaotic. This compels us to probe the dynamical information in spectra more closely. We find that hierarchial molecular spectra have hierarchial classical dynamics, with well-defined sequences of classical events. We can assign spectra in terms of events in the time domain, and in addition give new quantum numbers to augment traditional spectral assignments. For explicitly time dependent pump-probe experiments, the new results imply a more direct connection between the experiments and classical mechanics than was previously believed.

\*Acknowledgements: The recent work I shall describe was done in collaboration with Miguel Sepulveda and Steve Tomsovic.

## 2-Dimensional growth of surfactant aggregates: The Role of Spontaneous Curvature

R. Granek and W. M. Gelbart

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Hilgard Avenue, Los Angeles, CA 90024-156905*

### ABSTRACT:

We study the 2-Dimensional structural evolution in Smectic-A (Lamellar) phases of self-assembling surfactant systems, in which the rim associated with a bilayer edge has a preferred curvature. This property was not considered in previous studies of 2-Dimensional aggregation, in which case an infinite bilayer emerges already at very low concentrations.

We use a lattice model to describe the bending energy of the rim. An occupied lattice site corresponds to a minimum disk-like micelle. There is a bending energy penalty associated with corners and smooth interfaces depending on the value of the spontaneous curvature. When the spontaneous radius of curvature (of the rim) is small and the bending modulus is large, we find that the liquid-liquid condensation transition is postponed to high concentrations. At low concentrations this bending energy leads to an effective repulsive interaction between the aggregates, which in turn can lead to ordered (modulated) structures for not too large ratios of thermal energy to bending energy (which is the expected situation in most systems of interest).

Our model should be applicable for systems of decylammonium chloride and cesium perfluorononanoate studied by N. Boden (NMR and conductivity measurements) and J. Zasadzinski (freeze-fracture). In the latter systems a modulated stripe-phase of disk-shaped aggregates appears within the Smectic-A layers, which seems to fit our picture. Experimental studies of the structural evolution under further condensation of the system are not yet available.

## ACCURATE NONLINEAR OPTICAL PROPERTIES OF POLYACETYLENE FROM *AB INITIO* FINITE OLIGOMER CALCULATIONS

Bernard Kirtman, Joseph L. Toto, Muhammad Hasan and Robyn M. Carrillo  
Department of Chemistry, University of California, Santa Barbara, CA 93106

At the present time, the only theoretical method for obtaining reliable nonlinear optical properties of conjugated polymers is through *ab initio* finite oligomer calculations. But the finite oligomer approach is not without its own set of difficulties among which are:

- (1) extrapolation to the infinite chain limit,
- (2) including electron correlation for static and oscillatory fields
- (3) accounting for vibrational distortion and
- (4) treating interchain interactions.

All of these will be analyzed using the prototype  $\pi$ -conjugated polymer, polyacetylene, as the primary example.

## Role of Microscopic Solvation in Cluster Reaction Dynamics

Craig C. Martens and Xiche Hu  
Department of Chemistry  
University of California, Irvine  
Irvine, CA 92717-2025

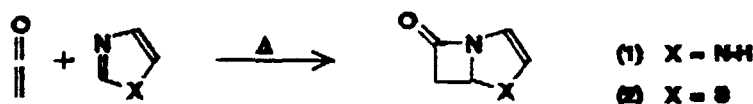
Molecular dynamics simulations of a prototypical cluster association reaction  $\text{IAr}_n + \text{I} \rightarrow \text{I}_2 + n\text{Ar}$  are described. The overall association reaction is found to be composed of three fundamental processes: (1) capture of the incident iodine atom by the  $\text{IAr}_n$  cluster; (2) migration of the captured I atom by a diffusive process on the surface or in the interior of the cluster, leading ultimately to an encounter with the other I atom to form a highly excited  $\text{I}_2$  molecule; (3) evaporative cooling of the diatomic product by energy transfer from the excited molecule into the Ar cluster, leading to decomposition of the cluster and vibrational relaxation of molecular iodine. A point-continuum model for evaluating atom-cluster interaction potentials is developed and applied to the calculation of capture cross sections and thermal association rate constants for atom-cluster association in the framework of the Langevin model, yielding good agreement with direct simulation. The accuracy of the model improves with  $n$ , illustrating the emergence of bulk-like continuum behavior as cluster size is increased.

# An Ab Initio Study of the Reaction of Ketenes with Imidazoles and Thiazole

Jake Pacansky and Karl-Heinz Pfeifer

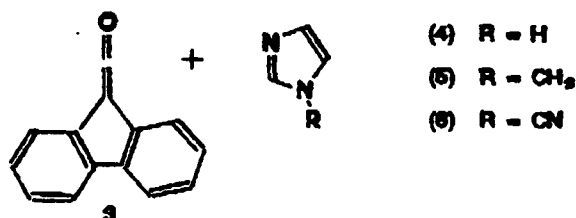
IBM Almaden Research Center, San Jose

The  $\beta$ -lactam antibiotics, i. e. Penicillin, are important drugs because of their broad spectrum of activity and their low toxicity. The common acknowledged model, explaining the reason for their effect, says, that these substances interfere in the final stage of the biosynthesis of peptidoglycan. Furthermore,  $\beta$ -lactamases are a family of bacterial enzymes which convert the  $\beta$ -lactams into inactive compounds by hydrolysing the amid-bond of the  $\beta$ -lactam ring. As an access to understand the mechanism of the effect of the above mentioned substances we conduct calculations on the following two simple model reactions as a first step:



We used the HF-SCF method with the basis sets 3-21G<sup>+</sup> and 6-31G<sup>++</sup>. The force constants of the geometry optimized structures of the adducts, transition states, intermediates and products were calculated with these methods as a proof that minimas or transition states were indeed found. We additionally optimized the structures with the MP2/6-31G<sup>++</sup> method in order to get reasonable values of the transition state energies.

In a second step we conducted calculations on the reaction of the substituted ketene (3) with the three imidazoles (4) - (6). using only the 3-21G<sup>+</sup> basis set:



Among other things Jake Pakansky et al. carried out experiments with these molecules about 1981. Using a simple matrix isolation technique, they succeed in detecting an intermediate of this type of reaction. So we are able to compare the theoretical findings with experimental results.

In this talk I will discuss the results gained with the calculations and some of their consequences for subsequent experiments. Further on I will discuss a model for the different stability of the three zwitterions, build by the attack of the nitrogen lone pair of the imidazoles (4) - (6) on the middle C-atom of the ketene.

## Density Functional Analysis of Phase Transition Models

Brian G. Moore and John D. Mize

*Department of Chemistry/Biochemistry MS-74  
Eastern Washington University, Cheney, WA 99004*

The density functional approach in statistical mechanics, namely the expansion of the non-ideal part of the free energy about a reference state, is illustrated by application to two phase transition models. The first model is the Zwanzig model of the isotropic-nematic (liquid crystal) transition. For this model, the virial coefficients have been calculated to 8th order, and there is evidence of a convergence in the solutions for the co-existing phases. Thus, this model provides a good test for the convergence of the DF expansion; e.g. does the third-order DF truncation provide a better result than second-order? Previous DF calculations for hard-sphere freezing indicate that the extension to third order does not necessarily improve the results. We will also examine the application of the DF expansion to the liquid-gas phase transition derived from the van der Waals equation of state. The vdW model provides a much simpler free energy to illustrate the technique, and yet recovers many of the qualitative features of the DF calculations based on more sophisticated models.



Abstract for talk to be presented at West Coast Theoretical Chemistry Conference, UCLA, Los Angeles, CA, June 19, 1993

**FIRST PRINCIPLES-DERIVED DYNAMICS OF F<sub>2</sub> REACTIVE SCATTERING ON Si(100)-2x1**

Lawrence E. Carter, Shervin Khodabandeh, Paul C. Weakliem,  
and Emily A. Carter

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Los Angeles, CA 90024-1569*

We have simulated via molecular dynamics the zero coverage limit of the interaction of F<sub>2</sub> with the clean Si(100)-2x1 reconstructed surface. Using a Stillinger-Weber-type many-body potential with the Si-F interactions refit to ab initio data, we found that both vibrational and translational excitation in the incident F<sub>2</sub> can lead to increased reactivity, but they do so in different ways. The dominant reaction channels are a) F-atom abstraction, leading to the formation of one Si-F bond while the remaining fluorine atom is ejected away from the surface, and b) dissociative chemisorption, where both fluorine atoms in the incident F<sub>2</sub> molecule form Si-F bonds on the surface. As a result, increased reactivity is mainly characterized by an increase in dissociative chemisorption events at the expense of F-atom abstraction events and by a corresponding increase in the initial reaction probability  $S_0$ . We find  $S_0$  ranges from  $0.57 \pm 0.04$  for the lowest excitational energies to  $0.78 \pm 0.04$  for the largest translational excitation of 20.9 kcal/mol. For cases where F-atom abstraction occurs, the exit velocities of fluorine atoms ejected from the surface are found to be independent of the incident F<sub>2</sub> energy and with kinetic temperatures much higher than the surface temperature, suggesting that the exiting fluorine atom does not equilibrate with the surface, yet loses memory of its initial state. Finally, for dissociative chemisorption trajectories, we find that the adsite location of the two fluorine atoms is strongly dependent on the incident orientation.

**Saturday, 19 June 1993**

**Session V** (California Room)

**Chair: Professor Craig Martens, University of California, Irvine**

2:30-2:50	Professor Chi Mak, University of Southern California
2:50-3:10	William McCarthy, University of Arizona
3:10-3:30	Srihari Kesharamurthy, University of California, Berkeley
3:30-3:50	Frank Grossman, University of Washington
3:50-4:10	Dr. Sotiris Xantheas, Pacific Northwest Laboratories
4:10-4:30	<i>Coffee Break</i>
4:30-4:50	Monique Chacon, University of Utah
4:50-5:10	Mark Sharlow, University of California, Los Angeles
5:10-5:30	Dr. Grant Smith, Pacific Northwest Laboratories
5:30-5:50	Richard Muller, California Institute of Technology
7:00	<i>Banquet (Sequoia Room)</i>

After-dinner speaker: Professor Howard Reiss, University of California, Los Angeles

## **Quantum Monte Carlo Simulations of Electron Tunneling in the Bacterial Photosynthetic Reaction Center**

**Reinhold Egger and C.H. Mak  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90089-0482**

Real-time quantum Monte Carlo (QMC) simulations have been used to compute the ultrafast electron tunneling rates in a tight-binding model of the bacterial photosynthetic reaction center. The simulations show that a dissipative three-state tight-binding model reproduces all experimentally observed characteristic features of the reaction center, including the negative temperature dependence of the transfer rate. The QMC simulations suggest that the initial electron transfer proceeds with a coherent mechanism that is different in nature from superexchange. The best efficiency is observed for a BChl<sub>L</sub> bridge energy close to the special pair and a small electronic coupling between them ( $\approx 60 \text{ cm}^{-1}$ ). The time constant of the charge separation is 0.6 ps at 237 K and decreases to 0.3 ps at 24 K. The bridging BChl<sub>L</sub> population is less than 20% throughout.

***ab initio* dynamics of the large amplitude  
ring puckering motion in 2-sulpholene**

W.J. McCarthy, M.A. Rochrig, Qi-Qi Chen, G.L. Henderson,

L. Adamowicz, and S.G. Kukolich

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

**Abstract**

Microwave measurements made on the rotational spectrum of 2-sulpholene provided limited information on the low frequency, large amplitude ring-puckering vibration. To supplement this experimental evidence, an *ab initio* potential energy curve was calculated at the SCF/3-21G\* level in terms of a single parameter ( $\omega$ ) describing the large amplitude motion (LAM) of the ring puckering. Vibration-coordinate dependence of the effective reduced mass associated with the LAM and the resultant kinetic energy expansion were determined. The solutions of a one dimensional Schrodinger equation solved within the double well potential yield a separation between the  $\nu = 0$  and  $\nu = 1$  LAM vibrational states of  $8\text{cm}^{-1}$ . The  $\nu = 0$  and  $\nu = 1$  eigenvalues for the SCF ring puckering potential were found to give vibrationally averaged rotational constants in good agreement with those obtained from the microwave spectrum.

# Multidimensional Tunneling - a semiclassical model using locally conserved actions

Srihari Keshavamurthy and William H. Miller

*Department of chemistry, University of California*

*Berkeley, California 94720*

Hydrogen atom transfer reactions are common in organic chemistry and in certain biological systems. At low temperatures this motion of Hydrogen atoms manifests itself in the form of tunneling. In complex chemical systems tunneling typically involves a large number of degrees of freedom which makes an exact quantum treatment very difficult. It is however, easier to do classical dynamics on the multidimensional potential surface but the classical approach cannot account for tunneling from one classically allowed region of phase space to another. Hence one is interested in semiclassical mechanics to investigate the tunneling dynamics. There do exist "rigorous" semiclassical theories to study tunneling but they are not easily applied to a complicated chemical system. For systems with large number of degrees of freedom it thus becomes important to develop *simple* semiclassical models which would give some insights into the complex nature of the tunneling dynamics.

In this paper we present a simple semiclassical model which can be easily incorporated into standard classical trajectory simulations. We use locally conserved actions associated with the saddle point to obtain tunneling rates. Application to a model two dimensional system to obtain state-specific tunneling rates is discussed. In addition applications to higher dimensional systems will be outlined.

# **A Semiclassical Approach to Relaxation in Quantum Systems**

**Frank Grossman and Eric J. Heller**

*University of Washington, Department of Chemistry, BG-10*

*Seattle WA 98159, USA*

## **Abstract**

We study a nonlinear quantum system (test-system) coupled to an environment, consisting of (i) a single harmonic degree of freedom and (ii) infinitely many harmonic oscillators. In the first case, starting from the functional integral for the propagator, a multidimensional cellular dynamics method is shown to produce good results compared with the full quantum mechanics. In the second case a simple semiclassical approximation to the propagator of the reduced density matrix for Ohmic dissipation (of damping strength  $\gamma$ ) and high temperatures,  $T$ , is derived. Implemented using cellular dynamics it is shown to lead to remarkably good agreement with the solution of the corresponding quantum master equation when the product  $\gamma T$  is small. The exact numerical results for the Morse oscillator show the suppression of high frequency oscillations and the approach to thermal equilibrium. Finally we discuss the relevance of our results to ultrafast pump-probe spectroscopy of molecules in the solid state and the relaxation of atoms absorbed at a surface.

*Abstract of presentation at the West Coast Statistical Mechanics / Theoretical Chemistry Conference, June 17-19, 1993, Univ. of California, Los Angeles, CA.*

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## AB-INITIO STUDIES OF WATER CLUSTERS<sup>†</sup>

Sotiris S. Xantheas and Thom H. Dunning Jr.

Molecular Theory Group, Molecular Science Research Center,  
Pacific Northwest Laboratory<sup>‡</sup>, Richland, WA 99352, USA

The optimal structures and harmonic vibrational frequencies of cyclic water clusters,  $(\text{H}_2\text{O})_n$ ,  $n=2-6$ , have been determined at the Hartree-Fock and MP2 levels of theory. Analysis of the structural trends reveals that the separation between neighboring oxygen atoms decreases exponentially with increasing cluster size. The trends in the harmonic vibrational frequencies suggest that, for large clusters, the intramolecular bends are blue-shifted by  $\sim 70 \text{ cm}^{-1}$  with respect to the monomer frequency, whereas the ones corresponding to the "bridge" hydrogens are red-shifted by  $\sim 400 \text{ cm}^{-1}$  with respect to the symmetric stretch in water. The magnitudes of the many-body interactions are also computed through an energy decomposition scheme including basis set superposition error (BSSE) estimates.

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<sup>†</sup> Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract No. DE-AC06-76RLO 1830.

<sup>‡</sup> Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U. S. Department of Energy.

# An $N^4$ method for static polarizabilities.

Monique Revoredo Chacon<sup>1</sup> and Michael C. Zerner

*Quantum Theory Project*

*University of Florida*

*Gainesville, Florida 32611*

## ABSTRACT

We present a method closely related to Configuration Interaction over Single excitations (CI-S) for the calculation of static dipole moment and polarizabilities, which we call Modified Configuration Interaction over Single excitations (MCI-S). This method allows for orbital relaxation through the inclusion of single excitations on a correlated 1st order Rayleigh-Schroedinger wavefunction.

An approximation to our Modified Configuration Interaction over Single excitations results in an inexpensive method to calculate polarizabilities that yields good results when compared with the Full Configuration Interaction (CI-F) results. This method, called Modified Configuration Interaction over Single excitations without triple excitations (MCI-S\_WT), seems particularly suitable to applications for large systems.

Examples are presented using the Intermediate Neglect of the Differential Overlap Model Hamiltonian (INDO/1) which indicates that the MCI-S\_WT procedure presents an error of less than 15% with respect to the Full Configuration Interaction (CI-F) values in a fraction of the computational effort.

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<sup>1</sup> Present Address:

University of Utah

Chemistry Department

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## ABSTRACT FOR PRESENTATION BY MARK F. SHARLOW

Title: COMPARATIVE PHASE BEHAVIOR OF HARD ROD AND DISK FLUIDS

The phase behavior of fluids of hard spherocylindrical particles has been the subject of much theoretical work. Since some molecules which form liquid crystals are disk-shaped rather than rod-shaped, similar results for disk-shaped particles are important to pursue. Some studies of disk-shaped particles (using quasi-analytical methods and simulations) already exist in the literature. We describe here our calculations of the phase behavior of disk-shaped hard particles using both density-functional theory and Monte Carlo computations. The particle shape we study consists of a cylindrical core with a half-torus edge, i.e., the oblate analogue of the cylindrical core with half-sphere caps (spherocylinder). We compare and contrast our results with existing results for fluids of rods and disks, focusing attention in particular on the presence and absence of partially positionally ordered (e.g., smectic and columnar) states.

**CONFORMATIONAL ENERGIES OF SMALL MODEL MOLECULES FOR  
POLY(TETRAFLUOROETHYLENE) AND POLY(PERFLUOROOXYETHYLENE)  
FROM ELECTRONIC STRUCTURE CALCULATIONS.**

Grant D. Smith, Elore Institute, Sunnyvale, CA 94087

Richard L. Jaffe, NASA Ames Research Center, Moffett Field, CA 94035

Do Y. Yoon, IBM Almaden Research Center, San Jose, CA 95120

In previous work we successfully developed a rotational isomeric state (RIS) model and conformational energy force field for poly(oxyethylene) based upon ab initio electronic structure calculations on small model molecules. In the present work we extend the practice of employing results of ab initio electronic structure calculations on small molecules for the study of conformational properties of polymers to fluorine-containing systems. Here we present results of ab initio calculations of the conformational energies of perfluoropentane as a model for poly(tetrafluoroethylene) (PTFE) and perfluoro-1,2-dimethoxyethane and perfluorodiethylether as models for poly(perfluorooxyethylene) (PFPOE). Also presented are RIS models for these polymers which were developed based on the computed conformational energies of these model molecules. These models are used to predict gauche populations and other conformational properties of the fluorinated polymers. The effects of the fluorine atoms on the conformational energies of these model compounds and on the properties of PTFE and PFPOE are considered by comparison of conformational energies and RIS models of the fluorine containing molecules with similar calculations for analogous non-fluorine containing molecules.

### ***Ab Initio* Calculation of Porphyrin Excited States**

**Richard P. Muller and William A. Goddard, III**

**Materials and Molecular Simulation Center**

**Beckman Institute**

**California Institute of Technology**

The excited states of porphyrin-like molecules have long been described using the Gouterman four orbital model in which the highest two occupied MO's (a and b) are combined with the lowest two excited MO's (c and d) in the combination

$$\begin{aligned} & (a^2bc \pm b^2ad) \\ \text{and} & \\ & (a^2bd \pm b^2ac) \end{aligned} \tag{1}$$

to obtain the visible and the Soret bands.

Gouterman's model has long been used as a qualitative aid to the interpretation of porphyrin spectra. However the size of the porphyrin ring and the multi-configurational nature of the excited state wavefunction have made *ab initio* calculations sufficiently difficult that most calculations thus far have been performed using semiempirical wavefunctions.

We modified the pseudospectral generalized valence bond (PS-GVB) program to allow an MCSCF wavefunction of the form of (1) where all  $\sigma$  and  $\pi$  orbitals are calculated self-consistently. Using the 6-31G\*\* basis set (with 430 basis functions) we solved for all four excited states using the newly developed MCSCF/DIIS convergence method. These results show that the Gouterman four orbital model is indeed an excellent description.

***Poster Session I, Thursday, June 17, Noon – 2:30 pm (California Room Patio)***

Dr. Douglas Beck, University of Washington  
Dr. Paul C. Weakliem, University of California, Santa Barbara  
Dr. Pawel M. Kozlowski, University of Arizona  
Miguel Angel Sepulveda, University of Washington  
Erik Bierwagen, California Institute of Technology  
Dr. Ito Chao, University of California, Los Angeles  
Dr. Roberta P. Saxon, SRI International  
D. C. Benn, University of California, Los Angeles  
Professor Douglas Henderson, University of Iztapalapa, Mexico  
Kirsten Eurenus, University of California, Los Angeles  
Dr. Hans Horn, IBM Almaden  
Dr. Paul Rejto, University of California, Berkeley  
Professor Robert J. Cave, Harvey Mudd College  
Douglas A. Gibson, University of California, Los Angeles  
Dr. Siddarth Dasgupta, California Institute of Technology  
Dr. Marcy Rosenkrantz, Edwards AFB, California  
Dr. Stephen P. Walch, NASA-Ames  
Dr. Sergio Maluendes, Molecular Research Institute  
Dr. Bruce C. Garrett, Pacific Northwest Laboratories  
Dr. Michael Ellerby, University of California, Los Angeles  
John Cullen, California Institute of Technology, Pasadena  
Nathan Oyler, University of Arizona  
Willard Brown, University of California, Berkeley  
Dr. Liem Dang, Pacific Northwest Laboratories

Abstract of poster to the WCTC-Conference 1993:

## Nonclassical Franck-Condon Factors

Douglas Beck and Eric J. Heller

*University of Washington, Department of Chemistry, BG-10,*

*Seattle, WA 98195, USA*

### Abstract:

Franck-Condon factors govern many important molecular processes, including electronic spectroscopy and radiationless transitions. Whereas the "vertical" Franck-Condon processes with good overlap are well understood, the weaker, nonvertical (classically forbidden) transitions are more problematical. Thus, a better understanding of the propensities for exciting various kinds of motion in nonclassical, nonvertical transitions is of great importance to attaching the right significance to certain experiments. For example, in benzene under very low pressure conditions ( $p < 0.1$  Torr) the transition from a particular vibrational state of the  $B_{1u}$  electronic state occurs with a quantum yield of  $\phi_F \approx 0.2$ . Thus, 4 out of 5 molecules decay without radiating or transferring energy via collisions with other molecules (lifetime is on the order of 70 ns). We present a technique which sheds light on these types of processes while avoiding Franck-Condon factor calculations. Results obtained for the radiationless transition of benzene from the  $B_{1u}$  electronic state to the  $A_{1g}$  electronic state are shown.

## RATE OF SODIUM DIFFUSION IN SODALITE.

Paul C. Weakliem, Nick P. Blake, and Horia Metiu

Departments of Chemistry and Physics

University of California

Santa Barbara, CA 93106.

Zeolites are solids with cage like structures which can hold other atoms or molecules in these interconnected cages. Interest in zeolites has generally been in their use for separation of gases, since smaller atoms and molecules can diffuse through the cages, while larger molecules or atoms are unable to pass through. However, we are studying zeolites with the hope of revealing interesting electronic properties which may be quite unlike those of semiconductors or metals.

Sodalite is a zeolite which consists of cages of  $([\text{AlSiO}_4]^-)_3$  with  $(\text{Na}_3)^{3+}$  clusters contained within each cage. In this state, the zeolite is white. When the sodalite is exposed to sodium vapor, the sodium atoms diffuse into the zeolite forming  $(\text{Na}_4)^{4+}e^-$  clusters within the cages. This leads to a change in color where the sodalite becomes blue, and upon further doping the sodalite turns to black. This is due to the adsorption of light by the excess electron. At higher doping concentrations it is likely that two excess sodium atoms occupy neighboring cages whereby the overlap of their wavefunctions could lead to very interesting electronic behavior.

In the current study, we have been examing the paths and rates of diffusion of the excess sodium ion and the electron. This process is important in that it is the first step in understanding the changes that take place as the sodalite is doped. We use wavepacket propagation and semiclassical dynamics to study the diffusion path, and correlation function theory to calculate the rates. We are also studying the effect of orientations and positions of the sodium ions on the diffusion.

# **AN EFFECTIVE METHOD FOR GENERATING NON-ADIABATIC MANY-BODY WAVE FUNCTION FOR HIGHER ROTATIONAL STATES USING EXPLICITLY CORRELATED CARTESIAN GAUSSIAN TYPE- FUNCTIONS**

**Pawel M. Kozlowski and Ludwik Adamowicz**

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA*

## **ABSTRACT**

A general formalism for the application of explicitly correlated Cartesian Gaussian-type basis functions for nonadiabatic calculations on rotationally excited states of many-body systems is presented. In this approach the wave function is expressed in terms of Cartesian coordinates of the positions of all the particles involved in the system and the correlation of the motion of the particles involved in the system and the correlation of the motion of the particles is achieved through exponential functions explicitly dependent on the interparticle distances. The energy associated with the external degrees of freedom, *i.e.* the motion of the center of the mass, is eliminated in an effective way from the total energy of the system. This is achieved by defining the variational principle based on the internal Hamiltonian, which is a difference between the total Hamiltonian and the kinetic energy of the motion of the center of the mass. The particular rotational state is reached by performing variational calculation with the variational functional which includes a penalty term forcing the variational wave function to become an eigenfunction of the total angular momentum operator with the desired eigenvalue. Test calculations on some model systems are presented and comparison with the exact results is discussed.

# ***Semiclassical Calculation and Analysis of Spectra***

***Miguel Angel Sepulveda \*, Eric J. Heller***

***University of Washington, Department of Chemistry BG-10***

*The use of classical trajectories for the solution of the time-dependent Schrodinger equation has been the object of recent study<sup>1</sup>. Since the standard EBK theory is only applicable to classically integrable systems recent research has begun to estimate the validity of semiclassical dynamics when the underlying dynamics is chaotic or mixed<sup>1</sup>. The later case is perhaps the most generic in chemical physics and a new method<sup>2</sup> for the propagation of wave packets in this context is presented. The technique is based on the time-dependent semiclassical Green's function and can be used to write the absorption spectra as a sum over classical orbits. This is illustrated by studying the UV absorption spectra of the Benzophenone molecule.*

*\* Supported by the Ministry of Science (Spain).*

*1 M. A. S., S. Tomsovic, E. J. Heller Phys.Rev Lett. 69, 402 (1992),*

*E. J. Heller, S. Tomsovic, M. A. S., Chaos 2, 102 (1992).*

*2 M. A. S., E. J. Heller, in preparation.*



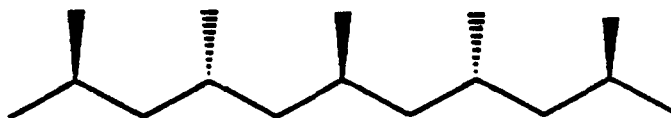
## Theoretical Studies of Model Ziegler-Natta Catalysts. Structural Variations and Tacticity Control.

Erik P. Bierwagen,<sup>†</sup> John E. Bercaw,<sup>‡</sup> and William A. Goddard, III<sup>†</sup>

<sup>†</sup>*Materials and Molecular Simulation Center  
Beckman Institute, 139-72  
California Institute of Technology  
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<sup>‡</sup>*Arnold and Mabel Beckman Laboratories of Chemical Synthesis  
California Institute of Technology  
Pasadena, CA 91125*

Ziegler-Natta (ZN) catalysts are used to polymerize  $\alpha$ -olefins to produce industrially important polymers such as polyethylene, polypropylene, polystyrene, etc. In some cases it has been possible to synthesize syndiotactic polymers:



with homogeneous group 4 cationic catalysts, and isotactic polymers:



with early metal homogeneous catalysts. For homogeneous ZN catalysts, the active species is believed to be:  $x \text{ } \begin{smallmatrix} \text{X} \\ \diagup \\ \text{M} \end{smallmatrix} \text{---R}$ , where R is the alkyl unit, X is cyclopentadienyl or a related ligand, and M = Sc, Ti<sup>+</sup>, Y, Zr<sup>+</sup> etc.

We use the ab initio General Valence Bond (GVB) methods to study how the nature of these metals and ligands affects stereochemistry. The catalysts were modeled as X<sub>2</sub>M-R where X = Cl, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) = Cp; M = Ti<sup>+</sup>, Sc, Zr<sup>+</sup>, Y, Hf<sup>+</sup>, La; and R = H, CH<sub>3</sub>, SiH<sub>3</sub>. We find that M = Ti<sup>+</sup>, Zr<sup>+</sup>, Hf<sup>+</sup> exhibit a strong preference for pyramidal geometries whereas M = Sc, Y, La leads to planar configurations. These results explain the origin of stereospecificity in the syndiotactic polymerization of propylene by unsymmetric metallocene catalysts.

# Theoretical Study of the Conformational Preference of CavitanDs

## in Gas and Solution Phases - Kite vs. Vase

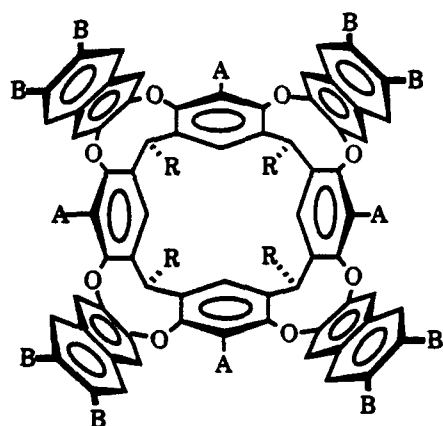
Ito Chao and K. N. Houk\*

*Department of Chemistry and Biochemistry*

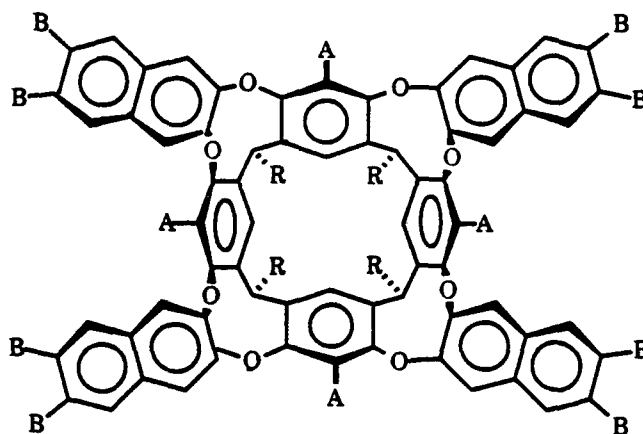
*University of California, Los Angeles*

*Los Angeles, California 90024*

**Abstract:** Energetics and structures of vase and kite conformers of a series of Cram's quinoxaline- and pyrazine- bridged cavitanDs were examined by molecular mechanics and molecular dynamics simulations. The effect of solvent in solution phase was simulated with a continuum solvation treatment. To improve the AMBER force field in program MACROMODEL, a torsional potential function for dihedral angle  $N_{sp^2}-C_{sp^2}-O-C$  was constructed by fitting the torsional barrier of 2-methoxypyrazine obtained by ab initio calculations at theory level RHF/6-31G\*//RHF/3-21G. Comparisons of gas and solution phase results revealed the subtle balance between solvent stabilization and intrinsic strain of a molecule in determining the preferred conformation observed in experiment. In addition, predictions were made for fluoro cavitanDs that have not been synthesized. Finally, our studies of a complexed cavitanD implied the possible existence of a disordered solvent molecule in the X-ray structure.



Vase



Kite

## **Theoretical Studies of Boron Compounds**

**Roberta P. Saxon  
Molecular Physics Laboratory  
SRI International  
Menlo Park, CA 94025**

Electron-deficient compounds can exhibit a variety of forms due to the large number of empty molecular orbitals and thus have been of fundamental interest in investigations of chemical bonding mechanisms. All the hydrides of boron, for example, from BH to BH<sub>5</sub> have been identified directly or indirectly. Boron compounds are of interest, as well, as potential components of fuels for rocket propulsion. Calculations of the structure and stability of the radical BH<sub>4</sub> will be presented. Geometries have been optimized at the MCSCF level and the energy with respect to dissociation to BH<sub>2</sub> + H<sub>2</sub> and BH<sub>3</sub> + H has been determined by MCSCF/CI calculations. A consistent set of values for the heats of formation of the boron hydrides will be compared with literature values. Calculations on the excited state spectrum of BH<sub>2</sub> will also be reported. The correlation diagram linking BH<sub>2</sub> states to those of B + H<sub>2</sub> and of BH + H has been established and rough estimates of excited state lifetimes will be provided.

Supported by AF Phillips Laboratory, Contract No. F04611-90-K-0012

**Nucleophilic Behavior in Electrophilic Reactions: The  
Higher Reactivity of Difluorocarbene with Alkynes than  
with Alkenes**

D. C. Bern and K. N. Houk

UCLA Department of Chemistry and Biochemistry, Los Angeles, CA

This poster presents the reasons why an alkyne reacts faster than an alkene with difluorocarbene, an electrophile. The surprising experimental observation<sup>1</sup> is in contrast to the fact that alkynes are usually less reactive than alkene with electrophiles<sup>2</sup>. Using Hartree-Fock *ab initio* theoretical calculations, the transition states (TS) of various reactions of alkynes and alkenes with difluorocarbene have been determined. From inspection of the activation energies and geometries of these TS, we notice that the substituents of the olefins and alkynes bend out of plane. This out of plane bending is a common phenomena when a nucleophile reacts with alkynes and alkenes. It can be reasoned, therefore, that there is some nucleophilic character in these electrophilic reactions. Furthermore, alkynes react faster than olefins in nucleophilic reactions<sup>3</sup>. Hence, we believe that the higher reactivity of alkynes with difluorocarbene than with alkenes is due to the stronger nucleophilic interaction of difluorocarbene with alkynes than with alkenes.

References:

1. *Tetrahedron*, 1991, 47, 7323.
2. *Tetrahedron*, 1985, 41, 1555.
3. *J. Am. Chem. Soc.*, 1979, 101, 1340.

DOES DIELECTRIC SATURATION PROVIDE A PLAUSIBLE  
EXPLANATION OF THE HYDRATION SOLVATION FORCE?

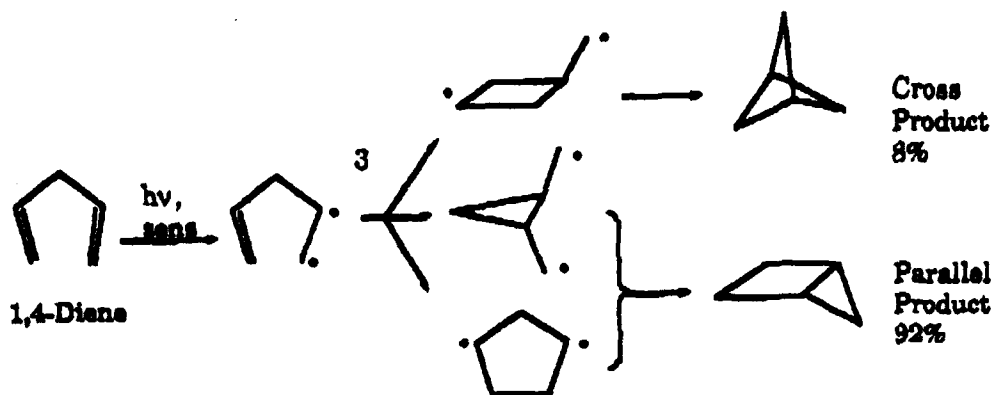
Douglas Henderson and Marcelo Lozada-Cassou  
Departamento de Fisica  
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Some years ago(1), we proposed an extension of the DLVO theory for the solvation force between macroions in an electrolyte which contained two new terms. The first term was an oscillatory core exclusion term resulting from the finite size of the solvent molecules. This we obtained from the PY theory for a mixture of large and small spheres. The second term was obtained by postulating a region of lower dielectric constant near the macrospheres. We suggested that this was due to the alignment of the solvent dipoles near the macrospheres. There seems to be general agreement about the first term. However, Curry and McQuarrie(2) have questioned the usefulness of the second term. They claim that the second term should result in an attraction, rather than a repulsion as we claimed. If Curry and McQuarrie are correct, this is a problem because Israelachvili(3) finds the experimental force to be more repulsive than the prediction of the DLVO theory. We show that, properly interpreted, the second term results in a repulsion and Curry and McQuarrie are in error.

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2. J. E. Curry and D. A. McQuarrie, J. Colloid Interface Sci. 154, 289 (1992).
3. J. N. Israelachvili, "Intermolecular and Surface Forces" (2nd Ed.), Academic Press, London (1992).

**THEORETICAL STUDIES OF INTRAMOLECULAR [2+2]  
PHOTOCYCLOADDITIONS:  
TRANSITION STATES AND INTERMEDIATES**

Kirsten Eurenus, K. N. Houk  
Department of Chemistry and Biochemistry  
University of California, Los Angeles  
Los Angeles, California 90024



Triplet-sensitized intramolecular [2+2] photocycloadditions were examined using a transition state force field model developed from an MP2/6-31G\* study of triplet ethylene addition to ethylene. Further calculations were performed using the GAUSSIAN92 and GAMESS programs at the (2,2) and (4,4) CASSCF/3-21G level with subsequent single points with the 6-31G\* basis set. Calculations of the spin orbit coupling constant were performed on relevant structures. QCI calculations were performed to avoid the differences in active space used in the calculations on the various transition structures and diradical intermediates. We determined that the competition between the diradical closure and reversion back to starting diene is the key factor in determining product ratios.

## **A Parallel Direct SCF and Gradient Program for Workstation Clusters**

**Stefan Brode, Hans Horn, Michael Moldrup, Julia E. Rice, Reinhart Ahlrichs**

A parallel Direct SCF and gradient program for workstation clusters has been implemented on the basis of the ab initio program package TURBOMOLE. Applications on large molecular systems (up to 1500 basis functions) monitor an appreciable speed-up in computational performance.

# A polarizable model for water and its ionic dissociation

Paul A. Rejto and David Chandler  
Department of Chemistry  
University of California, Berkeley  
Berkeley, CA 94720

## Abstract

A novel polarizable model for water that incorporates ionic dissociation is introduced and discussed. Parameters for the model are fit to gas phase data, while liquid phase properties of the model are investigated by molecular dynamics. Good agreement with experiment is found for many properties including renormalization of the monomer dipole moment, increase of the average O-H distance, and decrease of the average O-O distance.

The structure and energetics of solvated  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  are calculated. The model predicts formation of the stable complex  $\text{H}_9\text{O}_4^+$ , providing support for the Eigen mechanism for proton transport. The pH of the model is determined via the coupling parameter method, and comparison with experiment is made. Ongoing work using umbrella sampling to examine the dynamics of excess protons in liquid water is briefly discussed.



**A Theoretical Investigation of the Low-Lying States  
of the  $\text{CH}_2\text{NH}$  and  $\text{CH}_2\text{NH}^+$**

Robert J. Cave  
Department of Chemistry  
Harvey Mudd College  
Claremont, CA 91711

Methanimine is a substituted analogue of ethylene but it possesses low-lying  $n \rightarrow \pi^*$  electronic transitions in addition to the expected  $\pi \rightarrow \pi^*$  transitions. Since  $n \rightarrow \pi^*$  electronic transitions are expected to be important in larger substituted systems a detailed study is presented of several low-lying states of  $\text{CH}_2\text{NH}$ . Using Dunning "Correlation Consistent" basis sets excitation energies to the two lowest triplet states of  $\text{CH}_2\text{NH}$ , as well as ionization potentials to the two lowest states of the ion have been calculated. The convergence of the total energies and excitation energies is explored as a function of basis set size and theoretical method using a) perturbation theory selected multi-reference singles and doubles configuration interaction b) multi-reference averaged coupled-pair functional theory, c) coupled cluster singles and doubles (CCSD) theory, and d) CCSD(T). The necessary levels of theory for converged excitation energies is discussed, as well as an approximate G2-like perturbative method for inclusion of effects due to basis set extensions.

Abstract for poster to be presented at West Coast Theoretical Chemistry  
Conference, UCLA, Los Angeles, California, June 17, 1993

## **Ab Initio Molecular Dynamics with Reversible RESPA**

Doug A. Gibson and Emily A. Carter

Department of Chemistry and Biochemistry  
University of California, Los Angeles  
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Atomic clusters have potential energy surfaces with many local minima. A molecular dynamics simulated annealing approach can be used to find the global potential minimum, though this is a costly process in terms of computer time. However, it is widely known that changes in electronic degrees of freedom generally occur much more rapidly than changes in nuclear degrees of freedom. We have adapted Reversible RESPA, a multiple time step integrator originally developed by Berne and co-workers for empirical potential MD calculations, for use in ab initio MD simulations in a manner that takes advantage of this natural separation of nuclear and electronic time scales. This integrator offers a means of performing exact dynamics with multiple time scales. Evaluating the costly forces on the nuclei less often than the relatively cheap wavefunction forces shortens the time to solution.

## **The Hessian Biased Force Field for Molecular Dynamics Simulations of Poly-oxymethylene**

**Siddharth Dasgupta, Kenneth A. Smith\* & William A. Goddard, III**

**Materials and Molecular Simulation Center, Beckman Institute**

**Caltech, Pasadena, CA 91125**

**&**

**\*General Electric Central Research & Development**

**Schenectady, NY 12301**

Polyoxymethylene  $[-CH_2-O-]_n$  is a commercially important thermoplastic, which occurs in two crystalline forms: the stable trigonal form (t-pom) and the metastable (at room temperature) orthorhombic form (o-pom). It is an ideal system for validation of molecular dynamics methods because there is a large body of experimental data available for the highly crystalline forms.

To obtain force fields accurate enough to predict vibrational properties, we used the Hessian Biased Force Field/Singular Value Decomposition methodology (HBFF/SVD). This method was applied first to dimethyl ether where complete experimental vibrational frequency data is used to obtain scale factors for the theoretical frequencies. These scale factors were then applied to dimethoxy methane (which does not have complete experimental vibrational frequency data) to obtain force field parameters for the repeating  $CH_2O$  unit of polyoxymethylene.

The C-O-C-O dihedral angle is very different for the t-pom ( $77^\circ$ ) vs the o-pom ( $63^\circ$ ), which poses a challenge for the force field (to simulate both forms with the same parameter set). Additionally, the presence of the oxygen lone pairs stabilizes gauche dihedrals with respect to the trans dihedrals (the "anomeric" effect). Previously (MM2) this has been handled using explicit lone pairs but we avoid this because of problems for dynamics. We paid special attention to parameterizing the full torsional potential energy surface which is critical for high accuracy in the predicted macroscopic properties for the crystalline forms.

The force field was tested by simulations of tri- and tetra-methoxy methane where there is very limited experimental data. The stabilities of the conformers for tri-methoxy methane is in good agreement with that inferred from gas and solid phase IR and Raman spectroscopy for this molecule.

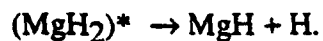
This force field is being applied to studies of semi-crystalline growth and macrocyclic pom.

## **Ab Initio Calculations of the Mg + H<sub>2</sub> and MgH + H Potential Energy Surfaces**

**Marcy E. Rosenkrantz**

The University of Dayton Research Institute  
Air Force Phillips Laboratory  
Edwards AFB, CA

We are interested in the reaction:



We have calculated the potential energy surfaces of Mg (<sup>1</sup>S, <sup>1</sup>P) interacting with H<sub>2</sub>. Specifically, we will discuss the region of the two potential energy surfaces in the vicinity of a curve crossing between the <sup>1</sup>A<sub>1</sub> and <sup>1</sup>B<sub>2</sub> states of MgH<sub>2</sub>.

The MgH in the reaction above can be rotationally and vibrationally excited. To understand the mechanism for the formation of the rotationally excited MgH, we have calculated the potential energy surfaces for several geometries of the interaction between MgH and H. The results of those calculations will also be discussed.

## Potential Energy Surfaces for Combustion Reactions

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The high speed research program (HSRP) involves plans to build a fleet of supersonic ( $> \text{Mach } 2$ ) aircraft. Since these aircraft will fly through the stratosphere, there is considerable concern about  $\text{NO}_x$  emissions from the jet engines. In response to the need to model  $\text{NO}_x$  production from these aircraft, potential energy surfaces are being computed for reactions which are important in hydrocarbon combustion, and in particular reactions involving nitrogen.

The potential energy surfaces (PES's) for these reactions involve four or more atoms and are typically quite complex. Such PES's commonly have numerous stationary points (both saddle points and minima) leading to multiple possible product channels. The results of complete active space SCF/gradient plus internally contracted configuration interaction (CASSCF/ICCI) calculations will be presented for selected systems, including  $\text{CH}({}^2\Pi) + \text{N}_2$ ,  $\text{NH}_2 + \text{NO}$ , and  $\text{CH}_3 + \text{O}_2$ .

<sup>a</sup> Supported by NASA Cooperative Agreement NCC2-478.

**Theoretical infra red spectra  
of carbon-chain carbene molecules**

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IBM Almaden Research Center  
San Jose, CA 95120-6099, USA  
and  
S. A. Maluendes  
Molecular Research Institute  
Palo Alto, CA 94304, USA

Carbon-chain carbene molecules ( $\text{H}_2\text{C} = (\text{C} = )_n\text{C}$ ) are candidates for astronomical observation because they are highly polar molecules presumably stable in the interstellar medium. Two members of this family,  $\text{H}_2\text{CCC}$  and  $\text{H}_2\text{CCCC}$ , have been detected in the laboratory and also identified in different astronomical sources (TMC-1, IRC + 10216). Astronomical searches and laboratory identifications have failed to detect the next two members of the cumulene series;  $\text{H}_2\text{C}_5$  and  $\text{H}_2\text{C}_6$ . In order to assist in the laboratory identification of these molecules we predict their infra red spectra. Comparison with experimental spectra is presented for  $\text{H}_2\text{CCC}$ . Finally, distortions along the carbon chain are discussed for  $\text{H}_2\text{C}_6$ .

*Abstract of poster presentation for the West Coast Theoretical Chemistry /Statistical Mechanics Conference, University of California, Los Angeles, California, June 17-19, 1993.*

**Dynamic Solvent Effects on Kinetic Isotope Effects for the Addition of  
Hydrogen to Benzene in Aqueous Solution**

Bruce C. Garrett, Gregory K. Schenter, and Michael Messina  
Molecular Science Research Center  
Pacific Northwest Laboratory  
Richland, Washington 99352

Variational transition state theory with semiclassical tunneling corrections is applied to a model of H atom addition to benzene in the gas phase and aqueous solution. The model allows the separation of equilibrium solvation effects on the free energy of activation from dynamic (nonequilibrium) solvent effects that enter through frictional terms. Within the model, the static effect of the solvent on the equilibrium free energy is independent of the mass of the solute, and for an equilibrium solvation model the kinetic isotope effect (KIE) for the aqueous and gas-phase reactions are the same. Therefore, changes of the KIE upon hydration are directly attributable to dynamic solvent effects. The model shows that the dynamic solvent effects are small for the H and D addition reactions but large for the addition reaction of muonium (Mu; a hydrogen isotope approximately one ninth the mass of H). These studies correctly account for the anomalous quenching of the Mu KIE by aqueous solution that has been observed experimentally [Roduner and Bartels, Ber. Bunsenges. Phys. Chem. **96**, 1037 (1992)].

*This work was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute which operates the Pacific Northwest Laboratory.*

## CONFIGURATIONAL ENTROPY OF MICROEMULSIONS: THE FUNDAMENTAL LENGTH SCALE

Howard Reiss, H. Michael Ellerby, and José A. Manzanares

### Abstract

Phenomenological lattice models of microemulsions have been quite successful in characterizing both the various complex phases and the corresponding phase diagram. In some approaches, e.g., the *random mixing model* (RMM), the lattice parameter is of the order of the dimension of a mesophase and have been used as a length scale for computing the entropy of mixing of the microemulsion. In the paper we prove that the fundamental length scale for the calculation of the entropy of mixing is of the order of the cube root of the volume per molecule — orders of magnitude smaller than the dimension of the mesophase. For the one-dimensional case, we indeed show that the random mixing model significantly underevaluates the entropy of mixing. Since the entropy of mixing plays a central role in determining the stability of the microemulsion, the determination of the fundamental length scale is of major importance in the thermodynamic characterization of microemulsions.



## Ab Initio Localized Electron Pair Theory

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We consider the efficacy of models describing the molecule as an ensemble of interacting localized electron pairs for the fast computation of the ab initio electron correlation energies. We compare various algorithms and discuss different schemes for localizing the occupied and correlating orbital spaces.

<sup>‡</sup>Permanent Address: Department of Chemistry, University of Manitoba, Canada

# *ELECTRON ATTACHMENT TO THYMINE, CYTOSINE, AND URACIL: A THEORETICAL STUDY*

*by Nathan Oyler and Ludwik Adamowicz*

*Dept. of Chemistry, University of Arizona, Tucson, 85721*

## **ABSTRACT:**

Despite a significant interest in the mechanism of excess electron location in DNA, the electron affinities of nucleic acids and related compounds in the gas phase are not well known. In our theoretical calculations of the tautomers of thymine, cytosine and uracil at the MP2/6-31+G\* level, we observed negative electron affinities indicating unstable anions. We also observed significant dipoles for many of the tautomers as well as uracil, which immediately suggested a dipole bound anion state. We were able to calculate the electron affinities of dipole bound anions by including a diffuse set of sp basis functions centered at the positive end of the dipole. At the MP2 level with the 6-31+G\* basis set for atoms and the set of diffused orbitals, we observed small positive electron affinities indicating stable anions. The present study shows that the crucial factor which allows one to locate the dipole-bound state in an ab-initio calculation is a proper selection of the basis set.

**Parallelization of correlation function quantum Monte Carlo.**  
**Willard R. Brown and William A. Lester, Jr.**

Correlation function quantum Monte Carlo (CFQMC)<sup>1</sup> is a method of calculating the excited state energies of polyatomic molecules. It is a hybrid of diffusion Monte Carlo and the Rayleigh-Ritz variational procedure. In cooperation with Rich Zwakenberg and Time Pierce<sup>2</sup>, we have implemented CFQMC on a CM-5 and obtained a significant speed-up compared to the implementation on the C-90. This research is supported in part by the Director, office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy.

<sup>1</sup>B. Bernu, D.M. Ceperley, and W.A. Lester, Jr., J. Chem. Phys. 93, 552 (1990)

<sup>2</sup>National Energy Research Supercomputing Center, LLNL, Livermore California, 94551

# Molecular Dynamics Simulations of Aqueous Ionic Clusters Using Polarizable Water<sup>(a)</sup>

Liem X. Dang  
Molecular Science Research Center  
Pacific Northwest Laboratory  
Richland, Washington 99352

## Abstract

We present a detailed study, based on state-of-the-art modern statistical mechanics, of the solvation properties of a chlorine ion in polarizable water. In these studies, we employed the polarizable water model developed recently by Dang [J. Chem. Phys. **97**, 2659 (1992)]. We developed the polarizable ion-water potential so that the successive binding energies for the ionic clusters, the solvation enthalpy, the bulk vertical binding energy, and the structural properties of the aqueous ionic solution agree with the best available results obtained from experiments. The minimum structures obtained from our molecular dynamics simulations qualitatively agree with recent quantum chemical calculations by Combariza, Kestner, and Jortner (Chem. Phys. Lett. **203**, 423 1993). The simulated vertical electron binding energies of the ionic clusters  $\text{Cl}^-(\text{H}_2\text{O})_n$ , ( $n=1-6$ ) compare reasonably well with recent data from photoelectron spectroscopy experiments. We explored the role of the  $\text{Cl}^-$  polarizabilities and found that the minimum structures of the ionic clusters are sensitive to the magnitude of the  $\text{Cl}^-$  polarizabilities.

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(a) This work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest Laboratory,

***Poster Session II, Friday, June 18, 12:20 – 2:30 pm (California Room Patio)***

Rigoberto Hernandez, University of California, Berkeley  
Dr. Tsun-Mei Chang, University of California, Los Angeles  
Nick Gonzales, University of Utah  
Professor J. Vince Ortiz, University of New Mexico  
David Maurice, University of California, Berkeley  
John Eksterowicz, University of California, Los Angeles  
Dr. Byron H. Lengsfeld III, Lawrence Livermore Laboratory  
Dr. Kerstin Andersson, IBM Almaden  
Dr. Dan Konowalow, Edwards AFB, California  
Jean-Marc Langlois, California Institute of Technology  
Zhenghong Zhang, University of Arizona  
Dr. Nick Blake, University of California, Santa Barbara  
Kenske Nakamura, University of California, Los Angeles  
Dr. Michael Messina, Pacific Northwest Laboratories  
Mark Roberson, University of Utah  
J. Daniel Gezelter, University of California, Berkeley  
Jens Fennen, University of California, Los Angeles  
M. Susan Melnick, California Institute of Technology, Pasadena  
Michelle R. Radeke, University of California, Los Angeles  
Professor William A. Parkinson, Southeastern Louisiana University  
Ersan Demiralp, California Institute of Technology  
Ian Ono, Harvey Mudd College  
Jim Na, University of California, Los Angeles

# A Semiclassical TST Method to Calculate Transmission Probabilities and Rates for Anharmonic Systems

Rigoberto Hernandez<sup>†</sup> and William H. Miller

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

## Abstract

A semiclassical method for obtaining transmission probabilities of non-separable systems was described by Miller several years ago.<sup>1</sup> Recent improvements in *ab initio* methods<sup>2</sup> have permitted the calculation of the cubic and quartic derivatives – at the saddle point of the potential energy surface – necessary to obtain the higher order corrections predicted by this theory. The non-separable Hamiltonian describing the transition state is obtained by perturbation theory in analogy to the construction of the vibrational spectroscopic Hamiltonian. The semiclassical theory then provides the transmission probabilities and thermal rates.<sup>3</sup>

In addition, a *new* semiclassical anharmonic thermal rate expression is presented as a sum over the reactive mode action of the activated complex. The expression is generally applicable to any system which can be characterized by a single transition state *region*. Anharmonicity – *i.e.* local reaction path curvature – is included perturbatively, as before, and consequently offers an improvement over standard harmonic TST expressions. The expression is illustrated by application to the bimolecular reaction,  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ , and to the unimolecular dissociation,  $\text{D}_2\text{CO} \rightarrow \text{D}_2 + \text{CO}$ . Moreover, we show how the method can be extended to systems with large amplitude motions in the perpendicular degrees of freedom by treating some of the modes perturbatively and diagonalizing the remaining effective Hamiltonians.

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<sup>†</sup> NSF Fellow and AT&T CRFP Fellow

<sup>1</sup> W. H. Miller, *Faraday Disc. Chem. Soc.* **62**, 40 (1977).

<sup>2</sup> W. H. Green, D. Jayatilaka, A. Willetts, R. D. Amos, and N. C. Handy, *J. Chem. Phys.* **93**, 4965 (1990).

<sup>3</sup> W. H. Miller, R. Hernandez, N. C. Handy, D. Jayatilaka and A. Willetts, *Chem. Phys. Lett.* **172**, 62 (1990); M. J. Cohen, N. C. Handy, R. Hernandez and W. H. Miller, *ibid.* **192**, 407 (1992).

Abstract for poster to be presented at West Coast Theoretical Chemistry Conference, UCLA, Los Angeles, CA, June 18, 1993

## **EFFECT OF TEMPERATURE AND LATTICE MISMATCH ON STRUCTURES OF METALLIC THIN FILMS**

Tsun-Mei Chang and Emily A. Carter

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University of California, Los Angeles  
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Los Angeles, CA 90024-1569

A mean-field approach is developed to investigate the commensurate-incommensurate phase transition of thin metallic films adsorbed on metal substrates at finite temperatures. The equilibrium configurations of the thin films can be obtained by evaluating the free energies. We apply this method to several fcc/fcc transition metal systems with various lattice mismatches, and are able to determine the critical thickness at the onset of commensurate-incommensurate transition. The results are then compared to static calculations (at 0 K) as well as Monte Carlo simulations.

# Structures and Energetics of the $\text{Al}_3\text{H}$ Molecule

Nick Gonzales and Jack Simons

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

## ABSTRACT

*Ab initio* electronic structure calculations on several  $\text{Al}_3\text{H}$  structures have been carried out using Dunning's aug-cc-pVDZ basis sets for both aluminum and hydrogen. Local minima, global minima, and transition states connecting these minima have been found using methods that incorporate electron correlation at the MCSCF level. Structures and energetics for  $\text{Al}_3\text{H}$  will be presented along with a comparison of the analogous boron structures.



# Total Energies and Gradients from Electron Propagator Theory: Applications to Carbon Clusters

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and

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

April 27, 1993

## Abstract

Electron propagator theory has been primarily a technique for the direct evaluation of vertical ionization energies and electron affinities. The formalism also generates one-electron reduced density matrices and total energies for a reference state. Recent derivations have shown how to obtain effective density differences pertaining to electron binding energies. Final state energy gradients can be calculated with related techniques in order to optimize geometries. From the second order self-energy of electron propagator theory, one can obtain total energies for the initial,  $N$ -electron state and the final,  $N\pm 1$ -electron states. Recent computational studies have demonstrated the feasibility of this approach to calculating adiabatic ionization energies and electron affinities, as well as properties of final states. Supplemental electron propagator calculations with larger basis sets and renormalized treatments of electron correlation at the optimized geometries provide excellent vertical and adiabatic energy differences. These techniques are applied to a variety of linear and cyclic clusters with ten or fewer carbon atoms.

## The Random Phase Approximation for Excited States: Direct Methods

David Maurice and Martin Head-Gordon

Department of Chemistry

The University of California at Berkeley

Berkeley, Ca. 94720

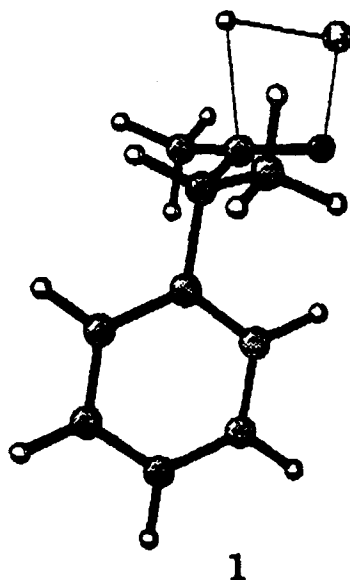
We are interested in finding excitation energies and transition and excited state properties for molecular system of significant size using the Random Phase Approximation (RPA) method. Excitation energies within this theory are obtained as the poles of the Hartree-Fock frequency dependent polarizability. The theory has the properties of size-consistency, and exactness for isolated electrons. We are using direct methods of calculation in which the two electron integrals are not stored, and iterative diagonalization procedures since the size of the RPA matrix in these cases is very large. Although the RPA matrix is non-symmetric, it is still possible (with small modifications) to use well-known methods for extracting the lowest eigenvalues. We discuss some preliminary applications and compare the RPA method with other approaches to molecular excited states.

# Transition Structures for Radical Hydrogen Abstractions and Lithium Hydride Additions

John E. Eksterowicz and K. N. Houk\*

Department of Chemistry and Biochemistry  
University of California, Los Angeles, California 90024

**Abstract:** Ab initio transition structures were obtained for the reactions of methane and hydrogen sulfide with the 1-hydroxyethyl radical, lithium hydride with acetaldehyde, hydrogen sulfide with 2-hydroxy-3-methylbutan-2-yl, and lithium hydride with methyl isopropyl ketone. The largest system studied, 1, contains a methyl and a phenyl substituent. Comparisons were made between the radical and hydride addition transition structures to determine whether the widely successful Felkin-Anh model can be used to predict the stereochemical outcome of radical reactions. All optimizations were performed at the 6-31G\* level, with MP2/6-31G\* single points on these geometries.



# Molecular Photoionization

Byron H. Lengsfeld III

Center for Computational Chemistry

IBM, Almaden Research Center

and

Tom Rescigno and Ann Woodin

Theoretical Atomic and Molecular Physics Group

Lawrence Livermore National Laboratory

The complex-Kohn scattering codes that were developed at Livermore to study electron-molecule and electron-ion scattering have been modified to treat photoionization. Our present work differs from earlier theoretical studies of this effect in that our formalism is capable of treating polyatomic molecules where correlated wave functions can be used to represent the target and the scattering wave functions. Previous scattering studies have been limited to either linear systems and/or single configuration descriptions of the ion states present in the scattering wave function. Our formulation of the photoionization problem will be presented and results of calculations on the photoionization of N<sub>2</sub> and CO will be discussed. Total, partial and differential cross sections ( beta parameters ) have been computed for these molecules.

## Multiconfigurational Second-Order Perturbation Theory

by Kerstin Andersson

Low-order perturbation theory in conjunction with multiconfigurational zeroth-order wave functions has proven to be a viable tool in quantum chemistry. The multiconfigurational (MC) SCF wave function has made possible calculations on molecular systems with complex electronic structures. For example, excited states, energy surfaces for chemical reactions, reactions, radicals and di-radicals, and transition metal chemistry are areas of research where the MCSCF wave function frequently is a prerequisite. Although MCSCF wave functions describe electronic structures qualitatively well, only a small fraction of the total correlation energy is obtained. The remaining part of the correlation energy—often referred to as the dynamical correlation energy—primarily originates from the failure of the MCSCF wave function to describe the two-electron cusp. There are several theoretical approaches to improve upon on MCSCF wave function and to recover a large portion of the dynamical correlation energy. Perturbation theory is such a technique and we have been able to implement it successfully up to first order in the wave function and second order in the total energy. In our implementation the zeroth-order MCSCF wave function is of the Complete Active Space (CAS) SCF type. A size-extensive formalism is thus achieved and dissociation processes as well as molecules with many electrons can therefore be properly described.

The performance of the method has been evaluated through a large number of applications covering a large range of properties of molecular systems. For example, a comprehensive study of about 30 molecules—in ground and excited states—was performed showing that bond distances and bond angles can be calculated with an accuracy of 0.01 Å and 2°, respectively, compared to experiment. For binding energies a systematic error is obtained making them too small by a few kcal/mol per electron pair formed. This is due to the construction of the zeroth-order Hamiltonian and work is in progress to eliminate it. Another example is the successful calculation of electronic spectra of conjugated and aromatic molecules. A large number of molecules have been studied like naphthalene, cytosine and porphine. The results for computed excitation energies are surprisingly accurate with errors smaller than 0.2 eV. Accurate results can also be obtained for transition metals as long as the number of open shells is small (again due to the construction of the zeroth-order Hamiltonian). For example, the following are the calculated values for the bond distance, dissociation energy, and vibrational frequency for Cu<sub>2</sub> in its ground state: 2.222 Å, 2.02 eV, and 269 cm<sup>-1</sup>. The corresponding experimental values are: 2.219 Å, 2.08 eV, and 266 cm<sup>-1</sup>.

In conclusion, our method is certainly not the most accurate approach to all quantum chemical problems but its versatility and simplicity to use in addition to its ability to handle fairly large molecules and producing rather accurate results altogether makes it an attractive approach.

# The Interaction of $\text{H}_2$ ( $1\Sigma_g^+$ ) with $\text{Li } 2s \ ^2S$ and $\text{Li } 2p \ ^2P$

Daniel D. Konowalow  
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Edwards AFB, CA 93524-7680

This study is directed toward the understanding of the structure and spectra of Li atoms trapped in a matrix of ground state  $\text{H}_2$  molecules. I present the potential surfaces for the four lowest-lying states and the electric dipole moment transition function for transitions connecting the ground and excited states. I present these data for three values of the H-H internuclear separation which correspond approximately to the left-hand and right-hand classical turning points and the equilibrium separation. The calculational method is 3 electrons in 6 orbital multireference CI which uses 9s,8p,2d,1f Gaussian functions on Li, 5s,3p on H, and 1s,3p,2d,1f on the  $\text{H}_2$  bond center for a total of 112 spherical basis functions.

Although this study was not designed to describe the long-range interactions with ultimate accuracy, various van der Waals features appear to have at least a qualitatively correct dependence on orientation. In the short range, the sigma (or  $A'$  or  $A_1$ ) states are entirely repulsive, but are relatively more attractive in  $C_{2v}$  than  $C_{\infty v}$ . In the short range, the doubly degenerate  $\Pi$  state is only weakly bound. As the  $\text{H}_2$  rotates, the states split and become more deeply bound with the deepest binding for the  $B_2$  state in  $C_{2v}$ . This trend is more pronounced the larger the H-H separation.

**Accurate numerical real-space approach to  
large scale *ab initio* electronic structure calculations**

**J.-M. Langlois, X. J. Chen and W. A. Goddard III**

*Materials and Molecular Simulation Center  
Beckman Institute  
California Institute of Technology  
Pasadena, CA 91125*

We have developed a real-space approach for density functional calculations of large molecular and crystalline systems. We use Gaussian type orbitals (GTO's) as basis set which significantly alleviates the  $N^3$  workload in the Fock matrix diagonalization as compared to the plane-wave approach. This is particularly important for all-electron calculations and for applications that include first-row atoms and transition metal elements where a soft pseudopotential is difficult to find. The matrix elements of the Coulomb and the exchange-correlation potential are evaluated numerically via integration over a grid. The numerical integration is partitioned into independent atomic integration using the Becke scheme and is found to be accurate in our modified implementation (total error less than 0.2mH for  $C_{60}$ ). The Coulomb field is computed by using a density-fitting procedure for the rapidly varying components of the density while using a Fourier transform procedure for the slowly varying components. The density-fitting procedure is decomposed into independent radial (angular-momentum resolved) atomic fits. This dual space approach allows for fast computation of the Coulomb field which is usually the time limiting step in GTO based methods. With efficient cutoff procedures, this approach leads to scaling better than  $N^2$  for large systems. In the SCF convergence each orbital is treated independently using a conjugate gradient method without line-minimization. Results will be presented for both molecules and crystals.

**NEWTON-RAPHSON OPTIMIZATION OF THE EXPLICITLY  
CORRELATED GAUSSIAN FUNCTIONS FOR CALCULATIONS  
OF THE GROUND STATE OF THE HELIUM ATOM**

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*Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA.*

**ABSTRACT**

Explicitly correlated Gaussian functions have been used in variational calculations on the ground state of the helium atom. The major problem of this application, as well as in other applications of the explicitly correlated Gaussian functions to compute electronic energies of atoms and molecules, is the optimization of the non-linear parameters involved in the variational wavefunction. An effective Newton-Raphson optimization procedure is proposed based on analytical first and second derivatives of the variational functional with respect to the Gaussian exponents. The algorithm of the method and its computational implementation is described. The application of the method to the helium atom shows that the Newton-Raphson procedure leads to a quite good convergence of the optimization process.

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## PHOTO-INDUCED CHARGE MIGRATION IN Na DOPED SODALITE

Nick P. Blake, Paul C. Weakliem, and Horia Metiu

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*University of California, Santa Barbara CA 93106*

Sodalite may be loosely thought of as a periodic lattice of aluminosilicate "Bucky-ball" type cages. Each cage is cubic with a hexagonal face along each of the (1,1,1) axes joined to each other via 6 square faces centered along the (1,0,0) axes of the cube. The  $\text{Na}^+$  ions sit approximately in the center of alternate hexagonal faces in a tetrahedral arrangement. In white sodalite, (stoichiometric formula  $(\text{Na}^+)_3(\text{AlSiO}_4)_3$ ) one of the vertices of these tetrahedra remains vacant. On doping with Na, the additional Na fills the vacancy and the valance electron autoionises. One immediate manifestation of this electron solvation is that the sodalite undergoes a color change from white to blue. Upon further doping we see a gradual change through purple to black when fully doped. We present results of simple wave packet propagation studies which examine the nature of these optical states of the electron. We demonstrate the existence of charge transfer states in which the electron leaves the impurity cage and localises in a neighboring cell. Quantum-semiclassical TDSCF calculations show that by optically accessing these states it is possible to induce color center migration where one of the  $\text{Na}^+$  ions follows the electron into the neighboring cage. We discuss such effects in the context of the resultant homogeneous broadening induced in the absorption spectrum and compare theory with experiment.

# THEORETICAL STUDIES OF DYNAMIC PROCESSES IN HOST-GUEST COMPLEXES

K. Nakamura and K. N. Houk

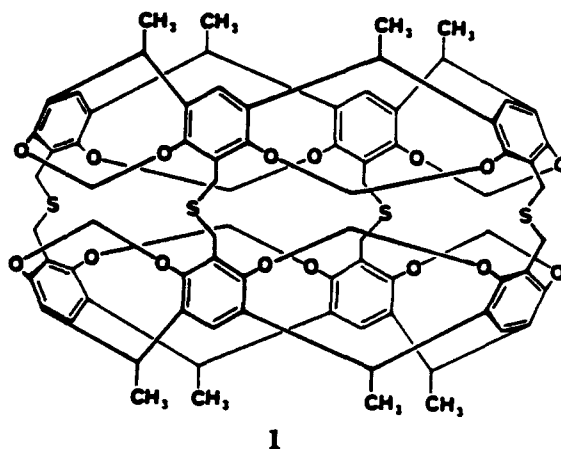
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Cram and coworkers have synthesized a series of molecules which incarcerate small molecules such as solvents.<sup>1</sup> Some of these host-guest complexes formed during the formation of the host molecule take in and/or release guest molecules under thermal conditions. We have investigated dynamic processes in one of these carceplexes in which 1 includes one or two acetonitriles as guests.<sup>2</sup> In the dynamics study with the AMBER force field,<sup>3</sup> the average orientation of the guest molecules in the cavity was examined and compared with experimental (NMR) results. The mechanism of the guest molecule escape process was also investigated. Both equatorial and polar escape pathways were examined with simple constrained optimizations and the potential of mean force (PMF) method to see which process is preferred.

Free energy differences( $\Delta\Delta G$ ) between losing the first and second acetonitriles calculated by free energy perturbation (FEP) method gave a good explanation for why the first escape occurs and the second does not.



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## Centroid Density Quantum Rate Theory: Variational Optimization of Dividing Surfaces

Michael Messina, Gregory K. Schenter, and Bruce C. Garrett  
Pacific Northwest Laboratory<sup>4</sup>, P. O. Box 999, Richland WA, 99352

We present a formal extension of the centroid density based quantum mechanical transition state theory of Voth, Chandler, and Miller<sup>1</sup> that allows for dividing surfaces that are arbitrary functions in phase space.<sup>2</sup> We use the formal prescriptions to calculate the quantum activated rate constants for a system consisting of an Eckart barrier coupled to a bath of harmonic oscillators. The results are shown to compare favorably to exact quantum mechanical calculations.

We also present a theory that corrects for the dynamical recrossings of the dividing surface in the centroid density based quantum transition state theory.<sup>3</sup> In this theory, reactive flux correlation functions are calculated from a classical-like expression where centroid variables replace their classical phase space counterparts and are evolved on an effective quantum mechanical potential surface. Results are presented for an Eckart barrier coupled to a bath of harmonic oscillators. Again, the results are shown to compare favorably to exact quantum calculations.

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<sup>4</sup> Pacific NorthWest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

# Collisional Energy Transfer in Bimolecular Ion- Molecule Dynamics



Mark Roberson, Maciej Gutowski, Jon Rusho, Jeff Nichols<sup>a</sup>, and Jack Simons\*

Chemistry Department  
University of Utah  
Salt Lake City, Utah 84112

## Abstract

Guided ion beam kinetic energy thresholds in the ion- molecule reactions  $M^+ + H_2 \rightarrow MH^+ + H$ , where  $M^+ = B^+, Al^+, \text{ and } Ga^+$  exceed by 0.4 to ca. 5 eV the thermodynamic energy requirements or theoretically computed barrier heights of these reactions. In addition, the formation of  $MD^+$  occurs at a significantly lower threshold than  $MH^+$  when  $M^+$  reacts with HD. Moreover, the measured reaction cross- sections for production of  $MH^+$  product ions are very small ( $10^{-17}$  to  $10^{-20}$  cm<sup>2</sup>). These facts suggest that a "dynamical bottleneck" may be operative in these reactions. In this work, the eigenvalues of the mass- weighted Hessian matrix, which provide local normal- mode frequencies, are used to identify locations on the ground-state  $MH_2^+$  potential energy surfaces where collisional- to- internal energy transfer can readily take place. In particular, the potential energies at geometries where eigenvalues corresponding to inter- fragment and to internal motions undergo avoided crossings are related to the kinetic energies of apparent reaction thresholds. This near- resonance energy transfer model, applied to  $M^+ + HD$  reactions, displays the experimentally observed preference to form  $MD^+$  at lower collision energies than  $MH^+$  as well as the fact that reaction thresholds may greatly exceed thermodynamic energy requirements. This model explains the small reaction cross- sections in terms of high energy content and subsequent dissociation of nascent  $MH^+$  (or  $MD^+$ ) ions. Although the mass- weighted Hessian matrix is used as a tool in this analysis, the model put forth here is not equivalent to a reaction- path Hamiltonian dynamics approach.

a. Also with IBM/FSC Corporation and the Utah Supercomputing Institute.

# RESONANT TUNNELLING IN KETENE REARRANGEMENT

J. DANIEL GEZELTER AND WILLIAM H. MILLER

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CA 94720

Recent experimental work<sup>1,2</sup> on the rate of ketene dissociation has indicated a highly featured energy dependence in the rearrangement dynamics. One explanation of the features is that the reaction path passes through the oxirene structure, which *ab initio* calculations<sup>3</sup> have found to be a minimum on the potential surface. If the well that corresponds to the oxirene structure is deep enough to support quasi-bound states, then the features that are seen in the experimental rate constant may correspond to resonances through the M-shaped barrier.

In this poster, we discuss the one- and two-dimensional potentials that we are using to approximate the area of the full potential immediately around the oxirene structure. It is our hypothesis that only a small amount of information about the true potential is needed to construct a model potential that can accurately describe the interesting dynamics of the ketene rearrangement. This information includes barrier heights, frequencies, and a single coupling constant that is determined from *ab initio* work.<sup>4</sup> We believe that information about other modes that are not directly related to the dissociation dynamics will have only minor effects on the cumulative reaction probability.

We present the results of our dynamics calculations, which utilize a sinc-function discrete variable representation<sup>5</sup> with absorbing boundary conditions.<sup>6</sup> In particular, we have calculated the cumulative reaction probability,  $N(E)$ , using these methods. It is interesting to note that many of the features that are present in the experimental reaction rates are also present in our calculations.

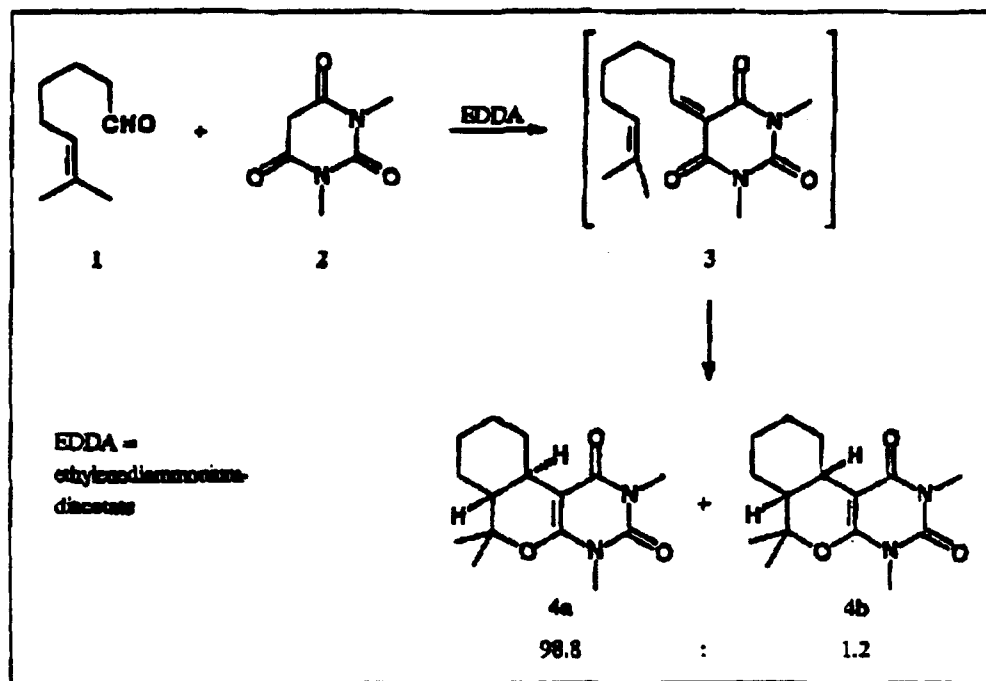
We also present results for the calculation which utilizes an indirect method of matrix inversion (*via* Fourier transformation of a polynomial approximation for the time evolution operator).<sup>7</sup> This gives us the added advantage of not having to store the full Green's matrix during the calculation, making it possible for us to perform this type of calculation on much larger systems.

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## AM1 and Molecular Mechanics Calculations of the Stereoselectivity in Intramolecular Hetero-Diels-Alder Reactions

Lutz F. Tietze and Jens Fennen

The intramolecular hetero-Diels-Alder reaction of alkylidenbarbiturates like 3, which are *in situ* formed by Knoevenagel condensation of an unsaturated aldehyde like 1 and a  $\beta$ -dicarbonyl compound like 2, proceeds with high diastereoselectivity.



Semiempirical AM1 calculations of transition states for model reactions as well as the experimentally investigated reaction of 3 were performed in order to determine the origin of the stereoselectivity. Four possible diastereomeric transition states, leading to the diastereomers 4a and 4b were considered for the reaction of 3. The calculated relative heats of formation predict a product ratio of 98.4 : 1.6, which is in good agreement with the experimentally found value of 98.8 : 1.2.

The calculated transition structures were used to generate additional force constants for the MM2-type force field of the PCMODEL program to allow the calculation of relative energies of transition states by molecular mechanics. The diastereoselectivities which were calculated with this modified force field were compared with experimentally obtained data for the reactions of several substituted alkylidenbarbiturates.

Abstract Submitted  
for the 1993 Meeting of the  
West Coast Theoretical Chemistry Conference  
17-19 June 1993

Halogen and Hydrogen Migration on Clusters Modeling the Diamond (110) Surface, M. S. MELNIK, D. G. GOODWIN, Caltech— Although many semiconductor growth processes are known to involve mobile surface adsorbates, for example silicon and gallium arsenide, growth mechanisms for diamond chemical-vapor deposition (CVD) to date have neglected the possibility of surface diffusion. One reason for this is that the diamond surface is terminated by hydrogen or halogens, blocking migration pathways. However, some fraction of the surface terminator is missing under typical growth conditions. If these vacancies are mobile, then pathways for surface migration of adsorbed hydrocarbon species may exist.

To examine this issue, we have computed activation energies for migration of chemisorbed H, F, and Cl to neighboring radical sites on the (110) surface. Energies for (1,2), (1,3), and (1,4) migrations were determined by *ab initio* SDCl computations using a TZP/VDZ basis set for small clusters modeling the surface. Transition states were estimated by fixing all atoms except the migrating one. Results indicate that vacancy diffusion occurs at least  $10^4$  times faster in the  $[1\bar{1}0]$  direction than in the  $[001]$  direction. Moreover, the characteristic (1,4) surface migration times for H and Cl are comparable to gas-surface reaction times. This indicates that (1,4) vacancy migration can compete with gas-surface reactions and play a role in both chlorine-assisted and hydrogen-based diamond CVD.

Prefer Standard Session

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**Abstract for poster to be presented at West Coast Theoretical Chemistry Conference, UCLA, Los Angeles, CA, June 18, 1993**

**MONTE CARLO SIMULATIONS OF METALLIC THIN FILMS**

Michelle R. Radeke, Tsun-Mei Chang, Benjamin C. Hitz,

Barry C. Bolding, Emily A. Carter

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*University of California, Los Angeles*

*405 Hilgard Avenue*

*Los Angeles, CA 90024-1569*

The growth of fcc metallic thin films is investigated using Monte Carlo simulations. A long-range Finnis-Sinclair potential models the adatom-adatom, adatom-substrate and substrate-substrate interactions. The systems studied are Pd/Ir(100), Ir/Pd(100), Pt/Ir(100) and Ir/Pt(100). Bulk Pd, Pt and Ir have similar lattice constants, but different cohesive energies. Therefore the lattice strain of the studied systems is small, while the cohesive energy difference between Pd-Ir is greater than that of Pt-Ir. Coverages of 0.5 to 3.5 monolayers at 300K, 500K and 800K are examined. In each of these scenarios, all systems are observed to grow pseudomorphically. Thus, the absence of interfacial strain seems to indicate that the film will grow commensurately with the substrate, despite significant differences in cohesive energies of the film versus substrate metals.



# Direct implementation for calculation of nuclear magnetic shielding.

William A. Parkinson<sup>1</sup>, Jeff Nichols<sup>2</sup>, Nick Gonzales, and Jack Simons  
Chemistry Department, University of Utah, Salt Lake City, UT 84112

Implementation and application of nuclear magnetic shielding calculations using direct SCF methods are discussed. The method is based on a direct atomic orbital integral driven algorithm which has recently been applied to the calculation of frequency-dependent polarizabilities<sup>3</sup> using the DISCO program system<sup>4</sup>. Property values in this study were computed at the first-order correlated level (known variously as coupled-perturbed Hartree-Fock, time-dependent Hartree-Fock, or the random phase approximation). This same machinery is utilized for computation of the paramagnetic contributions to the shielding tensor. The diamagnetic contributions are computed at the same level of correlation as an expectation value of the reference Hartree-Fock wavefunction. Benchmark examples are provided for a series of test cases.

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<sup>3</sup> M. Feyereisen, J. Nichols, J. Oddershede, and J. Simons, *J. Chem. Phys.*, **96**, 2978, (1992).

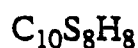
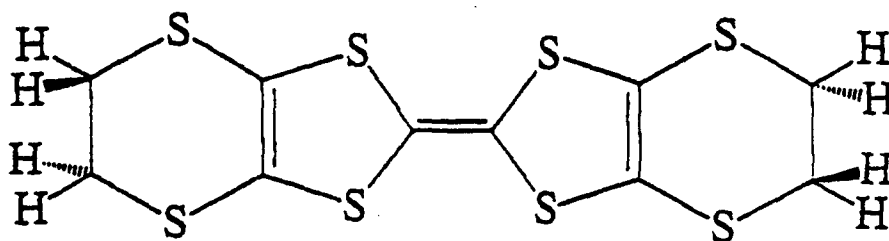
<sup>4</sup> J. Almlöf, K. Faegri, Jr., M. Feyereisen, and K. Korsell, DISCO, a direct SCF and MP2 code.

## Calculations on the (BEDT-TTF) Donor of Organic Superconductors

**Ersan Demiralp** and William A. Goddard, III

Materials and Molecular Simulation Center, Beckman Institute  
Caltech, Pasadena, CA 91125

The best two dimensional organic superconductors involve BEDT-TTF (from now on ET) as the donor (Figure 1). Examples include  $K - ET_2Cu(SCN)_2$  and  $K - ET_2Cu[N(CN)_2]Cl$  with  $T_c = 10.4K$  and  $12.8K$  respectively. We have developed a force field for treating the vibrational modes (phonons). We also carried out MNDO and Hartree-Fock calculations for the electronic status. The electronic bands are based on Hartree-Fock approximations coupled with the Hubbard model. We will summarize predicted properties with comparison to experiment.



bis(ethylenedithio)tetrathiafulvalene

Figure 1. bis(ethylenedithio)tetrathiafulvalene,  $C_{10}S_8H_8$ .

## Ab Initio Studies of LiF Clusters

Ian Ono\*

Robert J. Cave

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With the advent of nano-crystals and their possible applications in solid state electronics, there is a renewed interest in alkali halide clusters and crystals. We have conducted ab initio calculations on several LiF clusters, up to the quadmer, at the Hartree-Fock level, using several basis sets. Our calculations dealt with binding energies, vibrational frequencies, and geometry of the LiF clusters. In addition calculations at the coupled-cluster single and double level have been performed on the monomer and dimer, to examine correlation effects.

# THE ENERGETIC ADVANTAGE OF 5-EXO VERSUS 6-ENDO EPOXIDE OPENINGS: A PREFERENCE OVERWHELMED BY ANTIBODY CATALYSIS

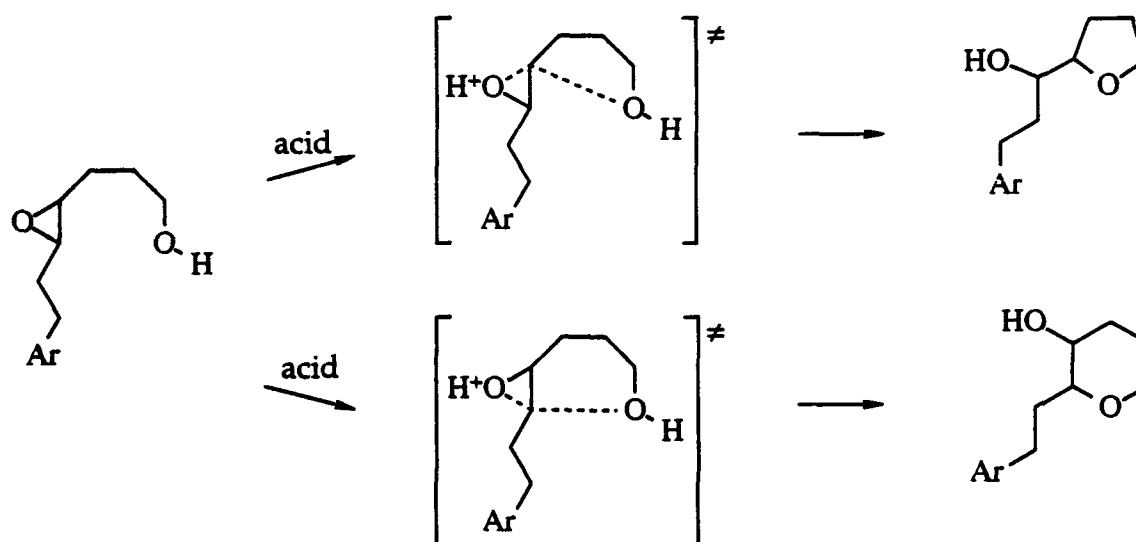
Jim Na,<sup>†</sup> K. N. Houk,<sup>\*,†</sup> Charles G. Shevlin,<sup>‡</sup> Kim D. Janda,<sup>‡</sup> and Richard A. Lerner<sup>†</sup>

*Department of Chemistry and Biochemistry, University of California*

*Los Angeles, California 90024, and Departments of Molecular Biology and*

*Chemistry, Scripps Research Institute, La Jolla, California 92037*

**Abstract:** Ab initio calculations were performed on the cyclization reactions of protonated trans-(3-hydroxypropyl)methyloxirane to form the corresponding five or six-membered products. Transition state for both cyclizations were located at the RHF/6-31G\* level. Formation of the five-membered product is energetically favored by 1.9 kcal/mol according to MP2/6-31G\* single point calculations on the 6-31G\* optimized geometries. Comparisons of the two transition structures with the reaction between water and protonated oxirane are made in order to rationalize why the Baldwin's rule (5-exo) process is favored. An electronic difference between the 5-exo and 6-endo transition states is identified which may account for the ability of an antibody to selectively stabilize the 6-endo ring opening.



<sup>†</sup> University of California, Los Angeles.

<sup>‡</sup> Scripps Research Institute.

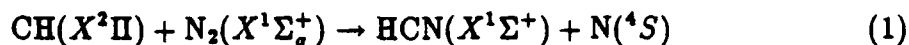
***Poster Session III, Saturday, June 19, 12:20 pm (California Room Patio)***

Dr. Tamar Seideman, NASA-Ames  
Deb Pearlman, University of California, Davis  
Dr. Eric Replogle, IBM Almaden  
Dr. Irina V. Ionova, University of California, Los Angeles  
Jason Perry, California Institute of Technology  
Dr. Vyacheslav Zakrzewski, University of New Mexico  
Dr. Gregory K. Schenter, Pacific Northwest Laboratories  
Hendrik Zipse, University of California, Los Angeles  
Dr. Kathleen Robins, University of Nevada, Las Vegas  
Brett Beno, University of California, Los Angeles  
Veronica Nefedova, University of Utah  
Dr. Sheng-Bai Zhu, IBM Almaden  
G. Gregg Reynolds, University of California, Los Angeles  
Ward H. Thompson, University of California, Berkeley  
Beatriz de Pascual-Teresa, University of California, Los Angeles  
Paul Gibbons, University of California, Los Angeles  
Joe Caddell, University of California, Davis  
Zoran Kurtovic, University of California, Berkeley  
Satomi Niwayama, University of California, Los Angeles  
Lionel F. X. Gaucher, University of California, Berkeley  
Dianne Meador, University of California, Davis  
A. Mehta, California Institute of Technology, Pasadena  
Hui Cu-Yang, California Institute of Technology, Pasadena  
Yuri Dakhnovskii, University of California, Santa Barbara

# Resonances in the CH+N<sub>2</sub> Reaction

Tamar Seideman<sup>‡</sup>  
Eloret Institute  
Palo Alto, CA 94303

## The reaction



is believed to be the first step in the production of NO in hydrocarbon flame fronts.<sup>1</sup> As such, the CH+N<sub>2</sub> reaction is one of the most important processes in combustion chemistry. In addition, reaction (1) plays an important role in the nitrogen-rich atmosphere of Titan.<sup>2</sup> The (as yet unknown!) mechanism, which allows the spin-forbidden process (1) to take place with significant probability, makes the CH+N<sub>2</sub> reaction a system of outstanding interest also from the basic research view point.

Experimental attempts to elucidate the reaction mechanism of process (1) and to measure it's rate constant began as early as 1967 with the pioneering work of Braun *et al.*<sup>3</sup> In spite of the many experimental studies which were conducted during the past twenty six years,<sup>4</sup> and are being conducted by several groups at present, the rate constant and the reaction threshold of process (1) are still a controversial.

Work in progress develops a dynamical model for the CH+N<sub>2</sub> reaction, based on two-dimensional *ab-initio* potential energy surfaces. Preliminary results are presented and discussed.

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  2. D.F. Strobel, Planet.Space Sci., 30, 839 (1982).
  3. W. Braun, J.R. McNesby and A.M. Bass, J.Chem.Phys. 46, 2071 (1967).
  4. See, for example, K.H. Becker, B. Engelhardt, H. Geiger, R. Kurtenbach, G. Schrey, and P. Wissen, Chem.Phys.Lett. 195, 322 (1992).

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<sup>‡</sup> Mailing address: NASA Ames Research Center, Mail Stop 230-3, Moffett Field, California 94035-1000

## Kinetics of the Hydrolysis of Anisole in Supercritical Water

*Deborah A. Pearlman and Susan C. Tucker*

*Department of Chemistry  
University of California, Davis, CA 95616*

Experimental studies of the hydrolysis of anisole in supercritical water indicate that the rate of this reaction increases dramatically with increasing pressure. We have begun to explain this trend by calculating the intrinsic (gas phase) rate constant for the hydrolysis of anisole from first principles (Hartree-fock level), and comparing this result with that extrapolated from the supercritical water experiments. From the *ab initio* data we have created a simple 1-dimensional effective solute potential which contains the necessary energy, frequency and charge transfer information for studying the solute-solvent interactions, and thus the solvent effects on the solute rate constants. In future work, we will use an embedded cluster model to study both the equilibrium and nonequilibrium effects of supercritical water on the solute reaction rate.

# ARCHEM - An Architecture for Computational Chemistry

Eric S. Replogle

IBM Almaden Research Laboratory  
650 Harry Rd, San Jose 95120-6099

June 19, 1993

## Abstract

If the world of computational chemistry was projected onto a geographical map, it would be best represented as a collection of islands separated by strong currents of incompatibility. On each island, various chemical calculations can be performed. On one island a scientist may be able to do a unique calculation; on another he may be able to do parts of that first calculation faster, but because of difficulties in communication it is difficult to take advantage of the better tools. Thus, at best, the scientist performs compromised experiments, and at worst, with necessary tools scattered over several islands, may not be able to do a desired experiment at all.

The ARCHEM project creates bridges between the different islands of computational chemistry. ARCHEM creates a framework whereby data, recognized and understood on all the islands, is easily transferred. With communication established, ARCHEM provides a mechanism for building an experiment that takes advantage of tools from all the islands, giving scientists the ability to put together powerful, flexible, seamless experiments that unify within and across many different scientific disciplines.

ARCHEM achieves this by constructing an open and standardized interface for communication between program modules. Each module will request data from and give data to the interface as a calculation proceeds. Any data given to the interface is potentially available to any other program that wishes to use it. The data that resides on the interface are called ARCHEM Scientific Datastructures (ASDs), each ASD being a computer representation of a scientific entity, such as a wavefunction, molecular geometry, or basis set, to take some examples from the field of quantum chemistry. ARCHEM provides utilities that allow a programmer to read, write, copy, and delete ASDs; where the ASDs are stored (it happens to be a file system in our implementation), or in what format, is all transparent to a programmer. The programmer needs to know only the format of data delivered to memory on an ASD read, or prepared in memory for an ASD write; these define ARCHEM's public standardized open interface.

In addition to the framework for allowing programs to communicate with the open interface, we have designed a scripting language and a language interpreter that allows a user (or a graphical user interface) to run a computational experiment of any degree of novelty.

*ARCHEM's goal is to provide two levels of independence. First, for program developers to be able to develop machine independent program modules with no knowledge of programming details in other modules. Second, for computational scientists to be able to run experiments using scripts and program modules that are machine independent.*

This poster will give a summary of the ARCHEM framework, both in an simple overview manner and a more detailed technical description.



# $O(N^3)$ Scaling of Two-Electron Integrals During Molecular Geometry Optimization

Irina V. Ionova and Emily A. Carter

Department of Chemistry and Biochemistry,  
University of California,  
Los Angeles, California 90024-1569

An evaluation of two-electron integrals is one of the bottlenecks in *ab initio* calculations since it scales as  $O(N^4)$ , where  $N$  is the number of basis functions. This burden becomes even heavier during the typical task of searching for an equilibrium structure of the molecule, because one needs to evaluate two-electron integrals for multiple geometries. Therefore, the optimization algorithms which require the least amount of energy evaluations are considered to be the most appropriate for molecular structure optimization.

We propose an alternative optimization technique which requires more energy evaluations than quadratically convergent quasi-Newton methods (including the CG (Conjugate Gradient) method) but each energy calculation is much cheaper due to  $O(N^3)$  scaling of the two-electron integrals evaluation. The proposed technique is a modification of quasi-Newton methods, i.e., it consists of repeated line searches for a minimum in a coordinate space. The scaling advantage is achieved at the expense of moving only one atom during each line search, so one needs to reevaluate only  $O(N^3)$  new integrals with the rest of them remaining unchanged. (In cases with symmetry, i.e., when symmetry-adapted functions are used instead of atomic orbitals, several atoms can be moved simultaneously without losing the scaling advantage). The center(s) to move and the direction of the search are determined from projecting the CG direction onto the direction corresponding to the movement of a single atom (in case of symmetry, specified group of atoms).

The statistics obtained from the numerous optimization runs with Lennard-Jones molecules shows that the number of energy and gradient evaluations for the proposed technique is only 1.5-5 times (for 3-27 atoms, respectively) larger than that for the CG method. Given the great advantage of  $O(N^3)$  scaling of the two-electron integrals in the former, one may achieve a substantial speedup of the overall computation in certain cases. We consider the factors which affect the performance of the proposed technique and we also present timings and other details of several molecular structure optimization runs on the *ab initio* level.

*Abstract of Poster for WCTCC 1993***Isosurface Visualization of some Monoatomic and Molecular Orbitals***James E. Kendall, Jason K. Perry, and William A. Goddard III**Materials & Molecular Simulation Center**Beckman Institute**California Institute of Technology**Pasadena, CA 91125*

Quantum mechanical approaches typically represent numerically or algebraically the wavefunctions of the electronic orbitals in three-dimensional space. The forms of these stable states are optimized to attain minimum energy, in accordance with the variational principle. Although such wavefunctions actually may be complex values through space, a real-valued wavefunction can be expressed which shows meaningful positive and negative regions, and preserves the probability density of the complex wavefunction.

To observe these wavefunctions resulting from numerical or algebraic calculations, the contour plot has traditionally been used, which slices the three-dimensional function with a plane, and represents the values of the wavefunction in this planar subspace by isocontour curves. The advantage of this method is that several isocontour levels can be shown on one plot, thus characterizing the function at various probability levels. The disadvantage is that only a subspace of three-dimensional physical space may be represented on one plot, necessitating that the viewer do a mental reconstruction in order to understand the three-dimensional nature of an orbital configuration.

Recently developed computational rendering methods make it possible to extend the isocontour concept to an isosurface in three dimensions. The AVS visualization software which we use extracts an isosurface of a specified value from a real-valued function in three dimensions. Although several different isosurface levels must be observed to fully characterize a probability cloud over its range of densities, in practice a very clear understanding of an orbital can be gained by viewing the isosurface at only one or two properly chosen values.

We show visualizations of some of the hydrogenlike orbitals, and molecular orbitals of water and benzene, to acquaint the viewer with the nature of the visualization technique on the orbitals of well-studied molecules. We then show a visualization of the GVB orbitals for  $Ir(H)_2(CH_2)^+$ , the intermediate in the reaction of  $Ir^+$  with  $CH_4$ .

Viewing the rendered isosurfaces of these wavefunctions allows a more immediate understanding of the spatial arrangement of the orbital lobes and nodal surfaces than does the traditional contour plot.

# Green Function Calculations on Vertical and Adiabatic Electron Binding Energies of Sulfur and Silicon Clusters

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Albuquerque, New Mexico 87131

and

Dept. of Chemistry, University of Utah  
Salt Lake City, Utah 84112

## Abstract

A new algorithm is developed to calculate third order self-energy diagrams of the one-particle Green function. It is possible to rearrange expressions for these contributions so that the innermost summations over two or three indices are performed as simple vector scalar products or as multiplication of a vector by a scalar. This procedure is facilitated by precomputing intermediate combinations of the transformed molecular integrals, in some cases together with the appropriate energy denominators. Abelian point group symmetry is used to reduce the storage requirements and the amount of computations. The program coded in FORTRAN may run together with MOLCAS-2 on an IBM-3090 (VM XA/CMS) and as a link in GAUSSIAN 90 or GAUSSIAN 92. Test runs on an IBM-3090 show that the present version runs 10-20 times faster than previous programs of this type. This program is used to calculate vertical ionization potentials and electron affinities of sulfur and silicon clusters. For  $S_3$ - $S_9$ , geometries of ionic states were optimized at the SCF level and adiabatic ionization potentials and electron affinities were calculated using CISD and an ANO basis set. These calculations employed MOLCAS-2. While the adiabatic electron affinities of  $S_3$  -  $S_9$  are positive, the vertical electron affinities are not. Geometries of several ionic states of small clusters are optimized using the second order propagator optimization technique.

## **Dependence of Solute Reaction Rate and Energy Transfer Mechanisms on Solvent Spectral Profile**

**Sabine K. Reese and Susan Tucker**

**Department of Chemistry, University of California, Davis, CA 95616**

**Gregory K. Schenter**

**Pacific Northwest Laboratory<sup>1</sup>, P.O. Box 999, Richland, WA 99352**

We report studies of reaction rates for solute activated dynamics in a linear-responding solvent bath. The results indicate that two distinct energy transfer mechanisms may be important in determining the solute reaction rate. The results also lead us to define an optimum collective bath coordinate that allows for a semiquantitative description of the dynamics using only two degrees of freedom.

The model system studied consists of a single solute reaction coordinate that has a cubic potential of mean force and solvent-solute dynamics described by a generalized Langevin equation (GLE). We numerically solve the GLE using an effective harmonic bath Hamiltonian to explore the difference observed in the rate constants for solvents described by exponential and Gaussian friction kernels in the case where the time scale associated with the solvent response is long relative to the time scale of the solute barrier motion. The differences are interpreted in terms of reactive flux correlation functions and energy transfer from the bath to effective collective solvent modes. Rate constants are further interpreted in terms of an effective one-dimensional bath.

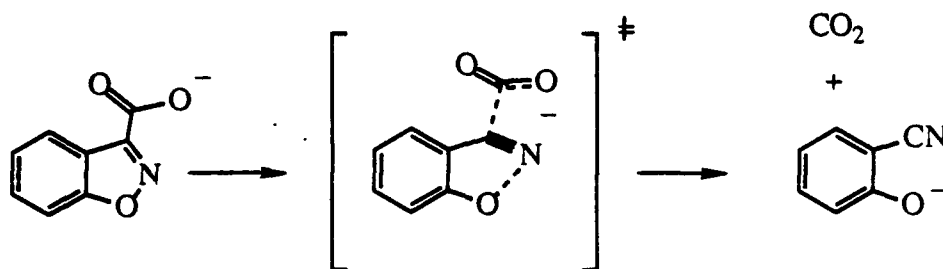
<sup>1</sup>Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830.

# A Theoretical Exploration of the Thermal Decarboxylation of Kemp's Other Acid (Benzisoxazole-3-carboxylic Acid). The Influence of Solvation on the Transition State Geometry of a Reaction with a Giant Solvent Effect.

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The decarboxylation of benzisoxazol-3-carboxylate has been investigated by ab initio molecular orbital calculations. The effects of solvation on transition state structure and energetics have been studied by inclusion of one or two water molecules into the ab initio calculations. Changes in activation barrier and kinetic isotope effects have been compared to experimental values.<sup>1,2</sup> The ab initio self consistent reaction field method has been used as well to model solvent effects via a continuum model. Changes in free energy of solvation along the ab initio reaction path have been calculated by Monte Carlo solution simulations. The question of solvent induced geometrical changes has been addressed by using three different structures for each the ground and transition state. Water, methanol, chloroform, acetonitrile, and tetrahydrofuran have been investigated as solvents. Results are compared with experimental rate data.<sup>1</sup> The model system has been extended to include a tetramethyl guanidinium ion to study the effects of counterions.



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# A Collaborative Experimental/Theoretical Study of $\text{HNO}^-$

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&

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## Abstract

The first theoretical *ab initio* calculations have been performed on nitroxide ion,  $\text{HNO}^-$ , in combination with a comparison study of two chemically similar systems, isoelectric peroxy radical,  $\text{HO}_2$ , and the neutral,  $\text{HNO}$ . Optimized geometries and vibrational frequencies are reported for all species with results compared to on-going experiments in autodetachment spectroscopy as well as previously reported theoretical values for the latter two systems. In addition, the Gaussian -1 and -2 methods developed by Pople and co-workers were used to determine the electron affinity of  $\text{HNO}$ , yielding a result in good agreement with experiment.

## **An Ab Initio Study of the Cycloaddition Reactions of SO<sub>2</sub> and 1,3-Butadiene**

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Vogel and co-workers recently reported that BF<sub>3</sub>·Et<sub>2</sub>O and CF<sub>3</sub>COOH catalyze stereoselective endo Diels-Alder reactions of SO<sub>2</sub> with isoprene and piperylene at low temperatures.<sup>1</sup> At high temperatures, the more stable sulfolenes are formed.

We are currently carrying out an ab initio investigation of the Diels-Alder reaction of 1,3-butadiene with SO<sub>2</sub> in an attempt to determine the origin of the stereoselectivity observed by Vogel. RHF transition structure optimizations give a gas phase endo preference ranging from 0.4 to 3.4 kcal/mol depending on the basis set used. Utilization of the SCRF method for determination of the exo and endo transition structures in CH<sub>2</sub>Cl<sub>2</sub> gives an endo preference of 0.3 to 2.1 kcal/mol.

Inclusion of electron correlation in the transition structure energies leads to 0.4 and 0.1 kcal/mol exo preferences at the MP2/6-31G\* and MP2/6-31+G\*//MP2/6-31G\* levels, respectively, while MP2/6-311+G\*//MP2/6-31G\* calculations yield an endo preference of 0.3 kcal/mol. MP2/6-31G\*//RHF/6-31G\* SCRF calculations predict a 0.1 kcal/mol endo preference. These results suggest only a small degree of stereoselectivity for the uncatalyzed Diels-Alder reaction of SO<sub>2</sub> with 1,3-butadiene. We are currently examining the BH<sub>3</sub> catalyzed reaction to determine whether the catalyst increases the stereoselectivity.

We have also examined the cheletropic reaction of 1,3-butadiene with SO<sub>2</sub> to form sulfolene. At the MP2/6-31G\*//RHF/6-31G\* level, this reaction has an activation barrier of 16.3 kcal/mol, 0.3 kcal/mol higher than the Diels-Alder reaction. The ΔE<sub>rxn</sub> for the cheletropic process is -9.3 kcal/mol at this level while that of the Diels-Alder is -7.6 kcal/mol. This result is probably qualitatively correct since the cheletropic reaction is known to be more exothermic than the Diels-Alder reaction.

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# GRAPHICAL DESCRIPTION OF THE SYMMETRIES OF POTENTIAL ENERGY SURFACES

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Shapes of the potential energy surfaces (PES) of "floppy" molecules can be represented by graphs in which vertices denote global minima and edges connecting the vertices describe energetically accessible paths connecting such global minima. Such graphical representations of PESs are characterized by (i) the number of vertices, (ii) edges that connect (or do not) various vertices and (iii) the symmetry of the PES, which may be obtained from the graphical figure. These characteristics are shown to be reflected in the vibration-rotation wavefunction's symmetry. Such a symmetry analysis reduces to that provided by the conventional point group for rigid molecules, but also provides a useful tool for characterizing vibrations of floppy molecules. In particular, it has been shown that for so-called complete graphs, the nonrigid group of the molecule is its full permutation-inversion group. PESs with complete graphs having three and six global minima are examined as examples, and relevant character tables are provided. PESs with incomplete graphs (which characterize species containing some inaccessible barriers), are also considered. In such cases, the graph connecting the  $n$  minima splits into two or more equivalent subgraphs each describing energetically accessible interconversions among subsets of  $n$  minima. The permutation-inversion group obtained according to these subgraphs can be used to label the vibration/rotation energy levels in these cases. The flexible molecules  $\text{ArH}_3^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{CH}_4^+$  and  $\text{LiBH}_4$  are considered as examples of the tools presented here.



# Modeling and Analysis of Electric Double Layers

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May 17, 1993

## Abstract

The structural properties of the electric double layers formed from aqueous electrolyte solutions adjacent to charged flat surfaces are studied, using constant temperature molecular dynamics method. Six systems constructed in a combination of three different water models (SPC/E, TIP4P, and ST2) and two types of monovalent ions (sodium cation and chloride anion) are investigated. These species are interacted with each other via potential functions optimized for the corresponding bulk phase. Their interactions with the surface remain the same type for all the systems, namely, 9-3 Lennard-Jones potential plus Coulomb potential between real and image charges. In addition, every point charges are acted with an external electric field. Through a detailed comparison of the data obtained from various systems, we are able to examine the model dependences of the results. This is a problem of primary importance in our effort to extend and improve the current models employed in studying interfacial phenomena. In order to test the possible artifacts introduced in choosing the location of image plane, which in itself is a topic involving much complication, we duplicate the simulation for the  $\text{Na}^+$ -SPC/E system except for shifting the image plane by  $\pm 0.5 \text{ \AA}$ .

**Abstract for poster to be presented at West Coast Theoretical Chemistry  
Conference, UCLA, Los Angeles, CA, June 19, 1993**

**AB INITIO INVESTIGATION OF LIGAND-TRANSITION  
METAL BONDING TRENDS OF PTZR**

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A study comparing metal-ligand (H, CH<sub>3</sub>) bond dissociation energies for bimetallic and monometallic-ligand complexes of Zr and Pt using Generalized Valence Bond (GVB) theory and Correlation-Consistent Configuration Interaction (CCCI) will be presented. The calculations indicate that the Zr-H and Zr-CH<sub>3</sub> bonds are more polar than those of Pt-H and Pt-CH<sub>3</sub>. In the dimer complexes, Zr acts as an electron donor and Pt as an electron acceptor, in contrast to the assumptions of the Engel-Brewer theory of early-late transition metal compounds. The hydride-dimer bond strengths are increased much more than the dimer-methyl bond strengths, relative to the monometallic bond energies. This holds promise that PtZr alloys might be used effectively to dehydrogenate hydrocarbons selectively.

# State-Specific Reaction Probabilities from a DVR-ABC Green's Function

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Seideman and Miller<sup>1</sup> have recently introduced a direct, efficient method for calculating cumulative reaction probabilities by using a discrete variable representation (DVR) to represent the Green's function and absorbing boundary conditions (ABC) to enforce the outgoing wave boundary conditions. Here we show that this method for representing the Green's function can also be used to calculate *state-specific* reaction probabilities. Application to the collinear reaction  $H + H_2 \rightarrow H_2 + H$  demonstrates that the method is an efficient way to calculate state-to-state and partially state-resolved reaction probabilities.<sup>2</sup> In addition, distorted waves are useful in reducing the size of the DVR basis. Present work on the application of this method to calculate initial state-selected reaction probabilities for the  $OH + H_2 \rightarrow H_2O + H$  reaction is discussed.

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<sup>1</sup>T. Seideman and W. H. Miller, *J. Chem. Phys.* **96**, 4412 (1992); *ibid* **97**, 2499 (1992).

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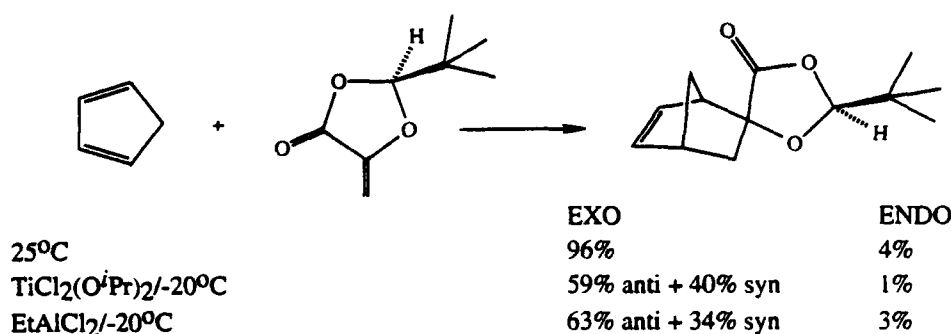
# Theoretical Study on the Origin of the Anomalous Donor-Endo, Acceptor-Exo Stereoselectivity in Diels-Alder Reactions of Captodative Dienophiles

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The Alder rule of maximum accumulation<sup>1</sup> of unsaturation has been a venerable guide to the stereochemistry of the exo and endo type found in Diels-Alder reactions.<sup>2</sup> In general, carbonyl groups of  $\alpha,\beta$ -unsaturated aldehydes, ketones, esters and anhydrides take the endo position in the transition state of Diels-Alder reactions.<sup>2</sup> The origin of this preference has been attributed to secondary orbital interactions, dipole-dipole interactions, steric effects and van der Waals attractions, but there is no general accord about the magnitudes of these effects.

Interestingly this rule is violated in a large number of examples showing in most of the cases a very high exo-selectivity ( $C=O$  exo; d.e. =70-90) in both thermal and catalyzed reactions for different dienes (cyclopentadiene, acrolein, and butadiene differently substituted) with  $\alpha$ -alkoxy,  $\alpha$ -amino or  $\alpha$ -alkyl  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>3</sup>



In this work we report a theoretical study using *ab initio* molecular orbital calculations on the reactions of butadiene and cyclopentadiene with vinyl alcohol, acrolein, 2-hydroxypropenal, and 5-methylene-1,3-dioxolan-4-one. Calculations were carried out with the restricted Hartree-Fock method, using the GAUSSIAN 90 and 92 programs. Transition structures were optimized using 3-21G basis set and the energies were also evaluated by single-point calculations with 6-31G\* basis set on the 3-21G geometry. The use of 6-31G\*//3-21G calculations has shown to give reasonable results in similar systems on substituent effects and stereoselectivities.<sup>4</sup>

We have addressed a variety of interesting effects involved in this reaction and emphasize those responsible for the unexpected high exo ( $C=O$ ) selectivity found in  $\alpha$ -donor- $\alpha,\beta$ -unsaturated dienophiles.

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# **The Methyl Carbene Radical Cation: Classical (Open) or Nonclassical (Bridged)?**

**Paul A. Gibbons and K. N. Houk\***

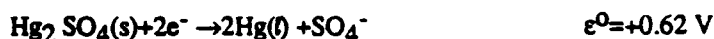
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**Abstract:** Ab initio molecular orbital calculations using basis sets up to 6-31G\* and with electron correlation incorporated at the second-order Moller-Plesset level have been used to study the 1,2 hydrogen shift in the ethene radical cation. Previous calculations on other cationic and radical species have shown the existence of classical structures for the ethyl radical and dication as well as non-classical bridged structures for the ethyl cation. The ground state structure for methyl carbene radical cation is predicted to have the classical structure using HF but the inclusion of electron correlation gives a structure that is bridged.

# Dynamics Of The Mercury Beating Heart System

Joe Caddell and Donald A. McQuarrie

The mercury beating heart system was first reported over a century ago by G. Lippmann in connection with his work on electrocapillarity. The original system consists of approximately one cubic centimeter of mercury on a watch glass covered with a dilute aqueous solution of a strong acid, such as  $\text{H}_2\text{SO}_4$  which has a few crystals of a strong oxidizer, such as  $\text{K}_2\text{Cr}_2\text{O}_7$ , and an iron nail. A film of  $\text{Hg}_2\text{SO}_4$  is thought to form on the surface of the drop. This in turn reduces the surface tension of the drop, causing it to spread out. If the iron nail is in a position such that it will touch the drop when it spreads out, the contact between the Fe and the surface of the drop allows the nail to reduce the  $\text{Hg}_2\text{SO}_4$  film according to



When the film is reduced this way, it dissolves, allowing the surface tension of the drop to increase again, causing the drop to "rise". When it does this, it breaks contact with the Fe, allowing the film to form again, causing oscillations to set up. The mechanism by which the surface tension changes with reduction and oxidation of the surface is electrocapillarity. The drop will oscillate in various modes, the three sided, or three-fold mode, is similar in appearance to a beating heart, thus the name.

Laidlaw, Olson and coworkers have shown that the same behavior can be obtained by connecting a drop of mercury, in pure water and an inert atmosphere, to an oscillating external voltage. This is a much simpler system, with qualitatively similar dynamics. Thus this is the system modelled in this work. Rayleigh, again over a century ago, developed a method by which to treat the oscillations of a charged sphere. His method was to expand the radius of the drop in a series of Legendre Polynomials, obtain expressions, to low order, for the kinetic energy, electrostatic potential, and potential energy due to capillarity, and then write down the Lagrangian equations of motion for the drop. He showed that the coefficients of expansion for the Legendre Polynomials may be used as generalized coordinates, and the equations of motion are written in these variables.

In this work, the Rayleigh method is extended to 3<sup>rd</sup> order in the expansions. This is done so that the coupling between modes may be studied, allowing the various modes of oscillation to exchange energy with other modes, and thus allowing the mode of oscillation to change dynamically. The time-dependent potential is also treated, as an extension of this method. This is done by using an electrical potential of the form  $A \sin \pi v + V_0$ . The electrocapillary effect is also taken into account in that the surface tension is now allowed to vary with the time (the applied voltage). Lagrange's equations of motion for the coefficients of the Legendre Polynomials in the expansion of the radius of the drop are solved numerically, steady states are found, and a stability analysis is conducted for the critical points. This is done for first the electrostatic problem, in which the external voltage is held constant, and then for the time dependent voltage. The simplifying assumption that only the modes through the 5-fold one are found is made, otherwise the Lagrangian equations of motion would be an infinite set of coupled nonlinear differential equations.

## Dynamics of Solvation Response, A Linear Model

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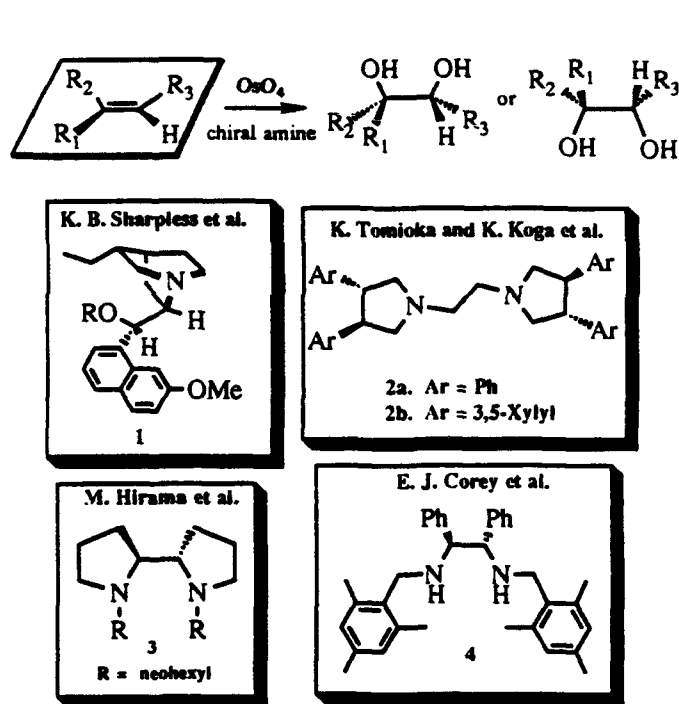
A chemical reaction is affected by the response of a solvent to solute changes, such as charge redistributions, which occur during the course of the reaction. A simple model is developed to describe the dynamics of this response. Within the linear response regime, the dynamics of a fluid responding to a perturbation are determined by its equilibrium fluctuations. For a pure fluid, the structure factor is used to define an energy surface. Momenta conjugate to the normal-mode coordinates are introduced, and the complete dynamics are known once the short-time behavior is used to fix the corresponding masses. In the presence of a solute, the exclusion of the fluid from a region of space leads to changes in the normal modes and their frequencies. The change can be calculated for a solute-solvent potential with a hard-core repulsive part. Computer simulations are used to evaluate the validity of the model.

# MM2 MODELING STUDY OF THE DIHYDROXYLATIONS OF ALKENES BY CHIRAL AMINE COMPLEXES OF OSMIUM TETRAOXIDE

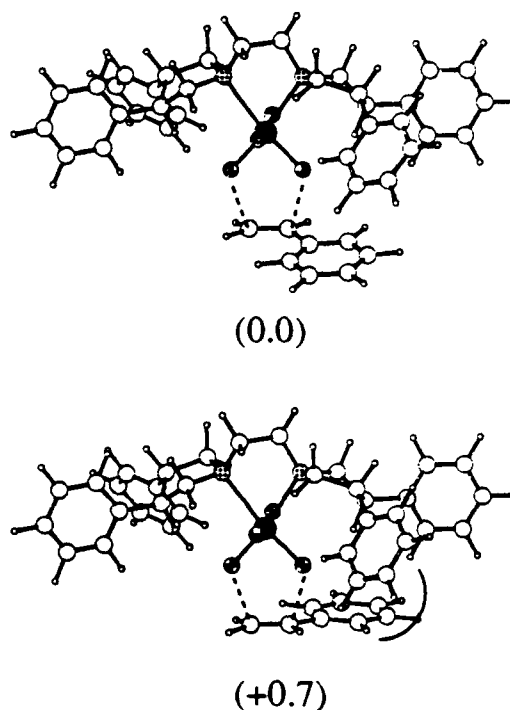
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Asymmetric dihydroxylations (ADH) with osmium tetroxide in the presence of chiral amine ligands are important reactions in organic synthesis. A number of excellent chiral amine ligands have been investigated up to the present as in Figure 1. Although two mechanisms have been proposed for the reaction of osmium tetroxide and olefins ( [2+2] and [2+3] cycloaddition ), we have so far investigated a five-membered [3+2] transition structure model for this reaction. This MM2 force field is based upon X-ray crystal structures of OsO<sub>4</sub>-amine complexes and osmate esters along with empirical knowledge from ab initio transition structures of analogous reactions. These models are still qualitative, but shows consistent results with available experimental results. Useful geometrical information about the transition states of the reaction is obtained. In this presentation, the modeling study of the amine ligands of Tomioka and Koga et al. and Sharpless et al. will be mainly described as in Figure 2.



**Figure 1** ADH and amine ligands: 1-Sharpless, 2a, b-Tomioka-Koga, 3-Hirama, 4-Corey



**Figure 2** Transition structures of 2a-OsO<sub>4</sub>-styrene

## Reference:

- [1] Y-D. Wu, Y. Wang and K. N. Houk, *J. Org. Chem.*, **1992**, 1362 and references cited therein.



# H + e<sup>-</sup> Scattering for Total J=0 using the S-Matrix Kohn Variational Principle with an Asymptotic Laurent Expansion

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The Kohn Variational Principle<sup>1</sup> has been used extensively in the study of nuclear and chemical scattering phenomena. Unfortunately, the K-Matrix formulation of this method is marred by the presence of anomalous numerical singularities which complicate the interpretation of energy-dependent phase shifts. The S-Matrix formulation<sup>2</sup> has been shown to be free of these anomalies. Converged phase shifts are presented for inelastic total J=0  $H_{nlm} + e^- \rightarrow H_{n'l'm'} + e^-$ . Asymptotic free waves are represented with a Laurent expansion in the scattering coordinate to reduce the size of the  $\ell^2$  basis set in the presence of long range interactions caused by a non-spherically symmetric asymptotic state.

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## **Ab Initio Studies of the Isotropic Hyperfine and Nuclear Quadrupole Coupling Constants of Imidazole radicals**

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In calcium depleted Photosystem II a signal is seen in the Electron Spin Resonance spectrum that is attributed to an amino acid radical near the manganese cluster in the reaction center. There has been experimental evidence that suggests this amino acid is histidine. In order to elucidate the source of this radical ab initio calculations have been performed on model system of histidine. Imidazole has been chosen as the model system, since the major portion of the unpaired electron density is localized on the imidazole ring of histidine.

The spin densities that determine the isotropic hyperfine coupling constants are calculated as well as the electric field gradients that determine the nuclear quadrupole coupling constant for the nitrogens. Restricted and Unrestricted Hartree-Fock calculations have been performed in the basis sets, STO-3G, 6-31G, and 6-31G\* on possible imidazole radical structures. Higher levels of calculations, such as limited configuration interaction and Møller-Plesset perturbation theory, will be reported.

# DYNAMIC TUNNELING MECHANISM OF INTRAMOLECULAR VIBRATIONAL RELAXATION IN $(\text{CH}_3)_3\text{YCCH}$ MOLECULES

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Quantum calculations are reported for the dynamics of intramolecular vibrational energy redistribution of the acetylenic CH stretch in  $(\text{CH}_3)_3\text{CCCH}$  molecules. This work is an extension of our previous publication (J. Chem. Phys. 98, 6044, 1993) where the linewidths of the CH overtone transitions were calculated in several molecules of a general class  $(\text{CX}_3)_3\text{YCCH}$  and it was found that the relaxation is due to a sequence of many weak off-resonance vibrational transitions between tiers of directly coupled states. The coupling of the CH stretch to a manifold of quasis resonant states resembles the superexchange mechanism of coupling between donor and acceptor states in long distance electron transfer reactions. The light state is separated from the quasicontinuum by a dynamic barrier. It is explicitly shown that the relaxation dynamics occurs via tunneling in tiers space of the system under this barrier. Details of the time evolution of population under the dynamic barriers in the course of relaxation is discussed. Also, the localization properties of the tier system of  $(\text{CH}_3)_3\text{YCCH}$  molecules are studied with a method originally developed for random solids by Skinner and co-workers. In this method connectivity of vibrational states along the tier coordinate of the molecule is calculated. The connectivity is used then to describe the average distance along the tier coordinate ("localization length") at which the light state is strongly coupled to other states in a molecule. The observed absence of relaxation in Si- compound in numerical simulation is discussed in relation to the localization phenomenon.

## **Calculation of Scanning Tunneling Microscopy Image of an Adsorbate: Application to Adenine Adsorbed on a Graphite Surface**

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An expression is obtained for the current in scanning tunneling microscopy (STM) between the tip and the sample in the presence of a single adsorbate molecule. For this purpose the "Newns-Anderson" treatment (a discrete state in a continuum) is used to obtain wave functions and other properties of the adsorbate/system. The current is expressed in terms of an effective local density of states at the adsorbate and the adsorbate-tip matrix elements, the local density of states incorporating the adsorbate-solid (substrate) interaction. The treatment is applied to the STM image of adenine adsorbed on a graphite surface, and the results are compared with experiment. The orientation of adenine with respect to the underlying graphite and the dependence of the image on the orientation are considered. The need for using, for the present system, more than only the HOMO and the LUMO orbitals of the adsorbate is seen both in the results and in the comparison with experiment.

## TUNNELING IN A TIME-DEPENDENT ELECTRIC FIELD

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If a particle is initially located in one of the wells of a two-well potential it coherently oscillates between the wells with a frequency equal to the splitting between the levels. When a time-dependent cw electric (laser) field is applied, this simple coherent motion is changed, and one observes a low frequency oscillation with a frequency much smaller than the frequency of the field. For high intensity of the field it is even possible to obtain localization of a particle in one of the wells. For the description of such an effect a simple two-level model is proposed. The condition for particle localization was found. The localization occurs when  $2Ed/\hbar\omega$  coincides with the zeros of zero-order Bessel function where  $E$  and  $\omega$  are the amplitude and the frequency of the field, and  $d$  is a transition dipole moment. For a biased system or a system in a constant electric field the physical picture is rather different. Initially the particle is localized in a deeper well, and can stay in this state forever. If the number of absorbed quanta of the cw electric field is exactly equal to the bias, a particle becomes delocalised, coherently oscillating between the wells.

Besides low frequency motion one also obtains high frequency oscillations commensurate with  $\omega$ . Despite the inversion symmetry of the two-well system it is possible to observe the effect of second harmonic generation. In a strong field even harmonics are split into two lines of different amplitudes. The frequency difference between them is the doubled low frequency of the slow component. When localization occurs this doublet shrinks into one line giving rise to even harmonic generation. The results are obtained both analytically and numerically by solving a time-dependent Schrodinger equation.

The effects described may be applied for any physical system which can be considered as a two-level system driven by an electric field: it may be an atom or a molecule in a laser field, an electron in quantum wells, a nuclear spin in a strong magnetic field, tunneling of a superconducting phase in Josephson junctions under the irradiation of a microwave field or a chemical reaction driven by a strong time dependent electric field.

Andersson, K. - 86	Gibbons, P. - 120
Atlas, S. -	Gonzalez, N. - 81
Auerbach, S. - 6	Granek, R. - 32
Bagdassarian, C. - 14	Grossman, F. - 44
Barker, J. - 8	Heller, E. - 31
Beck, D. - 53	Henderson, D. - 59
Benn, D. - 61	Hernandez, R. - 79
Beno, B. - 114	Horn, H. - 63
Berry, R. - 4	Ionova, I.V. - 108
Bierwagen, E. - 57	Keshavamurthy, S. - 43
Blake, N. - 88	Kirtman, B. - 33
Boldyrev, A. - 17	Konowalow, D. - 87
Brown, W. - 75	Kozlowski, P.M. - 55
Caddell, J. - 121	Krause, J. - 12
Carter, L. - 37	Kurtovik, Z. - 122
Cave, R.J. - 65	Langlois, J-M. - 87
Chacon, M. - 46	Lengsfield, B.H. III - 85
Chang, T-M. - 80	Lim, K-T. - 24
Chao, I. - 58	Liu, A. - 28
Colvin, M. -	McCarthy, W. - 42
Cullen, J. - 73	McLean, D. - 25
Dakhovskii, Y. - 128	Madden, P. - 3
Dang, L. - 76	Maitre, P. - 13
Dasgupta, S. - 67	Mak, C. - 41
Demiralp, E. - 99	Maluendes, S. - 70
Ellerby, M. - 73	Mandelshtam, V. - 21
Eksterowicz, J. - 84	Martens, C. - 34
Eurenius, K. - 62	Martinez, T.J. - 15
Fennen, J. - 95	Maurice, D. - 83
Garrett, B.C. - 71	Meador, D. - 125
Gaucher, L.F.X. - 124	Mehta, A. - 126
Gezelter, J.D. - 95	Melnick, M.S. - 94
Gibson, D.A. - 66	Messina, M. - 92
	Moore, B. - 36

Muller, R. - 49  
 Na, J. - 101  
 Nakamura, K. - 91  
 Nefedova, V. - 115  
 Nickolas, J. - 16  
 Niwayama, S. - 123  
 Ono, L. - 100  
 Ortiz, J.V. - 82  
 Ou-Yang, H. - 127  
 Oyler, N. - 74  
 Parkinson, W.A. - 98  
 Pascual-Teresa, B. - 119  
 Pearlman, D. - 106  
 Perry, J. - 109  
 Pfeifer, K-H. - 35  
 Piecuch, P. - 6  
 Radeke, M.R. - 97  
 Rejto, P. - 64  
 Replogle, E. - 107  
 Reynolds, G.G. - 117  
 Roberson, M. - 93  
 Robins, K. - 113  
 Rosenkrantz, M. - 68  
 Rost, J.M. -  
 Saxon, R.P. - 59  
 Schenter, G.K. - 111  
 Seideman, T. - 105  
 Sepulveda, M. - 56  
 Sharlow, M. - 47  
 Smith, D. - 27  
 Smith, G. - 48  
 Thompson, W.H. - 118  
 Walch, S.P. - 69

Weakliem, C. - 5  
 Weakliem, P.C. - 54  
 Wheeler, J. - 21  
 Williams, S. - 11  
 Wu, C. - 22  
 Xantheas, S. - 45  
 Zakrewski, V. - 110  
 Zeng, X.C. - 26  
 Zhang, Z. - 89  
 Zhu, S-B. - 116  
 Zipse, H. - 112