# Program and Abstracts
# Programme et Résumés

McGill

Université de Montréal

350 ANS
MONTRÉAL
*fête*

**11th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY**
**11e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE**

*AUGUST 2-7, 1992* *MONTREAL, CANADA*

# 11th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

# 11e SYMPOSIUM CANADIEN SUR LA CHIMIE THÉORIQUE

## INTERNATIONAL CONFERENCE INTERNATIONALE

**AUGUST 2 - 7, 1992**

**2 - 7 AOÛT 1992**

**MONTRÉAL, QUÉBEC**

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We gratefully acknowledge The Chemical Institute of Canada, Cray Canada, IBM Canada Ltd., NSERC/CRSNG, McGill University, and Université de Montréal for their support, without which this symposium would not have been possible.

Bryan Sanctuary
McGill University

Dennis R. Salahub
Université de Montréal

**11th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY**
**11e SYMPOSIUM CANADIEN SUR LA CHIMIE THÉORIQUE**

# PROGRAM/PROGRAMME

**SUNDAY, August 2**

| | |
|---|---|
| 15h00 - 17h00 | Registration, Lobby of Gardner Hall (Coed residence) |
| 19h00 - 21h00 | Registration, Otto Maas Building |
| 20h00 | Mixer |

*Lectures are in Otto Maas Building, Room 112*

| | MORNING | | AFTERNOON |
|---|---|---|---|
| **MONDAY, August 3** | 8h45 | Opening Remarks<br>Welcome by Prof. T.H. Chan | 14h00 R. Fournier |
| | 9h00 | J. Polanyi | 14h40 R.B. Gerber |
| | 9h40 | A. DePristo | 15h20 G.C. Corey |
| | 10h20 | BREAK | 16h00 POSTER SESSION |
| | 10h50 | H. Nakatsuji | |
| | 11h30 | J.P. Malrieu | |
| | 12h10 | LUNCH | |
| **TUESDAY, August 4** | 9h00 | P. Kusalik | 14h00 D. Ringe |
| | 9h40 | G. Patey | 14h40 D. Nguyen |
| | 10h20 | BREAK | 15h20 M. Zerner |
| | 10h50 | R.M. Stratt | 16h00 Buses leave for Université de Montréal |
| | 11h30 | M. Fixman | 17h15 H. Kroto |
| | | | 18h15 COCKTAIL |

| | MORNING | | AFTERNOON | |
|---|---|---|---|---|
| **WEDNESDAY, August 5** | 9h00 | K. Raghavachari | 14h00 | H. Metiu |
| | 9h40 | S. Clough | 14h40 | R. Dumont |
| | 10h20 | BREAK | 15h20 | POSTER SESSION |
| | 10h50 | C.A. Mead | 16h30 | BARBECUE OTTO MAASS LOBBY PATIO |
| | 11h30 | R.F. Haglund | | |
| | 12h10 | Business meeting of Canadian Theoreticians | | |
| **THURSDAY, August 6** | 9h00 | W. Kohn | 14h00 | I. Oppenheim |
| | 9h40 | R.G. Parr | 14h40 | D. Ronis |
| | 10h20 | BREAK | 15h20 | R.F. Snider |
| | 10h50 | A.D. Becke | 16h00 | A.R. Allnatt |
| | 11h30 | G. Stell | 17h00 | BUSES LEAVE FOR BANQUET |
| **FRIDAY, August 7** | 9h00 | M.S. Child | 14h00 | N.C. Handy |
| | 9h40 | T. Carrington, Jr. | 14h40 | R. Friesner |
| | 10h20 | BREAK | 15h20 | W. Kutzelnigg |
| | 10h50 | B.A. Hess | | |
| | 11h30 | T. Ziegler | | |
| | 12h10 | LUNCH | | |

# 11th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

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## INTERNATIONAL CONFERENCE INTERNATIONALE

## PROGRAM/PROGRAMME

***** N.B. Allotted times include discussion *****

**Lectures are in Otto Maas Building, Room 112**

### SUNDAY, August 2

| | | |
|---|---|---|
| 15h00 | - 17h00 | Registration, McGill University, Lobby of Gardner Hall (Coed residences) |
| 20h00 | - 22h00 | Mixer, Otto Maass Chemistry building (on the patio) |

### MONDAY, August 3

| | | |
|---|---|---|
| 8h45 | - 9h00 | Opening Remarks<br>Welcome by Professor T.H. Chan, Dean of Science, McGill University |
| *Chair: F. Grein* | | |
| 9h00 | - 9h40 | J. Polanyi "Photoreactions in adsorbates: theory and experiment" |
| 9h40 | - 10h20 | A. DePristo "Structure, dynamics and reactivity of mono- and bi-metallic clusters" |
| 10h20 | - 10h50 | BREAK |
| 10h50 | - 11h30 | H. Nakatsuji "Quantum-chemical approach for excited states and surface molecule interactions" |
| 11h30 | - 12h10 | J.P. Malrieu "Size-consistent CI's through self-consistent Intermediate Hamiltonians" |
| 12h10 | - 14h00 | LUNCH |
| *Chair: R. Wallace* | | |
| 14h00 | - 14h40 | R. Fournier "Classical potentials for metal and semiconductor clusters" |
| 14h40 | - 15h20 | R.B. Gerber "Quantum dynamics of reactions in clusters and in solids" |
| 15h20 | - 16h00 | G.C. Corey "A pseudospectral method for solving the time-dependent Schrödinger equation in spherical coordinates" |
| 16h00 | - 17h30 | POSTERS - I |

**TUESDAY, August 4**

*Chair: D. Wardlaw*

| | | |
|---|---|---|
| 9h00 | - 9h40 | P. Kusalik "Molecular dynamics studies of polar liquids" |
| 9h40 | - 10h20 | G. Patey "Ferroelectric liquid crystal and solid phases formed by strongly interacting dipolar spheres" |
| 10h20 | - 10h50 | BREAK |
| 10h50 | - 11h30 | R.M. Stratt "The excited states of liquids" |
| 11h30 | - 12h10 | M. Fixman "Stress relaxation in polymer melts and solutions" |
| 12h10 | | LUNCH |

*Chair: B. Roux*

| | | |
|---|---|---|
| 14h00 | - 14h40 | D. Ringe "Stopping them dead; the relationship of protein flexibility to protein function" |
| 14h40 | - 15h20 | D. Nguyen "A density functional theory study of DHFR enzyme mechanism" |
| 15h20 | - 16h00 | M. Zerner "A simple model for solvent effects in electronic spectroscopy" |
| 16h00 | | Buses leave for Université de Montréal |
| 17h15 | - 18h15 | H. Kroto "The discovery of $C_{60}$ Buckminsterfullerene and the implications for chemistry on earth and in space" |
| 18h15 | - 19h15 | COCKTAIL |

**WEDNESDAY, August 5**

*Chair: T. Dingle*

| | | |
|---|---|---|
| 9h00 | - 9h40 | K. Raghavachari "Structures and stabilities of spheroidal carbon clusters" |
| 9h40 | - 10h20 | S. Clough "The quantum phase and coherent dynamics of hindered methyl groups" |
| 10h20 | - 10h50 | BREAK |
| 10h50 | - 11h30 | C.A. Mead "The geometrical phase in molecular systems" |
| 11h30 | - 12h10 | R.F. Haglund "Photon-stimulated bond-breaking on non-metallic surfaces" |
| 12h10 | | Business meeting of Canadian Theoreticians |
| | | LUNCH |

*Chair: M. Casida*

| | | |
|---|---|---|
| 14h00 - 14h40 | | H. Metiu "Coherent effects in excitation with short laser pulses" |
| 14h40 - 15h20 | | R. Dumont "Tunneling time probability distribution" |
| 15h20 - 17h00 | | POSTERS - II |

**THURSDAY, August 6**

*Chair: K. Darvesh*

| | | |
|---|---|---|
| 9h00 - 9h40 | | W. Kohn "Density Functional Theory and Generalized Wannier Functions?" |
| 9h40 - 10h20 | | R.G. Parr "Recent advances in density functional theory" |
| 10h20 - 10h50 | | BREAK |
| 10h50 - 11h30 | | A.D. Becke "Density-functional molecular energetics" |
| 11h30 - 12h10 | | G. Stell "Solving nonequilibrium problems in statistical mechanics using equilibrium methods" |
| 12h10 | | LUNCH |

*Chair: N. Snider (tentative)*

| | | |
|---|---|---|
| 14h00 - 14h40 | | I. Oppenheim "Statistical mechanical theory of inelastic granular systems" |
| 14h40 - 15h20 | | D. Ronis "Structure and dynamics in colloidal suspensions" |
| 15h20 - 16h00 | | R.F. Snider "Aspects of moderately dense gas kinetic theory" |
| 16h00 - 16h40 | | A.R. Allnatt "Kinetic theory of matter transport in concentrated alloys" |
| 17h00 - | | BUSES LEAVE FOR BANQUET |

**FRIDAY, August 7**

*Chair: A. Thakkar*

| | | |
|---|---|---|
| 9h00 - 9h40 | | M.S. Child "Rydberg spectroscopy of $H_2O$" |
| 9h40 - 10h20 | | T. Carrington Jr."Isolated effective Hamiltonians for two nearly degenerate modes coupled by Coriolis and centrifugal terms" |
| 10h20 - 10h50 | | BREAK |
| 10h50 - 11h30 | | B.A. Hess "Relativistic electronic structure calculations in the framework of the Douglas-Kroll transformation" |
| 11h30 - 12h10 | | T. Ziegler "Density functional theory as a practical tool for the study of elementary reaction steps in homogeneous catalysis" |
| 12h10 - 14h00 | | LUNCH |

*Chair: J. Goddard*

| | | | |
|---|---|---|---|
| 14h00 | - | 14h40 | N.C. Handy "The harmonic frequencies of benzene" |
| 14h40 | - | 15h20 | R.A. Friesner "Pseudospectral methods for electronic structure calculations" |
| 15h20 | - | 16h00 | W. Kutzelnigg "Wave functions with linear $r_{12}$-dependent terms" |

| | SPECIAL SPEAKERS | TITLES |
|---|---|---|
| S.1 | Polanyi, J.C. | "Photoreaction in Adsorbates; Theory and Experiment" |
| S.2 | DePristo, A.E. | "Structure, Dynamics and Reactivity of Mono- and Bi-Metallic Clusters" |
| S.3 | Nakatsuji, H. | "Quantum-Chemical Approach for Excited States and Surface Molecule Interactions" |
| S.4 | Malrieu, J.P. | Size-Consistent CI's Through Self-Consistent Intermediate Hamiltonians" |
| S.5 | Fournier, R. | "Classical Potentials for Metal and Semiconductor Clusters" |
| S.6 | Gerber, R.B. | "Quantum Dynamics of Reactions in Clusters and in Solids" |
| S.7 | Corey, G.C. | "A Pseudospectral Method for Solving the Time-Dependent Schrödinger Equation in Spherical Coordinates" |
| S.8 | Kusalik, P.G. | "Molecular Dynamics Studies of Polar Liquids" |
| S.9 | Patey, G.N. | "Ferroelectric Liquid Crystal and Solid Phases Formed by Strongly Interacting Dipolar Spheres" |
| S.10 | Stratt, R. M. | "The Excited States of Liquids" |
| S.11 | Fixman, M. | "Stress Relaxation in Polymer Melts and Solutions" |
| S.12 | Ringe, D. | "Stopping them Dead; The Relationship of Protein Flexibility to Protein Function" |
| S.13 | Nguyen, Dzung T. | "A Density Functional Theory Study of DHFR Enzyme Mechanism" |
| S.14 | Zerner, M.C. | "A Simple Model for Solvent Effects in Electronic Spectroscopy" |
| S.15 | Kroto, H. | "The Discovery of C60 Buckminsterfullerene and the Implications for Chemistry on Earth and in Space" |
| S.16 | Raghavachari, K. | "Structure and Stabilities of Spheroidal Carbon Clusters" |
| S.17 | Clough, S. | "The Quantum Phase and Coherent Dynamics of Hindered Methyl Groups" |
| S.18 | Mead, C. A. | "The Geometrical Phase in Molecular Systems" |
| S.19 | Haglund, Jr., R.F. | "Photon-Stimulated Bond-Breaking on Non-Metallic Surfaces" |
| S.20 | Metiu, H. | "Coherent Effects in Excitation with Short Laser Pulses" |
| S.21 | Dumont, R.S. | "Tunneling Time Probability Distribution" |
| S.22 | Kohn, W. | "Density Functional Theory and Generalized Wannier Functions?" |
| S.23 | Parr, R.G. | "Recent Adances in Density Functional Theory" |
| S.24 | Becke, A.D. | "Density-Functional Molecular Energetics" |

| SPECIAL SPEAKERS | | POSTER TITLES |
|---|---|---|
| S.25 | Stell, G. | "Solving Nonequilibrium Problems in Statistical Mechanics Using Equilibrium Methods" |
| S.26 | Oppenheim, I. | "Statistical mechanical Theory of Inelastic Granular Systems" |
| S.27 | Ronis, D. | "Structure and Dynamics in Colloidal Suspensions" |
| S.28 | Snider, R.F. | "Aspects of Moderately Dense Gas Kinetic Theory" |
| S.29 | Allnatt, A.R. | "Kinetic Theory of Matter Transport in Concentrated Alloys" |
| S.30 | Child, M.S. | "Rydberg Spectroscopy of H2O" |
| S.31 | Carrington, Jr., T. | "Isolated Effective Hamiltonians for Two Nearly Degenerate Modes Couples by Coriolis and Centrifugal Terms" |
| S.32 | Hess, B.A. | "Relativistic Electronic Structure Calculations in the Framework of the Douglas-Kroll Transformation" |
| S.33 | Ziegler, T. | "Density Functional Theory as a Practical Tool for the Study of Elementary Reaction Steps in Homogeneous Catalysis |
| S.34 | Handy, N.C. | "The Harmonic Frequencie of Benzene" |
| S.35 | Friesner, R.A. | "Pseudospectral Methods for Electronic Structure Calculations" |
| S.36 | Kutzelnigg, W. | "Wave Functions with Linear R12-dependent terms" |

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| S.5 | Fournier, R. | "Classical Potentials for Metal and Semiconductor Clusters" |
| S.35 | Friesner, R.A. | "Pseudospectral Methods for Electronic Structure Calculations" |
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| S.8 | Kusalik, P.G. | "Molecular Dynamics Studies of Polar Liquids" |
| S.36 | Kutzelnigg, W. | "Wave Functions with Linear R12-dependent terms" |
| S.4 | Malrieu, J.P. | Size-Consistent CI's Through Self-Consistent Intermediate Hamiltonians" |
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# S.1 PHOTOREACTION IN ADSORBATES; THEORY AND EXPERIMENT

John C. Polanyi, University of Toronto, Toronto, Canada M5S 1A1

Photochemistry has always been appealing to chemists since they can select the bonds to be broken and, with pulsed ultraviolet light, can initiate photoinduced processes at a well-defined time. The new field of photochemistry in the adsorbed state has the additional attraction (a) that one can catalyse photodissociation (particularly through charge-transfer from the substrate), altering its probability, wavelength and molecular dynamics, and (b) that one can catalyse photoreaction by the (in theory) simple expedient of aiming adsorbed reagents at one another. The field of 'surface aligned photoreaction' is the youngest of all the endeavours in this broad area. This talk will review the experimental evidence and especially the theoretical basis for our understanding of photoinduced reaction between co-adsorbed species, and will argue that the infant field shows promise for the future.

# S.2

## STRUCTURE, DYNAMICS AND REACTIVITY OF MONO- AND BI-METALLIC CLUSTERS

Mark S. Stave, Hsing Lee and Andrew E. DePristo
Ames Laboratory,‡ USDOE, and Department of Chemistry, Iowa State University, Ames, IA 50011.

I will detail the density functional based corrected effective medium (CEM) theory. (The fundamental development was reviewed in T. J. Raeker and A. E. DePristo, Int. Rev. Phys. Chem. 10, (1991) 1.) This method replaces a real many electron N-atom system in arbitrary geometry by N reference systems, currently taken to be each atom bound in a homonuclear diatomic and a homogeneous bulk system. Current implementation also utilizes the approximation of additive atomic electron densities for all systems. The correspondence between an atom in the N-atom and the same atom in its reference system is made by identification of the same average electron density around the atom in both systems. Corrections to the zero'th order model are calculated non-self-consistently and include differences in coulomb and kinetic-exchange-correlation energies between the N-atom and N reference systems. I will also discuss the relationship of the CEM theory to related approaches such as the embedded atom method of Daw, Baskes and Foiles, the effective medium theory of Norskov and coworkers, the "glue" model of Ercolessi, Parrinello and Tosatti, and the Finnis-Sinclair method.

Applications will be presented to illustrate the capabilities and limitations of these methods. These will include the structure of $Ni_N$ and $Pd_N$ with N=5-23, adsorption and absorption of H-atoms on these clusters, and the structure of bimetallic clusters in the size range of 200-2000 atoms.

‡ Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences. Computer time was supplied by the DOE Lawrence Livermore Lab (CRAY 2), the Scalable Computer Laboratory of ISU and the Ames lab-USDOE (64 processor NCUBE) and the Massively Parallel Research Lab at Sandia National Lab at Albuquerque (1024 processor NCUBE).

# S.3 QUANTUM-CHEMICAL APPROACH FOR EXCITED STATES AND SURFACE MOLECULE INTERACTIONS

Hiroshi Nakatsuji
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto 606, Japan

We have developed exponentially generatd wave functions for studying electron correlations in ground and excited states. The SAC-CI method[1] is particularly useful and extended recently to quasi-degenerate cases[2] and high-spin states.[3] Surface electronic processes often involve several lower electronic states and electron stransfer, so that the above method is very useful for studying surface molecule interactions and reactions. Further, for surface-molecule interactions, the effect of bulk solid is sometimes important and considered by the dipped adcluster model (DAM).[4] We apply these methods to halogen adsorptions on alkali metal furfaces, particularly to harpooning and surface chemiluminescence processes.[5]

1) H. Nakatsuji, Chem. Phys. Lett. 59, 362 (1978); 67, 329, 334 (1979).
2) H. Nakatsuji, J. Chem. Phys. 94, 6716; 95, 4296 (1991).
3) H. Nakatsuji and M. Ehara, submitted.
4) H. Nakatsuji, J. Chem. Phys. 87, 4995 (1987); H. Nakatsuji, H. Nakai, and Y. Fukunishi, J. Chem. Phys. 95, 640 (1991).
5) H. Nakatsuji, R. Kuwano, and H. Morita, submitted.

# S.4 SIZE-CONSISTENT CI'S THROUGH SELF-CONSISTENT INTERMEDIATE HAMILTONIANS.

**J.P. Malrieu**, Laboratoire de Physique Quantique, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France

The theory of intermediate effective Hamiltonians provide a tool to eliminate the unlinked contributions introduced by the diagonalization of a CI matrix. This is achieved through proper dressings of the CI matrix. For a single state research the diagonal dressing is the most convenient. The dressing may be perturbative or self consistent. Self-consistence insures a strict additivity of the energy when localized MOs are used. The here-proposed size-consistent self-consistent truncated or selected CIs are calculated with a negligible extra cost through an efficient management of the EPV diagrams and the results of a direct version of this algorithm are presented. The derivation of a size-consistent Multireference MP2 method is also given.

**S.5**

# CLASSICAL POTENTIALS FOR METAL AND SEMICONDUCTOR CLUSTERS.

René Fournier, Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Ontario K1A 0R6

I studied small clusters of silicon, nickel and niobium with an accurate density functional method. The calculated binding energies were empirically scaled and used to make a database of (binding energy/geometry) points. The free parameters of empirical potential functions for clusters of these elements were then adjusted to fit the database. I will discuss the physical basis for the form of the potential functions chosen. The ability (or lack of it) of these potentials to reproduce more exact potential surfaces obtained with more costly methods and the prospects for their future use in dynamics studies of small and intermediate size clusters will be discussed.

# S.6

## *Quantum Dynamics of Reactions in Clusters and in Solids*

*R.B. Gerber, Physical Chemistry Dept., Hebrew University, Jerusalem 91904, Israel and Dept. of Chemistry, University of California, Irvine, CA 92717, USA*

A new method is presented for time-dependent quantum-mechanical simulations of processes in polyatomic systems, which is applicable also in cases where a substantial number of degrees of freedom is involved. As a first approximation, the method treats each particle by a wavepacket determined by a mean field. A perturbation theory is used to correct this approximation, and it can be made exact in principle.

Tests of the validity of the method are presented. Applications are given to molecular photodissociation in low temperature matrices and clusters, e.g. photolysis of HCl in solid Ar, and in the clusters of $Ar_N HCl$. The results show very interesting quantum effects on the photodissociation dynamics. Also, interesting effects are predicted on observable spectroscopic quantities, pertinent both to CW spectroscopy and to time-domain spectroscopy in the sub-picosecond regime.

**S.7** A PSEUDOSPECTRAL METHOD FOR SOLVING THE TIME-DEPENDENT SCHRODINGER EQUATION IN SPHERICAL COORDINATES.

Gregory C. Corey, Département de chimie, Université de Montréal, C.P. 6128, succursale A, Montréal, Québec, Canada H3C 3J7

The theory and application of a recently developed wave packet method for molecule-surface scattering problems is reviewed. The algorithm is based on a synthesis of grid techniques: In this method the wave function is propagated in the coordinate representation where the potential energy operator is diagonal. The dynamical coupling is contained in the off-diagonal matrix elements of the kinetic energy operators. A fast Fourier transform method is used for the Cartesian centre-of-mass coordinates (translational kinetic energy) and a generalized discrete variable representation is used for the angular coordinates (rotational kinetic energy). State-to-state transition probabilities can be obtained over a broad range of collision energies from a single wave packet propagation. The algorithm can be easily vectorized or parallelized and it makes minimal demands on central memory. The computational expense scales nearly linearly with respect to the number of grid points or basis functions. Numerical tests show that the algorithm is exact and one to two orders of magnitude more efficient than alternative quantum mechanical methods.

**S.8**

# MOLECULAR DYNAMICS STUDIES OF POLAR LIQUIDS.

P. G. Kusalik, Department of Chemistry, Dalhousie University, Halifax, N.S. B3H 4J3, CANADA.

Experimentally, the dielectric properties of a polar liquid are determined by measuring its response to applied electric fields. Computationally, they are usually determined for a model system from the fluctuations in, or the relaxation of, its polarization, depending upon whether the static value or the full frequency-dependent dielectric function is desired. This paper will first describe results for the structural and dynamic properties of a highly polar fluid obtained from equilibrium molecular dynamics simulations. These results will then be compared with the behaviour observed in simulations of this same system in which static or oscillating electric fields have been applied. The response of the system to the applied fields, both linear and non-linear, will be discussed.

# FERROELECTRIC LIQUID CRYSTAL AND SOLID PHASES FORMED BY STRONGLY INTERACTING DIPOLAR SPHERES

**S.9**

Dongqing Wei and G.N. Patey
Department of Chemistry
University of British Columbia
Vancouver, British Columbia
Canada V6T 1Z1

Molecular dynamics simulations are used to show that strongly interacting dipolar soft spheres can form ferroelectric nematic and columnar phases. This is the first demonstration that dipolar forces alone can create orientationally ordered liquid states. It is also the first time that the existence of ferroelectric nematic and columnar phases has been established for a model fluid. The model freezes to form a ferroelectric solid which is shown to have a Tetragonal I crystal structure. A density functional theory for dipolar systems which is qualitatively consistent with the computer simulation results will also be briefly discussed.

# S.10 THE EXCITED STATES OF LIQUIDS

Richard M. Stratt
Department of Chemistry, Brown University, Providence, RI 02912, USA

The traditional broad, featureless, spectroscopy which has long been characteristic of liquids is starting to give way to far more detailed, microscopically revealing, measurements — led principally by a variety of sub-picosecond techniques. Similar progress has been made in devising experiments capable of following the evolution of electronic structure in metallic and semiconducting fluids. What is being probed by both of these kinds of measurements might be called the basic linear excitation spectra of liquids — the normal modes and molecular orbitals of the liquid. Interestingly, theoretical approaches to these same excitation spectra which transcend such useful, but purely macroscopic concepts as diffusion and dielectric constants, are also beginning to appear. In this talk, some genuinely microscopic routes to these excitations are presented and the implications for spectroscopic observables discussed.

**S.11** STRESS RELAXATION IN POLYMER MELTS AND SOLUTIONS.

Marshall Fixman, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

The mechanical stress in polymer systems is usually ascribed to local backbone forces and orientations. According to this view the extremely slow relaxation of stress shown by melts and concentrated solutions implies that local backbone motion freezes out with increasing chain length. Brownian simulations of model systems indicate on the contrary that the stress is due predominantly to intermolecular forces, in particular to the total force that one chain exerts on another. In a stress calculation this force is weighted by the vector separation of chain centers. The simulation results and their implications will be discussed.

# S.12 STOPPING THEM DEAD; THE RELATIONSHIP OF PROTEIN FLEXIBILITY TO PROTEIN FUNCTION

Dagmar Ringe, Bjarne F. Rasmussen, Ann M. Stock, Gerlind Wallon, Peter Zavodsky*, and Gregory G. Petsko
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The role of protein flexibility in the stability of protein structure is not understood. There is widespread belief, but no evidence, that increased flexibility must lead to, or accompany, the unfolding of a protein. We h ave studied this question by examining the temperature-dependence of a protein structure, dynamics and activity.

When any of the dynamic properties of proteins are plotted as a function of temperature, biphasic behaviour is observed with a transition at around 220K. Below this temperature, atomic fluctuations are small and harmonic; above it they are anharmonic and larger, with a steep dependence on temperature. We call this the "glass" transition temperature, since below it the ensemble of protein molecules are unable to relax rapidly from one conformation to another. Molecular dynamics simulations at different temperatures show that dihedral angle changes and other collective modes of motion are "frozen out" below 220K. We have shown that mesophilic enzymes are unable to bind substrate below this temperature, demonstrating that flexibility is required for activity. Extreme thermophilic enzymes seem to have a highly elevated glass transition temperature, which correlates with their rigidity and lack of activity at normal temperatures.

# S.13 A Density Functional Theory Study of DHFR Enzyme Mechanism

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**Abstract:**

Previously, we have applied DFT to examine the shift in the spatial electron density of Dihydrofolate Reductase (DHFR) substrates and inhibitors upon binding to the enzyme. The results shed light on fundamental electronic effects due to the enzyme that may contribute to catalysis. In particular, the enzyme induces a long range polarization of the substrates that perturbs their electron density distribution in a specific and selective way in the vicinity of the bond that is reduced by the enzyme.

Currently, in order to further elucidate the DHFR mechanism, we use DFT to study small model systems to model putative reaction intermediates. We examined the formamide-formimidic acid reaction using DFT and the results are in agreement with high level Hartree-Fock calculations. We also looked at the keto-enol isomerization of dihydropteridine using DFT. Our studies, thus far, suggest that DFT results are in good agreement with MP2 calculations.

**S.14** A SIMPLE MODEL FOR SOLVENT EFFECTS IN ELECTRONIC SPECTROSCOPY.

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A review is made of models for including solvent effects in Quantum Chemical Calculations, and special attention is paid to continuum models, on isolated solute molecules, and on clusters of solute plus solvent molecules. This theory is then developed for the calculation of electronic absorbtion and emission.

Examples are given ranging from simple molecules in non-polar solvents to the more complex systems in hydrogen bonding situations in which specific solvation effects are as important as continuum effects.

There are several possible ways to view the absorption process, and these are discussed.

S.15

# THE DISCOVERY OF $C_{60}$ BUCKMINSTERFULLERENE AND THE IMPLICATIONS FOR CHEMISTRY ON EARTH AND IN SPACE

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Almost exactly five years after $C_{60}$ Buckminsterfullerene was discovered serendipitously during a series of graphite laser vaporization experiments designed to simulate the chemistry in red giant carbon stars, the molecule has been isolated in macroscopic amounts and its structure confirmed. This breakthrough has triggered an explosion of research into its chemical and physical properties and already the molecule has exhibited a wide range of novel phenomena which promise exciting applications. The discovery of the molecule and endeavours made to isolate it and confirm its soccerball structure provide shining examples of the importance of fundamental science for strategic or applied scientific advances. The events leading to the discovery can be traced back to radioastronomy measurements carried out in collaboration with NRC (Ottawa) astronomers in the mid-70s. The discovery itself may also have some fascinating further astrophysical implications.

# S.16 STRUCTURES AND STABILITIES OF SPHEROIDAL CARBON CLUSTERS.

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The recent macroscopic preparation of spheroidal carbon clusters (fullerenes) has stimulated a wide variety of experimental and theoretical studies on these novel systems. In this work, the structures and stabilities of fullerenes and fullerene derivatives have been investigated by means of semi-empirical and ab-initio quantum chemical calculations. Techniques which are particularly appropriate for the study of large molecules have been used throughout this work.

$C_{60}$ and $C_{70}$ have unique ground state isomeric structures where each pentagonal ring in the spheroid is separated from the remaining pentagons by at least one hexagon. All other higher energy isomers are characterized by the presence of one or more pairs of adjacent pentagonal rings. Larger fullerenes such as $C_{76}$, $C_{78}$, $C_{82}$, and $C_{84}$, have several structural isomers which have all the pentagons isolated from each other. Energy minimization techniques have been used to determine the geometries and relative energies of these isomers. The stabilities of the isomers are analyzed in terms of the local environments of the pentagons and hexagons in the structures. Energy parameters have been derived which can characterize such isomers in a predictive manner. Correlations between the structural and electronic properties are discussed.

Fullerene derivatives such as $C_{60}O$, $C_{70}O$, and $C_{60}CH_2$ have a $-O$ or $-CH_2$ group bridging a $C-C$ bond in the fullerene. The bonding in the derivatized fullerenes is compared to that in $C_{60}$ or $C_{70}$. In particular, the nature of the bond length across the bridging $C-C$ bond is discussed in detail. Vibrational spectra of derivatized fullerenes are predicted.

S.17

# The Quantum Phase and Coherent Dynamics of Hindered Methyl Groups

S. Clough

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Quantum methyl rotation in solids resembles the Aharonov-Bohm effect in that a rotating methyl wavepacket acquires a phase change in each circuit. The phase, which is associated with the angular velocity of the wavepacket, can be attributed to a vector potential which is an inertial memory of the torque which established the state of motion. The rotation is described by a U(1) gauge theory like electromagnetism but with a single space coordinate. Since hindered methyl orientation is only sampled in three potential wells, a wavepacket is approximately described by a vector consisting of three complex amplitudes, propagated by a 3x3 matrix which incorporates the inertial vector potential. Methyl dynamics is therefore similar to spin dynamics though based on SU(3) rather than SU(2). Wavepackets are excited and accelerated or decelerated by low symmetry ripples on the static threefold hindering potential and they transport three quasi-particles (anyons) round the three lattice sites. The dipole-dipole interaction of the quasi-particles couples the rotation and spin coordinates and mediates the transfer of magnetic and rotational angular momentum. The usual density matrix treatment of the spin dynamics can be extended to encompass the similar though more complex structure of methyl rotation. As with NMR coherent trajectories, as opposed to incoherent transitions, provide a rich conceptual framework for experiments.

Experimentally there are two challenges, (a) to explore the continuous transition from low temperature coherent quantum tunnelling rotation to high temperature quasi-classical thermally activated hopping, and (b) to gain control of the low temperature tunnelling spectrum by using the externally modulated dipole-dipole interaction to excite and manipulate rotating wavepackets at low temperatures. Cross relaxation experiments show that even at low temperatures the narrow tunnelling spectrum has a low frequency wing, reflecting the slowing down of decaying wavepackets. At higher temperatures this leads to the collapse of the spectrum to the single Lorentzian peak of the hopping theory. A simple stochastic model gives a good fit to the data. Experiments will also be described whose objective is to modify the rotational tunnel spectrum at 4K. A new two frequency NMR technique enables a pure rotational spectrum to be observed free from the interference of magnetic transitions. The usual narrow peak at the tunnel frequency can be substantially broadened in an asymmetric way. A new peak is also observed near zero frequency, and is attributed to the lifting of a Kramers degeneracy as induced rotation breaks time reversal symmetry.

# S.18

## THE GEOMETRICAL PHASE IN MOLECULAR SYSTEMS

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We review the fundamentals of the geometric phase, as it appears in molecular systems through the Born-Oppenheimer formulation. It is shown how the requirement of a single-valued electronic wave function leads to a vector potential term in the effective hamiltonian for the nuclei, and the analogy with the Aharonov-Bohm effect is emphasized. We also discuss some current results and problems, including: The role of the geometric phase in magnetic screening of nuclei by electrons; the effect of the nonabelian geometric phase in molecules with odd numbers of electrons; and the seemingly deep problem of the effect of the geometric phase on permutations of identical nuclei, particularly when the number of identical nuclei exceeds four.

# S.19 PHOTON-STIMULATED BOND-BREAKING ON NON-METALLIC SURFACES.

Richard F. Haglund, Jr.,
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Surface bond-breaking by photon beams from lasers and synchrotron light sources is a significant area of chemical physics, and an integral part of materials-processing and analytical technology. Adsorbate bond-breaking has been extensively studied, and is generally understood to be the result of such relatively straightforward processes as: direct Franck-Condon transitions to an anti-bonding potential energy surface; heating of the surface with subsequent breaking of the adsorbate bond; and internal excitation of the adsorbate or the surface to an anti-bonding state of the adsorbate-substrate system. Our understanding of photon-stimulated surface bond-breaking ("photon sputtering") on the other hand, is still rudimentary. Photon-stimulated desorption (PSD) of surface atoms and molecules is dominated by complex relaxation processes in which the initial electronic excitation is dissipated into electronic and non-radiative channels. PSD experiments on insulator and semiconductor surfaces show that ejection of surface atoms, molecules and molecular clusters can be initiated by various electronic mechanisms, including: defect creation and migration in the near-surface bulk; selective excitation of surface states; and creation of dense electron-hole plasmas. On non-metallic surfaces, photon-stimulated bond-breaking is characterized by four distinct phases: (1) creation of free electron-hole pairs; (2) relaxation of the electron-hole pairs into a lattice-localized state; (3) evolution to a pre-dissociative state; and (4) excitation to an anti-bonding potential energy surface. From this perspective, laser ablation and wholesale destruction of the surface is governed by cumulative changes in surface stoichiometry and structure due to PSD. Under certain circumstances, bond-orbital theory can be used to provide a microscopic interpretation of the experimental results.

# S.20 COHERENT EFFECTS IN EXCITATION WITH SHORT LASER PULSES.

C. Dateo, Eloret Institute, 3788 Fabian Way, Palo Alto, California, 94303; N. Blake, R. Bavli and H. Metiu, Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California, 93106.

I will discuss two topics. (1) The use of two phase locked ultrashort pulses to create coherent effects that allow us to modify predissociation rate and study predissociation dynamics. (2) The use of pulses to localize electrons in quantum wells and generate low frequency radiation and high harmonics.

# S.21

## TUNNELING TIME PROBABILITY DISTRIBUTION

Randall S. Dumont & Thomas L. Marchioro II, Department of Chemistry, McMaster University, Hamilton Ontario L8S 4M1

Localized wave packet tunneling through a one dimensional barrier is investigated with respect to tunneling time distribution. First, we demonstrate that, strictly speaking, a tunneling time probability distribution does not exist. Nevertheless, in terms of the time evolution of an initially localized wave packet, we construct a quantity - the "tunneled flux"- with properties of a tunneling time distribution. This quantity is investigated both numerically and analytically, via a semiclassical steepest descent calculation. The semiclassical calculation qualitatively reproduces numerical tunneled fluxes, while affording means of extracting insight into tunneled flux characteristics. The main features of this "tunneling time distribution" are summarized as follows: Tunneling is faster than simple classical motion from one side of the barrier to the other, even with no accounting for transit between the turning points. Effectively, the barrier acts as a filter for the large momentum component of the initial wave packet. The distribution itself is modeled as an "exponential skewed Lorentzian", with width governed primarily by the inital wave packet x-space uncertainty. The principal conclusion resulting from this study is the essential disparity between the time and energy domain pictures of wave packet tunneling.

S.22

# Density Functional Theory and Generalized Wannier Functions?

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In the self-consistent Kohn-Sham version of DFT one has to solve the single particle equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r) - \epsilon_j\right)\phi_j(r) = 0,$$

where, at each stage of the iteration, $v_{\text{eff}}(r)$ is given. For a many atom system ($N \gtrsim 10^2$ or $10^3$) the solution of these equations is generally prohibitive, unless there is an important symmetry, such as periodicity. Computing time generally behaves at least as $N^3$. For many-electron ground states, separated by a substantial gap from excited states, the eigenstates $\phi_j(r)$ can in principle be replaced by localized Generalized Wannier Functions (GWF), $a_{\ell m}(r)$, where $\ell$ is the site index, such that

$$n(r) = \sum |\phi_j(r)|^2 = \sum |a_{\ell m}(r)|^2.$$

$a_{\ell m}(r)$ depends only on $v_{\text{eff}}(r)$ near the site $r_\ell$. It is possible that for such systems direct computation of the GWF's, instead of the eigenfunctions $\phi_j(r)$, may lead to a computing time behaving as $N$ or $N^2$.

# S.23 RECENT ADVANCES IN DENSITY FUNCTIONAL THEORY

**Robert G. Parr,** University of North Carolina, Chapel Hill, North Carolina 27599, USA

Density functional theory promises to contribute much to the understanding of molecular structure and behavior. Several new discoveries are described which illustrate the power and promise of this theory. These include (a) enunciation and proof of the maximum hardness principle, (b) the suggestion and test of a conjointness property of exchange energy and kinetic energy, (c) the suggestion and test of a new local exchange-correlation functional, and (d) the solution of the problem of how to go from an electron density to a wavefunction.

**S.24**

# DENSITY-FUNCTIONAL MOLECULAR ENERGETICS

Axel D. Becke, Department of Chemistry, Queen's University,
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A variety of density-functional theories have been assessed by comparing atomization energies, ionization potentials, electron affinities, and proton affinities of a large number of atomic and molecular systems (Pople's "G1" data base) with experimental data. We find reasonably good overall agreement with experiment, of the order of a few kcal/mol, with functionals containing density-gradient corrections to the local spin-density approximation. Also, a new combined Hartree-Fock/electron gas theory will be reported.

# S.25

## SOLVING NONEQUILIBRIUM PROBLEMS IN STATISTICAL MECHANICS USING EQUILIBRIUM METHODS

George Stell and James Given, Department of Chemistry, State University of New York, Stony Brook, N.Y. 11794-3400, U.S.A.

We have developed several complementary techniques in treating a class of nonequilibrium statistical mechanics problems that involve systems that can be regarded as differentially quenched. Such problems include random sequential adsorption, the behavior of spin glasses and the properties of equilibrated fluid particles contained in quenched random media. One of the ingredients of our treatment is an extension of a method devised by Boltzmann, which yields Kirkwood-Salsburg type equations. A second is based upon generalized Potts models that reduce to the systems of interest in certain special limits. A third is an Ornstein-Zernike integral-equation formalism used in conjunction with the Potts models. Representative results for the examples mentioned above are given. They include exact series expansions of correlation function and their approximate analytic assessment via integral equation.

S.26

# STATISTICAL MECHANICAL THEORY OF INELASTIC GRANULAR SYSTEMS

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A statistical mechanical theory of inelastic granular systems is formulated using projection operator techniques. The theory is based on the fact that each granular particle has many interacting internal degrees of freedom which, except for very short times, remain at equilibrium at a very low temperature. These degrees of freedom provide a sink for the translational relative momenta and lead to clustering of the particles.

S.27

# Structure and Dynamics in Colloidal Suspensions

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ABSTRACT

Dilute suspensions of highly charged colloidal particles can exhibit strong static and dynamic many-body correlations that at first glance are reminiscent of small molecule fluids. I will discuss theories of the equilibrium inter-colloid correlation functions, counter-ion double-layer profiles, and conformational equilibrium in systems where the colloid particles are formed from block copolymer aggregates containing a coblock that is both charged and flexible.

In addition to static properties, a theory of shear-induced melting of colloidal crystals, that proposes a different mechanism for the crystal lattice instability from what is believed to operate in molecular crystals, will be presented.

S.28

# ASPECTS OF MODERATELY DENSE GAS KINETIC THEORY

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A review of past theories used to estimate the density corrections to the transport coefficients will be given. Three different mechanisms contribute to these corrections. These are: 1) three-body collisions, 2) bound state effects, and 3) nonlocalized binary collisions. It is the latter mechanism that has occupied most of the theoretical and computational effort for the calculation of the density corrections. Crucial to that calculation for realistic intermolecular potentials has been whether a pair of particles are to be treated as free, bound or metastably bound, a problem vigorously tackled by Rainwater and colleagues at N.I.S.T. Recent work by Laloe and coworkers, and by the author, on the density corrections to the quantum Boltzmann equation has raised questions as to whether the earlier work is the proper starting point for these calculations. Specifically the question is whether pair particle correlations need to be explicitly taken into account in the initial formulation of the problem. The present state of this development is discussed.

S.29

# KINETIC THEORY OF MATTER TRANSPORT IN CONCENTRATED ALLOYS

A.R. Allnatt, Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7.

Irradiation of a metal alloy produces an inhomogeneous distribution of vacancy and dumb-bell lattice defects which create matter transport by making jumps between nearest-neighbour sites. Modelling the resultant concentration changes requires a knowledge of the dependence on the alloy composition and on the defect concentrations and jump frequencies of the phenomenological coefficients $L_{ij}$ appearing in the standard form of the flux equations in non-equilibrium thermodynamics. Approximate analytical calculations of the $L_{ij}$ which start from exact linear response formulae are described here and compared with Monte Carlo simulations based on the same formulae. The hierarchy of coupled kinetic equations for the lower order distribution functions for atoms and defects are decoupled by neglect of third and higher order fluctuations; useful results are obtained for simple models where the various jump frequencies do not span more than an order of magnitude in size. When the third order terms are approximated in a self-consistent manner very accurate results are obtained which even show the percolation effects characteristic of extreme jump frequency ratios.

# S.30

RYDBERG SPECTROSCOPY OF $H_2O$

[+]M.S. Child , [*]Ch. Jungen, [+]R.D. Gilbert and [≠]D.M. Hirst
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The Rydberg dynamics of polyatomic molecules will be presented as a topical challenge to the theoretician involving breakdown of the Born-Oppenheimer approximation, coupled with possibly competing predissociation and autoionization mechanisms. A preliminary multichannel quantum defect analysis of recent high resolution spectra of $H_2O$ will be presented and compared with other spectroscopic data, Implications for the general dynamics will be reviewed and reinforced by ab initio studies.

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S.31

# ISOLATED EFFECTIVE HAMILTONIANS FOR TWO NEARLY DEGENERATE MODES COUPLED BY CORIOLIS AND CENTRIFUGAL TERMS

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Highly excited rotational states of nearby vibrational energy levels are strongly coupled by matrix elements of the Coriolis terms in the ro-vibrational Hamiltonian and for these energy levels the usual uncoupled zeroth-order model becomes very poor. It is important to look for better zeroth-order pictures (which should include some of the ro-vibrational coupling) because they will facilitate assignment and calculation of energy levels. If zeroth-order energies of two vibrational states are close to each other it is not possible, using the standard perturbation theory approach, to decouple them so as to obtain effective rotational Hamiltonians for the quasi-degenerate states. We derive uncoupled effective Hamiltonians for nearly degenerate states using a Bogoliubov-Tyablikov (BT) transformation. By changing the orientation of the molecule-fixed axis at equilibrium and using a BT transformation we have obtained isolated effective Hamiltonians for molecules with two vibrational degrees of freedom coupled by Coriolis terms with two (or three) angular momentum components. Some off-block matrix elements due to centrifugal coupling are dealt with exactly, others are treated by perturbation theory.

# S.32

## RELATIVISTIC ELECTRONIC STRUCTURE CALCULATIONS IN THE FRAMEWORK OF THE DOUGLAS-KROLL TRANSFORMATION

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The Douglas-Kroll Transformation [1] provides an approach to relativistic electronic structure calculations that makes it possible to separate off explicitly the degrees of freedom of particles charge-conjugated to the electrons interacting with the external field of the nuclei. The resulting operator may be split into a part that does not explicitly depend on spin and incorporates relativistic kinematics, and a spin-orbit operator that, in contrast to the Breit-Pauli operator (as derived e.g. from a Foldy-Wouthuysen Transformation), is bounded below and may consequently be used in a variational procedure without running into the problem of a variational collapse [2]. Thus, it is possible to define consistent CI, ACFP, MBPT, Green's functions methods etc. that include relativistic kinematics.

We discuss the impact of relativistic corrections of the two-electron integrals on valence shell properties [3], leading to the conclusion that a relativistic correction of the one-electron integrals only is usually sufficient, resulting in a very economical way of implementation of relativistic kinematics. We report recent applications of the method, including calculations based on the spin-orbit operator that derives from the Douglas-Kroll Transformation [4].

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S.33

# DENSITY FUNCTIONAL THEORY AS A PRACTICAL TOOL FOR THE STUDY OF ELEMENTARY REACTION STEPS IN HOMOGENEOUS CATALYSIS

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Approximate density functional theory (DFT) has over the past decade emerged as a tangible and versatile computational method in the field of transition metal chemistry. It is shown that DFT affords molecular structures and bond dissociation energies of high quality for organometallic systems. The method is further able to trace energy profiles in elementary reaction steps of importance for homogenous catalysis. Results will be presented from calculations on C-H activation of early and late transition metals, olefin polymerization by early transition metals as well as olefin and acetylene metathesis.

S.34

# THE HARMONIC FREQUENCIES OF BENZENE

Nicholas C. Handy, Paul E. Maslen, Roger D. Amos, Jamie S. Andrews,
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**Abstract**

We report calculations for the harmonic frequencies of $C_6H_6$ and $C_6D_6$. Our most sophisticated quantum chemistry values are obtained with the MP2 method and a TZ2P+f basis set (288 basis functions), which are the largest such calculations reported on benzene to date. Using the SCF density, we also calculate the frequencies using the exchange and correlation expressions of Density Functional Theory. We compare our calculated harmonic frequencies with those deduced from experiment by Ozkabak et al. The Density Functional frequencies appear to be more reliable predictions than the MP2 frequencies and they are obtained at significantly less cost.

S.35

# PSEUDOSPECTRAL METHODS FOR ELECTRONIC STRUCTURE CALCULATIONS.

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We describe new pseudospectral algorithms for *ab initio* electronic structure computations. Major modifications of our previous algorithms have been implemented, including extensive use of analytical two and three center integrals which are integrated with numerical grid algorithms in an efficient fashion. In this talk we will focus on results for calculation of point charges of large molecules, where factors of 5-10 in CPU time have been gained as compared to our previous methods. A discussion of gradient and electron correlation methods will also be presented.

**S.36**

Wave functions with linear $r_{12}$-dependent terms.

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By inclusion of terms that depend linearly on the interelectronic coordinates, into a many-electron wave function it is possible to satisfy the correlation cusp condition and at the same time to speed up the convergence of a CI type expansion considerably. Results of atomic and molecular calculations are presented in the framework of Moller-Plesset-perturbation theory (MP2-R12, MP3-R12, MP4-R12) and of coupled-cluster theory (CC-SD-R12, CC-SDT-R12). The R12-variants yield a significant gain in accuracy without much additional cost in computer time. To make these calculations feasible, some approximations are necessary. However these become exact in the limit of a complete basis and they guarantee faster convergence to the complete-basis results than in conventional calculations.

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 1. Abbate, Sergio | "Transition from Normal Modes to Local Modes in A-B-A' Molecules" |
| 2. Abou-Rachid, Hakima | "Time-Resolved Adiabatic Wavepacket Photodissociation Dynamics of $H_2^+$ in Intense and Short Laser Pulses" |
| 3. Adams, William H. | "Summable and Nonsummable Perturbation Expansions of Intermolecular Interaction Energies" |
| 4. Aguda, Baltazar, D. | "Reversible and Irreversible Formulation of Unimolecular Reactions" |
| 5. Alberts, Ian L. | "The Molecular Structure of 1-(Dihaloboryl) Pentaborane Derivatives" |
| 6. Alencastro, Ricardo | "Semi-Empirical Studies on Some Phototoxic Drugs" |
| 7. Arteca, Gustavo A. | "Two-Dimensional Maps of Global Shape Features in Macromolecules" |
| 8. Aubanel, Eric E. | "Intense-Field Photodissociation of Hydrogen Molecule Ion" |
| 9. Beck, Thomas L. | "Molecular Dynamics of Tethered Alkanes: Melting in the RPLC System" |
| 10. Beck, Thomas L. | "Quantum Theory of Solubilities via Path Integral Generalization of Widom's Test Particle Theory" |
| 11. Bendazzoli, Gian Luigi | "A Vector and Parallel Full Configuration Interaction Algorithm" |
| 12. Bikker, J.A. | "A Comparison of AM1, MNDO, and PM3 Molecular Orbital Methods for Conformational Analysis of Experimental Anticonvulsants" |
| 13. Biemolt, W. | "A Potential Energy Surface from LDA Calculations for the Interaction of CO with Rhodium Surfaces" |
| 14. Bramley, Matthew J. | "A Study of Vibrational Resonance in Acetylene, Using a New Refined 6-Dimensional Forcefield and an Exact Variational Method" |
| 15. Branchadell, Vicenç | "Ab Initio Study of Complexes between $TiCl_4$ and Carbonyl Compounds" |
| 16. Bundgen, Peter | "Calculation of Atomic and Molecular G-Values" |
| 17. Burghgraef, H. | "NI Insertion in the CH Bond of Methane. Calculation of Electronic Structure and Dynamics" |
| 18. Burleigh, Darin C. | "An Investigation of Rotation-Vibration Mixing Using Random Matrices" |
| 19. Bussery, Béatrice | "The $O_2$-$O_2$ Dimer : Van der Waals Interaction Potential" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 20. Campolieti, Giuseppe | "Semiclassical Quantum Propagation with Applications to Molecular Photodissociation" |
| 21. Casida, Mark | "Dipole Polarizabilities of Alkali Metal Clusters: Basis Set Effects in All-Electron, Local-Density Calculations" |
| 22. Castro, Eduardo | "Further Remarks Concerning the Hartree-Fock Energies of N-Electron Atomic Systems" |
| 23. Castro, Miguel | "Electronic Structure of Small Iron Clusters, $Fe_1$ to $Fe_5$. A DFT Approach" |
| 24. Chaudhury, Rajat | "Equivalent Local Excitation Descriptions of Laser-Driven Multichannel Molecular Systems: A General Non-Perturbative Coupled-Wavepacket Propagation Method" |
| 25. Chen, Han | "Ab Initio Pseudopotential Density Functional Study of Small Molecules" |
| 26. Chermette, Henry | "LCGTO-DF Study of the $CuCl_2$ Molecule: Vibrational and Electronic Property Analysis" |
| 27. Custodio, Rogério | "Proton Affinities: Correlations with Atomic Charges and Electronegativities" |
| 28. Daniel, Chantal | "Photodissociation Dynamics of Organometallic Complexes: Dynamical Calculations Based on CASSCF/CCI Potential Energy Surfaces for $HCo(CO)_4$" |
| 29. Darvesh, Katherine V. | "Ab Initio Studies of Bonding within the Heteroindene Framework" |
| 30. Dateo, Christopher E. | "Vibrational Predissociation of Methylnitrite Using Phase-Locked Ultrashort Laser Pulses" |
| 31. Davis, William M. | "Dithia- and Diselena- Diazolyl Radicals and Dimers: Modelling Main Group Inorganic Ring Systems" |
| 32. de Brouckère, G. | "CI Calculations on the $^1\Sigma^+$, $A^1\pi$ and $^1\Delta$ States of PN" |
| 33. Dickson, Ross M. | "Molecular Geometries by a Numerical Density-Functional Technique" |
| 34. Edgecombe, Kenneth E. | "Application of Topological Analysis to Metal Cluster Charge Densities: Lithium and Sodium" |
| 35. Edgecombe, Kenneth E. | "Substituent Effects on Spatially Integrated Atomic Charges in Compounds of Pharmacologic Interest: Carboxylated Pyridine Derivatives" |
| 36. Esquivel, Rodolfo O. | "Lower and Upper Bounds for the Curvature of $\rho(r)$" |
| 37. Esquivel, Rodolfo O. | "On the Convexity of the Atomic Electron Density" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 38. Evangelisti, Stefano | "An Effective Hamiltonian for Cyclic Polyenes" |
| 39. Flock, Michaela | "Ab-Initio SCF Investigation of Glycolic Acid and 3-Hydroxy-Propionic Acid" |
| 40. Fournier, René | "Density Functional Study of 1:1 Complexes of Nickel with Small Molecules" |
| 41. Froese, Robert D. J. | "Potential Energy Surface Features of $CS_3$, $COS_2$, and $CO_3$" |
| 42. Gallego-Planas, Nuria | "Bonding Between Host and Guest in 18-Crown-6 Clusters |
| 43. Goddard, John D. | "Computational Studies of Main Group Inorganic Compounds: Thia-, Selena-, and Tellura- Pentalenes" |
| 44. Goodwin, L. | "Density Functional Study of Niobium Microclusters" |
| 45. Graham, Richard | "Accurate Electronic Potential Energy Hypersurfaces of Methyl Mercaptan Computed with the *ab-initio* Effective Valence Shell Hamiltonian Method ($H^V$)" |
| 46. Graham, Richard | "Application of a Quantum Based Molecular Dynamics: The Effects of Intermolecular Interactions on the Structure and Properties of Perfluorododecane" |
| 47. Grein, Fritz | "SCF and CI Studies on Thiocarbonyl and Corresponding Sulfur-Silicon Molecules" |
| 48. Guan, Jingang | "Comparison of Local-Density and Hartree-Fock Calculations of Molecular Polarizabilities and Hyperpolarizabilities" |
| 49. Hachey, Michel | "The $^1A_1$ Electronic Excited States of Formaldehyde, and Comparison to its Thio Analogue. An AB Initio MRD-CI Study" |
| 50. Halet, Jean-François | "Electronic Structure of Octahedral and Cubic Inorganic Clusters" |
| 51. Herman, Michael F. | "The Effect of Many Chain Interactions on Lateral Motion in Polymer Melts" |
| 52. Hiyama, Miyabi | "Theoretical Assignment of the Correlation Bands Observed in the Near-Threshold Photoelectron Spectra of $N_2$,CO and HCl" |
| 53. Hoffmeyer, Ruth E. | "Fast Electron and X-ray Scattering from $B_2H_6$" |
| 54. Hrusak, Jan | "The Evaluation of the Bond Dissociation Energy of the $FEF^+$ Ion by ab initio ECP-MCSCF Calculations and FTICR-Experiments" |
| 55. Hrusak, Jan | "The Reaction Pathway of the Unimolecular HF Loss from Protonated Fluorobenzene. A Combined Theoretical and Experimental Study" |
| 56. Ikegami, Tsutomu | "Theoretical Photoabsorption Spectra of Argon Cluster Ions" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 57. Ishida, Kazuhiro | "General Formula Evaluation of Electron-Repulsion-Integrals and Their Derivatives. II." |
| 58. Jiang, Xue-Pei | "Quantum Rate of Reaction Over a Dissipative Barrier" |
| 59. Kay, Kenneth G. | "Quantum Mechanics as a Form of Classical Mechanics" |
| 60. Knowles, Peter J. | "A State-Selective Multi-Reference Coupled-Cluster Formalism" |
| 61. Kobayashi, Hisayoshi | "Electronic Structure and Reactivity of Metals and Metal-Oxides by Density Functional Method" |
| 62. Komasa, Jacek | "Accurate Properties of $H_2$ and $D_2$ from Explicitly Correlated Wave Functions" |
| 63. Krauss, Morris | "Theoretical Assignment of RSS Anion and Indole Free Radical Spectra" |
| 64. Krishnan, Mangala | "Theory of Pulses and Spin Dynamics in Nuclear Quadrupole Resonance Spectroscopy" |
| 65. Krishnan, Mangala S. | "Quantum Canonical Transformation to Eliminate Coriolis and Centrifugal Terms Coupling Nearly Degenerate Vibrational States" |
| 66. Laakkonen, Liisa | "Cis-Trans Ratios in Substituted Prolines in Solution" |
| 67. Ladanyi, Branka M. | "Electron Transfer in Methanol: The Role of Hydrogen-Bonding" |
| 68. Le Quéré, Frédéric | "Vibrational Predissociation of $Ne_2Cl_2$ and $He_2CL_2$: A Quantum, Time Dependent Approach" |
| 69. Lee, Timothy J. | "Development of a New Open-Shell Coupled-Cluster Method" |
| 70. Lemoine, Didier | "Discrete Variable Representation in Wave Packet Scattering from Surfaces" |
| 71. Lo, Alan | "Long Time Dynamics of Regular and Chaotic Scattering Billiard Systems" |
| 72. Luo, Xincai | "Regioselectivity of Nucleophilic Additions to Cyclopentadienyliron Complexes of Subtituted Benzenes" |
| 73. Lushington, Gerry | "Molecular G-Tensor Calculations" |
| 74. Maclagan, Robert G.A.R. | "Gas Phase Ion Mobilities of $Li^+$ in $N_2$ and CO" |
| 75. Makri, Nancy | "Improved Feynman Propagators on a Grid and Non-Adiabatic Corrections within the Path Integral Framework" |
| 76. Malkin, Vladimir | "Calculations of NMR Shielding Constants Using a Combination of Pseudo-Potential and IGLO Methods" |
| 77. Mandy, Margot E. | "Monte Carlo Simulations of Dipolar Fluids" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 78. Manoli, Soheil | "Gauge Considerations in the Calculation of Laser-Induced Resonances in the Photodissociation of $H_2^+$ in an Adiabatic Electronic-Field Representation" |
| 79. Maroulis, George | "Hyperpolarizability of Some 10- and 18-Electron Systems" |
| 80. Marquez, Antonio M. | "Theoretical Study of the Thermal and Photolytical Decomposition of Gold-Alkyl Complexes" |
| 81. Marsh, Craig M. B. | "An Ab Initio Study of Four-Coordinate Organoaluminum-Nitrogen Ring Compounds" |
| 82. Matsuzawa, Hidenori | "Geometrical and Electronic Structures of Aluminum-Sodium Bimetallic Clusters" |
| 83. Mawhinney, Robert C. | "Some Trends in the Stabilized Nitrogen and Phosphorus Ylides" |
| 84. McNichols, André | "Variational Method for the Vibrational Energy Levels of Polyatomic Molecules" |
| 85. Michelson, Jeremy | "Does Electronegativity Have a Future?" |
| 86. Miyoshi, Eisaku | "The Electronic Structure of $Li^+_nF^-_m$ Cluster in Ionic Cage" |
| 87. Morrison, Robert C. | "Approximate Two-Matrices Which Satisfy the CUSP Condition" |
| 88. Murray, Christopher W. | "Quadrature Schemes for Integrals in Density Functional Theory" |
| 89. Nagaoka, Masataka | "A Theoretical Study on Chemical Reactions in Solution" |
| 90. Nakamura, Kensuke | "Theoretical Studies of Dynamic Processes in Host-Guest Complexes" |
| 91. Nanbu, Shinkoh | "Theoretical Study of the Photoabsorption and Photodissociation Dynamics of FCO" |
| 92. Negri, Fabrizia | "Vibrational Force Fields and Structure of the Anions of $C_{60}$" |
| 93. Nilar, S. H. | "Comparison of Some Kinetic Energy Density Functionals" |
| 94. Ochterski, Joseph W. | "Improved Basis Sets for *Ab Initio* Calculations" |
| 95. Ortiz, J. V. | "Electron Propagator Interpretations of Bonding and Spectra" |
| 96. Osamura, Yoshihiro | "Molecular Orbital Study on the Formation Reactions of the Interstellar Molecules Containing Carbons" |
| 97. Osman, Roman | "Molecular Dynamics Simulations of DNA with Primary Damage" |
| 98. Ouhlal, Abdelhak | "Model Systems for the Cr Interface with Polyimide Surfaces" |
| 99. Pang, Li | "Atom-Atom Potential Analysis of the Complexing Characteristics of Cyclodextrins (Host) with Benzene and p-Dihalobenzenes (Guest)" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 100. Papai, Imre | "Density Functional Study of $Ni(C_2H_4)_n$ Complexes" |
| 101. Petersson, George A. | "Vinylidene and the Hammond Postulate" |
| 102. Poulin, Martin | "Determination of the Potential Surface for Diatomics Using the Discrete Variable Representation" |
| 103. Proynov, E. I. | "On the Screened-Coulomb Exchange Energy in the Kohn-Sham LSD Scheme" |
| 104. Quelch, Geoffrey E. | "Phototdissociation of $C1_2O_2$: Implications for Ozone Depletion" |
| 105. Rice, Julia E. | "Solvent Effects on Hyperpolarizabilities" |
| 106. Røeggen, Inge | "The Potential Energy Surface of the $(H_2)_2$ Dimer" |
| 107. Roy, Pierre-Nicholas | "Wave Packet Propagation in a Discrete Variable Representation Using the Split Operator Method for Molecule-Surface Scattering Calculations" |
| 108. Rozas, Isabel | "Aromaticity Studies Using the Shape of the Electron Density" |
| 109. Ruiz-Lopez, Manuel F. | "Asymmetric Diels-Alder Synthesis: Solvent Effects and Catalytical Mechanisms" |
| 110. Russo, Nino | "LCGTO-NLSD Singlet-Triplet Gap of Substituted Carbenes" |
| 111. Sakai, Shogo | "Theoretical Study on the Chemical Reaction Mechanisms of Main Metal Atoms with Molecules" |
| 112. Sannigrahi, M. | "Theoretical Study of the Reaction $S_2^+ + S_2^+ \rightleftharpoons S_4^{2+}$ and Various Reactions with $SNS^+$" |
| 113. Schuch, Dieter | "On a Momentum-Space Version of Dissipative Wave Mechanics" |
| 114. Scuseria, Gustavo | "Comparison of Coupled Cluster Results with a Hybrid of Hartree Fock and Density Functional Theory" |
| 115. Sepp, Wolf-Dieter | "Accurate Calculation of Relativistic Effects on Molecular Properties of AU2" |
| 116. Shea, J. | "Average of Configuration Ionization Energies, Electronegativities and Hardnesses" |
| 117. Sibert III, Edwin L. | "Investigating Highly Excited Vibrational States of Acetylene" |
| 118. Smedarchina, Zorka | "Multimode Approach to Hydrogen Tunneling" |
| 119. Smedarchina, Zorka | "Combining Dynamics with Transition State Theory: Proton Transfer in a Model Opiate-Receptor System" |
| 120. Snider, Neil | "Broadening Factors in Unimolecular Rate Theory" |

| POSTER PRESENTERS | POSTER TITLES |
|---|---|
| 121. Snyder, Lawrence | "Mindo/3 Cyclic-Cluster Calculations of the Relative Stability of Siloxene Structures" |
| 122. Sodupe, Mariona | "A Theoretical Study of the Bonding in Transition-Metal-Legand Cations" |
| 123. Sosa, Carlos | "Electronic Structure of 1,3 Dipolar Cycloadditions Using the Local and Nonlocal Spin Density" |
| 124. Soscun, Humberto | "The Relationship Between the Homo Energies and the Experimental pKa's in Bicyclic Azines: An ab initio Study" |
| 125. Stave, Mark S. | "Parallel Full-Potential Linearized Augmented-Plane-Wave Calculations of Silica Sodalite" |
| 126. Suba, Slaven | "Molecular Problem: QFT Approach" |
| 127. Summerfield, John | "Large-*D* Limit for Correlation Methods in Atoms" |
| 128. Tasi, Ming-Sung | "Angular Dependence of Hydrogen Bond Strength in Several Complexes Involving Hydrogen Fluoride" |
| 129. Tasi, Ming-Sung | "Induced Rotation Barrier in Benzocyclobutanechromium Tricarbonyl" |
| 130. Temme, Francis P. | "Fundemental Wigner Unit Superoperators Defining $\varphi$ - Yamanouchi $\hat{O}(i_1\text{-}i_n)kqv>>$ Bases as an Aspect of $D_i$-Boson Pattern Algebra over $\{H_v\}$ Carrier Space Demonstrating Co-operative Effects over Liouville Space for MQ-NMR Clusters" |
| 131. Thakkar, Ajit J. | "Chain Length Dependence of Static Longitudinal Polarizabilities and Hyperpolarizabilities in Linear Polyynes" |
| 132. Topaler, Maria | "Path Integral Calculations with Quasi-Adiabatic Propagators: Exact Quantum Dynamics of IVR in Model Hydrocarbon Chains" |
| 133. Trindle, Carl | "Hydrogen Bonding and Proton Transfer in Polycyclic Triols and Triamines" |
| 134. Uno, Bunji | "Proton Accessibility and Electronic States of $\rho$-Quinone Dianions" |
| 135. Ushio, Jiro | "LCGTO-LDF Calculation of Transition States of Chemical Reaction: The Reaction of Pentacoordinate Allylsilicate with Aldehyde" |
| 136. Wang, Yeu | "Wavepacket Propagation Technique for Calculating Bound-State Energy Levels of Polyatomic Molecules: ArHCl" |
| 137. Wei, Hua | "The Discrete Variable Representation of a Triatomic Hamiltonian in Bond Length - Bond Angle Coordinates" |
| 138. Weinberg, Noham | "A Microscopic Theory of High-Pressure Processes: How Does High Pressure Affect a Potential Energy Surface?" |

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|---|---|
| 139. Weinberg, Noham | "A Novel and Highly Efficient Algorithm for the Theoretical Conformation Analysis of Cyclic Structures" |
| 140. Williams, C. I. | "The Decomposition of Bi- and Tri- Cyclic Tetrazepinones: A Molecular Mechanics/Semi-Empirical M.O." |
| 141. Yang, Weitao | "A Divide-and-Conquer Approach to Large Molecular and Solid-State Systems" |
| 142. Yu, Hengtai | "Application of the Finite Element Method to Solve the Time Dependent Hartree-Fock Equation in an Intense Laser Field" |

1

## TRANSITION FROM NORMAL MODES TO LOCAL MODES IN A-B-A' MOLECULES

Sergio Abbate, Giovanna Longhi, Danila Ghisletti, Antonio Giorgilli, Laure Lespade

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A system of two harmonically coupled identical Morse oscillators, A-B-A, was recently shown to exhibit a third kind of modes, besides normal and local modes, that were called transition modes(Longhi et al., Theor. Chim. Acta, 82(1992)321). They are characterized by phase locking, like normal modes, but not by complete energy interchange, like local modes.They were found classically at intermediate values of the total energy.

In this paper we investigate the case of the A-B-A' molecules by the same methods employed in the paper mentioned above, namely Poincaré Surfaces of Section, plots of the bonds energies and lengths vs. time and use of classical perturbation theory on a local mode basis. Besides, Lissajous trajectories of the system and perturbative calculations based on normal forms will be presented. A fourth type of motion is found, showing energy interchange between bond A-B and A-B' and no phase locking. A critical discussion of the meaning of normal modes and local modes will be presented.

2

## TIME-RESOLVED ADIABATIC WAVEPACKET PHOTODISSOCIATION DYNAMICS OF $H_2^+$ IN INTENSE AND SHORT LASER PULSES.

H. Abou-Rachid and T.T. Nguyen Dang
Département de chimie, Université Laval, Québec, GlK 7P4, QUÉBEC

The adiabatic coupled wavepacket propagation algorithm developed by Nguyen-Dang and Abou-Rachid (J. Chem. Phys. **96**, 256 (1992)) is applied to the study of the photodissociation of $H_2^+$ excited by a short and intense 329.7 nm laser pulse.

The dynamics of the process is systematically studied as a function of the parameters of the laser pulse (pulse length, pulse shape and peak intensity) within the electric-field (EF) gauge and the radiation-field (RF) gauge.

3

## SUMMABLE AND NONSUMMABLE PERTURBATION EXPANSIONS OF INTERMOLECULAR INTERACTION ENERGIES

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Rutgers University
New Brunswick, New Jersey 08903, U.S.A.

We have used the variational method to compare two perturbation expansions of intermolecular interaction energies with regard to convergence and summability. One is the Polarization expansion, which is derived by applying the Rayleigh-Schrödinger method to the Hamiltonian $H^\circ + \lambda V$, where $\lambda$ is the expansion parameter, $H^\circ$ is the sum of atomic/molecular Hamiltonians, and $V$ is the difference between the system Hamiltonian and $H^\circ$. The other expansion is derived from $H^\circ + \lambda A V$, where $A$ is the antisymmetric projector. This Hamiltonian was first explicitly considered by Hirschfelder. We contrast the behavior of these expansions for $He_2$ and LiH by considering the results of variational calculations of energy eigenvalues $E(\lambda)$ as functions of complex $\lambda$. In particular we have approximately determined the location of the branch points nearest to $\lambda = 0$ for the lowest $E(\lambda)$ of both Hamiltonians. We argue that the Polarization expansion is neither convergent nor summable for systems containing atoms with atomic numbers greater than 2, whereas the second expansion is likely to be convergent and can be summed.

4

## REVERSIBLE AND IRREVERSIBLE FORMULATION OF UNIMOLECULAR REACTIONS

Baltazar D. Aguda[1] and Huw O. Pritchard[2]

[1]Chemistry Dept., Lakehead University, Thunder Bay, Ontario P7B 5E1
[2]Chemistry Dept., York University, Downsview, Ontario M3J 1P3

A comparison is made between the reversible and irreversible formulations for a series of model isomerization reactions, and the conditions under which the differences are important are demonstrated.

5

# THE MOLECULAR STRUCTURE OF 1-(DIHALOBORYL) PENTABORANE DERIVATIVES

Ian L. Alberts

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ SCOTLAND.

*Ab initio* quantum mechanical methods have been used to determine the molecular structure of thermally stable, gas phase 1-(dihaloboryl)pentaborane derivatives, 1-($X_2B$)$B_5H_8$ (X=F, Cl). Specifically, SCF and MP2 levels of theory were employed in conjunction with two basis sets of double-zeta (DZ) and double-zeta plus polarization (DZP) quality. The results confirm a recent electron diffraction study of the dichloroboryl-derivative, undertaken at Edinburgh, that such molecules consist of a pentaborane $B_5H_8$ cage substituted at the apical boron atom by the dihaloboryl group ($BX_2$). The potential energy surface for the low frequency $BX_2$ twisting mode about the B-B (apex-exo) bond will be discussed in detail.

6

## SEMI-EMPIRICAL STUDIES ON SOME PHOTOTOXIC DRUGS

Joaquim Delphino da Motta Neto** and Ricardo Bicca de Alencastro* - **Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville, FL, 32611, USA. *Physical Organic Chemistry Group, Instituto de Química da UFRJ, Cidade Universitária, CT, lab. A622, Rio de Janeiro, RJ, 21910, Brasil.

2-[2-(4-chlorophenyl)benzoxazol-5-yl]propionic acid (benoxaprofen), 4-Hydroxy-2-methyl-N-(2-pyridinyl)-2H-1,2-benzothiazine-3-carboxamide-1,1-dioxide (piroxicam), and 2-chloro-N,N-dimethyl-10H-phenothiazine-10-propanamine (chlorpromazine) are non-steroidal anti-inflammatory drugs (NSAID) that have been widely used for therapy of arthritis. These drugs, however, present undesirable side effects. They tend to accumulate at the skin where they sensitize production of singlet oxygen, which in turn is supposed to be the active agent for its phototoxicity. In this work we have examined the photophysics of these compounds using quantum chemical calculations. Geometries were fully optimized with the AM1 method of Dewar. Absorption spectra calculated with the INDO/S method as parametrized by Zerner and coworkers. The calculated spectra are in fair agreement with experimental results. [CNPq - Brazil].

7

## TWO-DIMENSIONAL MAPS OF GLOBAL SHAPE FEAUTURES IN MACROMOLECULES.

Gustavo A. Arteca

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A methodology to analyze and characterize small- and large-scale shape and structural features in chain macromolecules is presented. The procedure involves the construction of the *spherical shape maps* of a molecular skeleton. These maps provide a full description of the overcrossing pattern of a molecule and give a characterization of its global folding features. In this communication, it is shown how the essential shape information contained in these maps can be presented by means of two-dimensional maps. The two variables used in these maps are the distance between crossovers of the molecular backbone when it is seen along a given direction of space and the radius of a spherical viewing window defined across the viewing direction. The function mapped in terms of these two variables is the area of the spherical shape maps. A number of examples of supersecondary structural features are analyzed and compared by this methodology. Other applications, such as the monitoring of unfolding in a-helices, are also discussed.

8

## INTENSE-FIELD PHOTODISSOCIATION OF HYDROGEN MOLECULE ION

Eric E. Aubanel and André D. Bandrauk

Département de Chimie, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Que., J1K 2R1

Intense-field photodissociation of $H_2^+$ at wavelength $\lambda$ = 212.8 nm is calculated using a split-operator time dependent method. The stabilizing effect of resonances arising from laser-induced avoided crossings shows up as minima in the dissociation probability as a function of intensity. The position and line width of the resonances, obtained from time-independent calculations, are compared to the kinetic energy distributions of products. The efect of rotational excitation on stabilization is examined.

9

MOLECULAR DYNAMICS OF TETHERED ALKANES: MELTING IN THE RPLC SYSTEM, Thomas L. Beck and S. J. Klatte, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

We present molecular dynamics simulations of the structure and dynamics of alkanes ($C_8$ and $C_{18}$) chemically tethered at one end to a silica surface. The system is modelled after the stationary phase of Reversed Phase Liquid Chromatography (RPLC). The temperature dependence of a high density phase is examined. Various equilibrium and dynamical quantities are computed, including z density profiles, radial distribution functions, torsional angle populations, mean square displacements, and power spectra. A gradual transition from a low temperature glassy state to a high temperature liquid-like state is observed. Our findings are consistent with available calorimetric, IR, NMR, and neutron scattering experimental data. The longer chains exhibit an appreciable collapse on the surface due to attractive interactions. The general effect of attractive interactions on structure and dynamics is probed and implications for retention mechanisms and mean-field approaches are discussed. Results concerning hydrodynamic behavior of a single Brownian solute particle at several z locations are presented.

10

QUANTUM THEORY OF SOLUBILITIES VIA PATH INTEGRAL GENERALIZATION OF WIDOM'S TEST PARTICLE THEORY, Thomas L. Beck, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

An extension of Widom's test particle theory for chemical potentials to the quantum domain is presented. A Fourier path integral formula is derived for the absolute chemical potential of a quantum solute in a quantum solvent (neglecting exchange). The resulting expression is formally equivalent to insertion of a ring polymer into a ring polymer solution. The classical and mixed classical-quantum cases are naturally recovered in the path integral theory. The exact formula is taken as a starting point to derive useful expressions for changes in system mass and potential. Numerical results are presented concerning relative solubilities of hydrogen isotopes in model harmonic and anharmonic solids. Good agreement between basis set and quantum Monte Carlo calculations is obtained. Discussion will be given of relations of this work to recently developed approaches for the computation of chemical potentials in dense polymer systems.

**11**

## A VECTOR AND PARALLEL FULL CONFIGURATION INTERACTION ALGORITHM

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A Full Configuration Interaction (FCI) algorithm is presented. It is an integral driven formalism which is based on the explicit construction of tables which realize the correspondence between the FCI vector X and the vector HX, H being the Hamiltonian matrix of the system. In this way no decomposition of the identity is needed, and in the simplest implementation only the two vectors X and H need to be kept on disk. Tests have been done on the cyclic polyene $C_{18}H_{18}$ in the Pariser-Parr-Pople Approximation, where the size of the FCI vector can be reduced to about 73 million components. Running on a CRAY Y-MP with 4 cpus and 32 Mw of core memory, we obtained an elapsed cpu time per iteration of about 300 seconds and a total elapsed time of 1000 seconds, which correspond to about 4 and 14 seconds per million determinants respectively.

**12**

## A COMPARISON OF AM1, MNDO, AND PM3 MOLECULAR ORBITAL METHODS FOR CONFORMATIONAL ANALYSIS OF EXPERIMENTAL ANTICONVULSANTS

J.A. Bikker (*) and D.F. Weaver(*+), Departments of Chemistry(*) and Medicine(+), Queen's University, Kingston, Ontario. K7L 3N6

Computer aided rational design of anticonvulsant drugs requires reliable methods of molecular conformational analysis. Semi-empirical molecular orbital techniques are now commonly used to evaluate structural and electronic properties of novel drug molecules. However, because of the parameterization inherent in these methods, the conformational energy hypersurface may not be correctly represented. A comparison of calculated results to either experimental data or high level ab initio calculations is therefore required to ensure method applicability and validity.

Recent evidence suggests that the dihydropyridine calcium channel blockers (DHPs) have promising anticonvulsant properties. The utility of AM1, MNDO, and PM3 as methods of conformational analysis of these molecules has been critically evaluated. The assessment comprised i) root mean square fitting of the optimized geometries of 14 DHPs to their crystal structures, ii) comparison of the heights and locations of rotational energy barriers, and iii) examination of specific functional groups. AM1 proved to be best suited to the conformational modelling of DHPs. PM3 performed substantially better than MNDO, yet not as well as AM1.

13

## A POTENTIAL ENERGY SURFACE FROM LDA CALCULATIONS FOR THE INTERACTION OF CO WITH RHODIUM SURFACES.

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We studied the CO/Rh interaction using density functional calculations in the Local Density Approximation. Starting with only one Rh atom we calculated the adsorption energy of CO as accurate as possible, including relativistic and non-local corrections, and performing spin-unrestricted calculations. From these calculations we developed a potential energy surface (PES) in spherical expansion form for Rh-CO. The expansion coefficients were fitted on Lennard-Jones or Morse functions. With this PES we were able to reproduce, and predict for new geometries, the adsorption energy within 10 kJ/mol. Attempts to obtain atom-atom potentials, which only depend on the Rh-C and Rh-O distances, were less satisfactory.

Next we calculated the interaction of CO with small Rh clusters (2-4 atoms) to test and improve the PES . The dominant multi-particle modification was due to the influence of CO on the Rh-Rh interaction. Finally this PES was tested by comparison of predictions made using the PES with calculations on larger Rh systems (7-13 atoms), and with experimental results, like site preference and adsorption energy, for infinite surfaces.

14

## A STUDY OF VIBRATIONAL RESONANCE IN ACETYLENE, USING A NEW REFINED 6-DIMENSIONAL FORCEFIELD AND AN EXACT VARATIONAL METHOD.

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It is now possible to calculate the 9-dimensional rovibrational wavefunctions of sequentially-bonded 4-atom molecules variationally without dynamical approximation and with basis sets well completed in all degrees of freedom [M. J. Bramley and N. C. Handy, *J. Chem. Phys.*, submitted]. For HCCH, the simplest case, it is straightforward to obtain many hundreds of rovibrational (J=0,1,2) levels converged to better than 1 $cm^{-1}$. This has allowed the refinement [M. J. Bramley, S. Carter, N. C. Handy, and I. M. Mills, *J. Mol. Spectr.*, submitted] of the well-known forcefield of Strey and Mills [*J. Mol. Spectr.* **59**, 103 (1976)] against experimental term values up to 3 C-H stretch quanta. Here we use the refined forcefield to obtain new insight into the resonances associated with the accidental degeneracies ($v_2+v_4+v_5,v_3$) and ($v_2+2v_5,v_1$) in the principal isotopomer. In particular: (i) calculated energies and wavefunctions shed new light on the assignment of the experimentally-detected states in the $2v_3$ and $3v_3$ polyads; and (ii) it is found that vibrational Coriolis (kinetic energy) terms, rather than quartic anharmonicities in the potential, are the primary cause of the resonant interactions. The other $^1HCC^1H$ isotopomers are also considered.

15

## AB INITIO STUDY OF COMPLEXES BETWEEN $TiCl_4$ AND CARBONYL COMPOUNDS

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The activation of carbonyl compounds by transition metal complexes plays an important role in many catalytic processes. The knowledge of the structure and properties of such complexes is necessary to understand the mechanism of activation and to obtain information useful for the design of efficient catalysts.

In this communication we present an ab initio study of complexes of carbonyl compounds of the type RR'CO with titanium tetrachloride. The formation of 1:1, 2:1 and dimeric complexes has been discussed. The interaction between the donor and acceptor moieties have been analyzed and the factors governing the preference for each kind complexation have been discussed.

16

## CALCULATION OF ATOMIC AND MOLECULAR G-VALUES

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The interaction of the net electronic spin of open shell atomic and molecular systems with an applied magnetic field is described by g-values that show small but clear deviations from the free electron g-value. The contributions of some operators that are held responsible for the observed shifts are computed in first order perturbation theory using correlated MRD-CI wavefunctions. Results will be presented for selected atoms and diatomic molecules.

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NI INSERTION IN THE CH BOND OF METHANE. CALCULATION OF ELECTRONIC STRUCTURE AND DYNAMICS

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The calculations were performed with a first principles packkage developped by the Theoretical Chemistry Group of Baerens et al. at the Free University of Amsterdam.
The insertion of Ni in the CH bond of methane is investigated by calculating a four dimensional grid in the NiC, NiH, and CH distances and the tilt of the methyl group.
A non-linear molecular state with a binding energy of about -5 kJ/mol and a transition state with a barrier of 60 kJ/mol, both with respect to gas fase Ni and CH4, were obtained.
The obtained potential hypersurfaces were used for dynamical calculations, in particular the calculation of rotational constants and vibrational frequencies in the transition state, the molecular state, and for the gas fase molecules.
According to transition state theory, rate constants were calculated in terms of partition functions together with sticking coefficients.
The dynamical calculations showed that the reaction coordinate consists mainly of the CH stretch.

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# AN INVESTIGATION OF ROTATION-VIBRATION MIXING USING RANDOM MATRICES

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In a previous study of the dynamics of $H_2CO$, we found that rotation-vibration mixing increases rapidly for total energy $E \geq 6000$ cm$^{-1}$, and $J \geq 4$, making assignment of specific states in this regime difficult or impossible. This is in qualitative agreement with the experimental results of Dai *et. al.* [ J. Chem. Phys. **82**, 1688 (1985)], who found significant spectral congestion in their stimulated emission pumping spectra in a similar energy regime. The present work focuses on statistical properties of the dynamics of $H_2CO$ and $D_2CO$, borrowing from some of the random matrix methods first pioneered by Dyson and Wigner for analyzing complex systems. The vibrational mixing between the normal modes is shown to have a strong influence on the breakdown of the separation between rotation and vibration. We find this mixing to be accurately reproduced by a model Hamiltonian with only a few parameters. This talk will discuss the important components of the model in detail. Our model also quantitatively reproduces the average rotation-vibrational mixing.

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## THE $O_2$-$O_2$ DIMER : VAN DER WAALS INTERACTION POTENTIAL

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Intermolecular potential surfaces of $(O_2)_2$ are presented for $O_2(^3\Sigma_g^-) + O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g) + O_2(^1\Delta_g)$ dissociations. The potential interaction energy is calculated following the Rayleigh-Schrödinger perturbation theory : the first order exchange and electrostatic terms are obtained using the ab initio treatment of Wormer *et al.* Based on the second quantification, the $32e^-$ problem is reduced to a $4e^-$ one and the non orthogonal basis problem is resolved.
Second-order polarization contributions are included using the Cambi *et al* treatment for generalized correlations in terms of polarizability, valid for interactions due to Van der Waals forces. Comparison with experimental data for the second virial coefficients and the cohesion energy of the crystal are presented as a check of the potential surfaces for the ground state dimer.

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## SEMICLASSICAL QUANTUM PROPAGATION WITH APPLICATIONS TO MOLECULAR PHOTODISSOCIATION

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**Abstract**

A semiclassical theory of quantum propagation which combines phase space integration and real-valued classical mechanics to compute the generally time-dependent quantum propagator in any representation is presented. The formalism has an asymptotic equivalence with uniform WKB theory but circumvents the trajectory root search problem. Based on this formalism, and the use of a classical interaction picture, an integral formula for polyatomic dissociation is derived whereby calculation of photofragmentation cross sections proceeds via phase space integration of dissociative classical trajectories only. Numerical application of integration techniques such as conditioned Monte Carlo methods render the theory amenable for multidimensional systems. Evaluation of photofragmentation t-matrix elements for the IBr diatom are shown to reproduce the exact numerical quantum results to high accuracy.

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# DIPOLE POLARIZABILITIES OF ALKALI METAL CLUSTERS: BASIS SET EFFECTS IN ALL-ELECTRON, LOCAL-DENSITY CALCULATIONS.

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Dipole polarizabilities are important for understanding both nonresonant (e.g. refraction and depolarization of scattered light) and resonant (e.g. Raman intensities) optical phenomena. Both types of phenomena provide useful probes of the "interior" and "surface" structures of clusters. Dipole polarizabilities can also be measured by beam deflection in molecular beam studies of metal clusters, giving additional clues about cluster structure.

A full interpretation of the structural information inherent in these experimental measurements cannot be made without the help of theoretical calculations. Yet there are still relatively few *ab initio* calculations of the polarizabilities of metal clusters. The calculations which have been reported generally use an effective core potential which is independent of the external electric field, hence neglecting core polarization effects. We present all-electron calculations, including geometry optimizations, on small sodium clusters, and consider the effect on polarizabilities, of different methods for choosing field-induced polarization functions.

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# FURTHER REMARKS CONCERNING THE HARTREE-FOCK ENERGIES OF N-ELECTRON ATOMIC SYSTEMS

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The 1/Z perturbation expansion provides a very useful framework for the study of the changes of some atomic expectation values along an isoelectronic series. Since the expansion coefficients are, in general, not known, it is not possible to make a detailed study of atomic systems. On spite of this drawback, several attempts have been made to surmount these difficulties to get energy formulas with accuracy enough to be taken as the reliable basis for the subsequent considerations. A way to obtain precise energy formulae is to resort to recurrence relations. The constancy of second differences in electronic energies has attracted considerable interest and led to a parameter-free energy formula provided the total energies of two adjacent members in a given isoelectronic series are known. The purpose of this communication is to re-examine the recurrence relationships based on the constancy of second differences in electronic energies in order to generalize their applications and to increase the exactitude of the resulting formulae.

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ELECTRONIC STRUCTURE OF SMALL IRON CLUSTERS, $Fe_1$ to $Fe_5$. A DFT APPROACH.

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The geometries, electronic and magnetic structures, as well as the binding energies (for both neutral and ionic species) and ionization potentials of small bare iron clusters are studied by means of a linear combination of Gaussian type orbitals-local/nonlocal spin density (DFT) method. At nonlocal level of approach and correcting by non-sphericity effects on the iron atom, the calculated binding energies are in reasonable agreement and follows the trends of the corresponding experimental results. The calculated ionization potentials, both in the vertical and adiabatic approaches, are close to the experimental values and to those obtained by means of highly correlated ab initio techniques. The magnetic energy gains enhances d-bonding and favours ferromagnetic three dimensional geometries, with maximum bond formation, and high magnetic moments per atom, greater than the bulk magnetization. In these clusters, the equilibrium bond lengths are shorter than the nearest neighbor distance in the bulk.

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**EQUIVALENT LOCAL EXCITATION DESCRIPTIONS OF LASER-DRIVEN MULTICHANNEL MOLECULAR SYSTEMS: A GENERAL NON-PERTURBATIVE COUPLED-WAVEPACKET PROPAGATION METHOD.**

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A general transformation of the time-dependent Schrödinger equation for a typical laser-driven multichannel molecular system is derived and permits the interpretation of molecular dynamics in the presence of a short and intense laser pulse in terms of coherent excitations in the equivalent local multi-level electronic systems. The transformation generalizes a previous construction by including R-dependent channel couplings. The resulting coupled-wavepacket propagation algorithm is third-order in time and denotes a generalization of the split-operator formula to incorporate arbitrary time-dependence of the couplings.

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AB INITIO PSEUDOPOTENTIAL DENSITY FUNCTIONAL STUDY OF SMALL MOLECULES

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We have implemented the ab initio norm-conserving pseudopotential method inside the program package DGauss. We have calculated bond-lengths, vibrational frequencies, and binding energies using the LCGO method. Good agreements with all electron calculations and experimental data were obtained.

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## LCGTO-DF STUDY of the $CuCl_2$ MOLECULE: VIBRATIONAL and ELECTRONIC PROPERTY ANALYSIS .

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The potential gas-laser $CuCl_2$ molecule is investigated with a density functional theory method developped by Saint-Amant and Salahub [1], based on a LCAO method with gaussian orbital basis sets and geometry optimization options. Some properties of the ground state and of some excited states are calculated, at two levels of theory for the exchange and correlation potential, namely the local spin density (LSD) approximation, with the Vosko, Wilk, Nusair functional [2], and a non-local approximation, with the GGA (Generalized Gradient Approximation) of Perdew [3].

These properties (equilibrium distances, total energies, electronic structure with Mulliken analysis, harmonic vibrational spectra) are compared with experimental data and other previous computational results. In every case, the ground state is found to be $^3\Pi$, the coordination is linear (as for the charge-transfer excited states), with Cu-Cl distances varying from 203 pm (LSD) to 210 pm (GGA) (experimental value: 203.5 pm); the symmetric and asymmetric vibration modes (346 and 493 $cm^{-1}$, LSD) are in good agreement with the recent experimental data (360 and 496 $cm^{-1}$).

References:

[1]: A. St-Amant and D.R. Salahub, Chem. Phys. Lett. **169**, 387 (1990).

[2]: S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200, (1980).

[3]: J.P. Perdew, Phys. Rev. **B33**, 8822 (1986).

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## PROTON AFFINITIES:CORRELATIONS WITH ATOMIC CHARGES AND ELECTRONEGATIVITIES.

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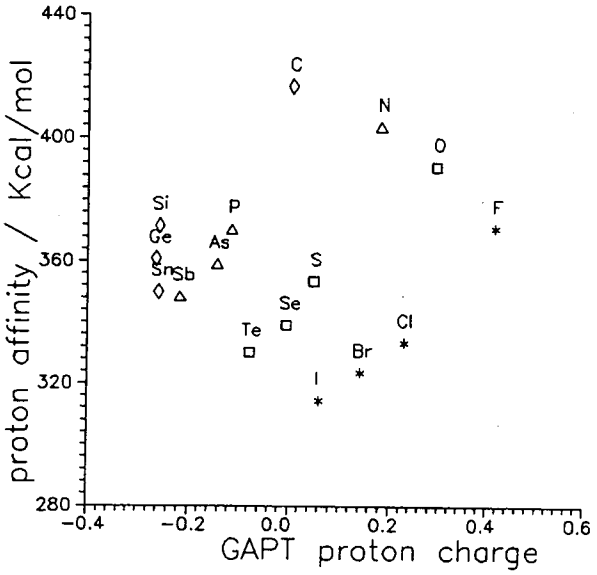


Proton affinities for $AH_{n-1}^-$ hydrides containing elements from the secondto the fifth periods and groups 14 to 17 were calculated at the MP2 level employing core potential and split valence plus polarization basis sets. Proton charges were calculated using the generalized atomic polar tensor method (GAPT). A linear correlation was found between the proton affinities and the GAPT proton chargesof the protonated molecules for the group 15 to 17 elements.Calculationsof the Iczkowski-Margrave group electronegativities revealed a similar relationship to proton affinities.

(Acknowledgments: NSERC and FAPESP)

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## PHOTODISSOCIATION DYNAMICS OF ORGANOMETALLIC COMPLEXES: DYNAMICAL CALCULATIONS BASED ON CASSCF/CCI POTENTIAL ENERGY SURFACES FOR $HCo(CO)_4$

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The dynamics of the photodissociation of $HCo(CO)_4$ have been studied through dynamical calculations based on ab initio potential energy surfaces for the metal-hydrogen bond homolysis and for the dissociation of the axial carbonyl ligand. The dynamics of the two competitive primary pathways are simulated by propagation of representative wavepackets on the two lowest triplet states by means of the Fast Fourier Transform (FFT) technique. Upon UV irradiation the molecule has the choice between two different channels: i) dissociation of a carbonyl ligand from the $^3E\ 3d_\delta \rightarrow \sigma^*$ state and ii) homolysis of the metal- hydrogen bond either from the $^3A_1\ \sigma \rightarrow \sigma^*$ state, or from the $^3E\ 3d_\delta \rightarrow \sigma^*$ state. The presence of an energy barrier on the $^3E$ potential energy surface along the metal-hydrogen bond elongation is responsible for an asynchronous decay mechanism yielding ultrafast ( 20fs) formation of $H + Co(CO)_4$, followed by much slower (200fs) decarbonylation.

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## AB INITIO STUDIES OF BONDING WITHIN THE HETEROINDENE FRAMEWORK

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The dithiaphospholium cation and related compounds have been examined using Gaussian 90, with the aim of obtaining optimised geometries, orbital energies and bond orders. Such compounds are of interest in that they are candidates for second row p-pi bonding. Results for these compounds will be presented, with particular emphasis on the extent of pi bonding observed. Hydrogenation thermochemical cycles have been used to estimate the strength of the phosphorus-sulfur pi bond in dithiaphospholium.

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## VIBRATIONAL PREDISSOCIATION OF METHYLNITRITE USING PHASE-LOCKED ULTRASHORT LASER PULSES

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The behaviour of a molecule interacting with two phase-locked ultrashort laser pulses is studied using a two-dimensional model for the ground and excited states of $CH_3ONO$. The results are obtained using time-dependent quantum wave packet theory to accurately solve the Schrodinger equation. We demonstrate how the total product populations and relative NO vibrational populations can be changed by varying the delay time between the pulses.

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# DITHIA- AND DISELENA- DIAZOLYL RADICALS AND DIMERS: MODELLING MAIN GROUP INORGANIC RING SYSTEMS.

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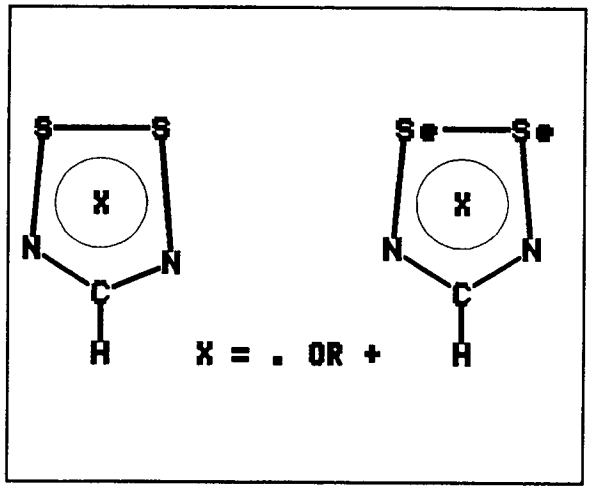


The ground state molecular electronic structures of some inorganic diazolyl ring systems were examined using three *ab initio* computational techniques: local density functional, all-electron Hartree-Fock and effective core potential Hartree-Fock. Electron correlation effects were included via Moller-Plesset perturbation theory. Predictions are made for the cations, radicals and radical dimers of these systems. Full geometry optimizations and vibrational frequency analyses were carried out.

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# CI CALCULATIONS ON THE $^1\Sigma^+$, $A^1\Pi$ AND $^1\Delta$ STATES OF PN

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A series of single and double multireference configuration interaction (MRSD-CI) calculations(x) using Gaussian triple-zeta quality basis set, on the $^1\Sigma^+$, $A^1\Pi$, $^1\Delta$ states of PN have been performed in order to accurately determine the respective potential energy surfaces in the vicinity of their minimas. The $^1\Delta$ is unknown experimentally. With the help of these curves, a wide assortment of spectroscopic data have been calculated and the overall agreement with experiment is good. Among the calculated observables are pure rotational transitions, spontaneous radiative lifetimes involving two distinct and a single spectroscopic state(s) and Franck-Condon factors.

(x) including energy corrections for higher order excitations,

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## MOLECULAR GEOMETRIES BY A NUMERICAL DENSITY-FUNCTIONAL TECHNIQUE

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Equilibrium geometries have been calculated for a range of small molecules using the NUMOL no-basis-set density-functional program. This program uses pointwise (grid) representations for functions instead of more traditional basis-set representations. Forces on the nuclei are calculated using the Hellmann-Feynman theorem with a correction only for frozen core electrons. These forces are not only inexpensive and accurate, but converge more quickly with respect to grid than does the energy surface itself. The geometry optimization method used, therefore, is a conventional quasi-Newton algorithm which takes greater account of the forces than of the energy. The geometries calculated are compared with those calculated by other density-functional and conventional methods, and with experiment.

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## APPLICATION OF TOPOLOGICAL ANALYSIS TO METAL CLUSTER CHARGE DENSITIES: LITHIUM AND SODIUM

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The theory of molecular structure, developed by Bader *et al*, is based on the topological properties of the charge density of isolated molecules. In this study we report on the application of this method of analysis to lithium and sodium metal clusters. The appearance/disappearance behavior of nonnuclear attractors is discussed. The extension of this method of analysis to the solid state is reported and results for *bcc* lithium and sodium discussed.

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## SUBSTITUENT EFFECTS ON SPATIALLY INTEGRATED ATOMIC CHARGES IN COMPOUNDS OF PHARMACOLOGIC INTEREST: CARBOXYLATED PYRIDINE DERIVATIVES

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The use of structure-activity relationships is widespread in the search for compounds with biological activity. In this study, we calculate spatially integrated atomic charges using the theory of molecular structure as proposed by Bader *et al* for substituted carboxylated pyridines such as quinolinic acid, known to be a neuro-active compound. Small compounds such as carboxylated pyridines are thus are logical candidates for investigations into the suitability of using such charges as indicators of biological activity. The charges are derived from Hartree-Fock wavefunctions at the 3-21G level.

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## LOWER AND UPPER BOUNDS FOR THE CURVATURE OF $\rho(r)$

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The curvature of the spherically averaged ground-state electron density of atoms is the subject of this study. We show that strict pseudo-convexity is the general structural property of the density of atoms which embodies all the structural features that have been empirically attributed to $\rho(r)$. Rigorous upper and lower bounds for the second derivative of $\rho(r)$ at the nucleus and at large distances are obtained. Within the bare Coulomb-field model atom, it is shown that the total electron density of the lowest set of closed shells is convex. Rigorous cusp conditions for the second derivative of the model atom density are derived and shown to be obeyed by model atoms with closed-shells. Upper bounds that constrain the curvature of $\rho(r)$ at the nucleus of open-shell model atoms are also developed. The Kohn-Sham formalism is used to obtain a general expression for the second derivative of $\rho(r)$ at the nucleus.

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# ON THE CONVEXITY OF THE ATOMIC ELECTRON DENSITY

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The curvature of the atomic electron density $\rho(r)$ is numerically studied. Within the model of the bare Coulomb-field (BCF), it is numerically shown that the total electron density of an arbitary number of closed shells is convex. The model atom density with electrons filling orbitals consistent with Stoner's restriction, shows that for model atoms with $Z \leq 92$, non-convexity is a periodic property appearing around closed-shell ground-state hydrogenic configurations. It is numerically found by using near HF accuracy wave functions that $\rho(r)$ is non-convex for atoms with Z=3-6, 16-32 and 45-92. The non-convexity region is shown to be closely related to the topological features of the Laplacian of $\rho(r)$. Highly correlated densities of configuration-interaction (CI)- and Hylleraas-type quality for atoms of the Li- and Be-isoelectronic sequences show that the non-convex region of $\rho(r)$ is not largely affected by the inclusion of electronic correlation as compared with HF-type densities.

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# AN EFFECTIVE HAMILTONIAN FOR CYCLIC POLYENES

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*Abstract: An Effective Hamiltonian for cyclic polyenes $C_nH_n$ in the Pariser-Parr-Pople approximation is constructed through the explicit definition of its 1-electron and 2-electron integrals. Its Self Consistent Field energy is proportional to the SCF energy of the original system, provided this is a closed shell. Test calculations have been performed on systems with 2, 6, 10, 14, 18 carbon atoms, and on the infinite polyacetilene case ($10^6$ carbon atoms). They show that the use of such an Effective Hamiltonian in Configuration Interaction calculations gives a good approximation of the correlation energy of the original system.*

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### AB-INITIO SCF INVESTIGATION OF GLYCOLIC ACID AND 3-HYDROXY PROPIONIC ACID

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The potential energy surfaces of glycolic acid ($HO–CH_2–COOH$) and 3-hydroxypropionic aci ($HO–CH_2–CH_2–COOH$) have been investigated by means of ab-initio SCF (RHF) calculations us ing the 4-31G basis set.

7 symmetry unique local minima were found in the potential energy surface (PES) of glycolic aci and 36 symmetry unique local minima have been located in the PES of 3-hydroxy propionic acic The characteristics of both potential energy surfaces will be summarized and selected minima will b discussed in detail with special emphasis on the intramolecular interactions between the functiona groups. The character of these interactions and their influence on the molecular properties, as th stabilization of the individual conformations, will be examined and compared with the correspondin amino acids.

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### DENSITY FUNCTIONAL STUDY OF 1:1 COMPLEXES OF NICKEL WITH SMALL MOLECULES.

René Fournier, Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Ontario K1A 0R6

The geometry and vibrational frequencies of the 1:1 complexes of nickel with carbon monoxide, water, methanol, acetylene, formaldehyde and propene have been determined by linear combination of gaussian-type orbitals-density functional calculations. The calculated binding energies in the singlet and triplet states will be compared to those deduced from recently measured association reaction rates (C.E. Brown, S. A. Mitchell and P. A. Hackett, Chem. Phys. Lett., in press). There is evidence, both from the kinetic data and from theory, that in some cases the association reaction takes place on more than one potential surface.

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## POTENTIAL ENERGY SURFACE FEATURES OF $CS_3$, $COS_2$, AND $CO_3$.

Robert D.J. Froese and John D. Goddard, Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph Guelph, Ontario, CANADA N1G 2W1.

The potential energy surfaces of three related molecular systems: $CS_3$, $COS_2$, and $CO_3$ were studied using *ab initio* Hartree-Fock and Møller-Plesset perturbation theory. Low energy reaction paths, isolable intermediates, and product vibrational and rotational excitation are predicted.

The reaction of excited state sulfur atoms with carbon disulfide is predicted to proceed through low lying singlet intermediate isomers with an intersystem crossing near the exit channel transition state allowing for the formation of the ground state diatomic products, $CS(^1\Sigma^+)$ and $S_2(^3\Sigma_g^-)$. The reaction of ground state oxygen atoms ($O(^3P)$) with carbon disulfide probably proceeds directly on the triplet potential energy surface forming *cis* and *trans* SCSO isomers which can dissociate into the major products observed experimentally, $CS(^1\Sigma^+)$ and $SO(^3\Sigma^-)$. The reaction of excited state oxygen atoms ($O(^1D)$) with carbon dioxide leads to low lying singlet $CO_3$ isomers, which, following an intersystem crossing, lead to the major products, $O(^3P) + CO_2(^1\Sigma_g^+)$.

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## BONDING BETWEEN HOST AND GUEST IN 18-CROWN-6 CLUSTERS

N. Gallego-Planas, L. Pang, C. Williams and M.A. Whitehead

The electronic structures of 18-crown-6 as an isolated molecule and as a host to differen metal ions were studied with the Quasi-Relativistic Self-Interaction-Corrected-Multiple-Scattering-Xα method. The degree of oxygen-metal bonding between the crown-ether and the two guest molecules, $HgCl_2$ and $CdCl_2$, was investigated. QR-Xα-SIC energy eigenvalues were compared to semi-empirical MO calculations.

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**COMPUTATIONAL STUDIES OF MAIN GROUP INORGANIC COMPOUNDS: THIA-,SELENA-,AND TELLURA- PENTALENES.**

**Rogerio Custodio, William M. Davis, and John D. Goddard**
**Guelph-Waterloo Centre for Graduate Work in Chemistry**
**Department of Chemistry and Biochemistry**
**University of Guelph**
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**Ab initio effective core potential and all electron SCF and Moller-Plesset computations have been carried out on a series of inorganic pentalene structures containing carbon and nitrogen along with sulfur, selenium, and tellurium. Both the ground and lowest excited electronic states have been examined. Emphasis has been placed on the UHF descriptions of formally closed shell species and on testing for Hartree-Fock instabilities and symmetry breakings. Trends in structures and stabilities upon the replacement of S by Se or Te are examined with reference to the dimerization and oligomerization of the monomers.**

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A DENSITY FUNCTIONAL STUDY OF NIOBIUM MICROCLUSTERS

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We have studied the energetically favourable isomers of niobium clusters containing up to seven atoms. These are the largest transition metal clusters so far studied using a *state of the art* density functional approach and geometry optimisation techniques. The experimental trends for the binding energy, the bond dissociation energy and the ionisation energy are well reproduced. The most favourable isomers are seen to maximise the atomic coordination, and hence the number of bonds. The detailed structures are presented.

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## ACCURATE ELECTRONIC POTENTIAL ENERGY HYPERSURFACES OF METHYL MERCAPTAN COMPUTED WITH THE *AB-INITIO* EFFECTIVE VALENCE SHELL HAMILTONIAN METHOD ($H^v$)

Jonathan Stevens, Richard L. Graham*, Karl F. Freed, and Laurie J. Butler, The James Franck Institute, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637

The size consistent Effective Valence Shell Hamiltonian method, which uses quasidegenrate multi-reference Reyleigh-Schrodiner perturbation theory, is employed to compute accurate *ab initio* adiabatic potential energy surfaces of methyl mercaptan along the C-S and S-H coordinates. Experimentally it has been observed that the electronic excitation of this molecule in the second absorption band leads to preferential cleavage of the stronger S-H bond over the weaker S-C bond. These calculations are used to explain these experimental observations. Also, this is the first time the $H^v$ method is used to study a molecule for which relatively little is known about its electronic structure. A computationally efficient systematic approach for studying such molecules is developed.

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## APPLICATION OF A QUANTUM BASED MOLECULAR DYNAMICS: THE EFFECTS OF INTERMOLECULAR INTERACTIONS ON THE STRUCTURE AND PROPERTIES OF PERFLUORODODECANE

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Molecular dynamics employing empirical force fields has had considerable success in elucidating molecular properties. However such force fields are inherently limited in that they do not include electronic degrees of freedom. Therefore, with such methods it is difficult to describe a variety of properties, such as the making and breaking of chemical bonds, polarization effects, and optical phenomena. We have combined classical molecular dynamics and semi-empirical electronic structure methods and performed molecular dynamics simulations. The first application of our method is to the study of Perfluorododecane which is a model for Teflon (TM), perfluoropolyethylene. Teflon is known to have twisted chains. *Ab initio* molecular orbital calculations have shown that single perfluoroalkane chains are twisted. We study how intermolecular interactions affect the twisting of the perfluoroalkane chains and how its molecular properties change.

Teflon is trademarked.

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SCF AND CI STUDIES ON THIOCARBONYL AND CORRESPONDING SULFUR-SILICON MOLECULES

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CI studies were performed on valence and Rydberg states of $H_2CS$, $C\ell_2CS$, HCS and $C\ell CS$, to obtain vertical excitation energies and potential energy curves. Of particular interest were the geometry and location of the $^1(\pi,\pi^*)$ and $^1(n^2,\pi^{*2})$ states of $H_2CS$.[1] The radicals HCS and $C\ell CS$ are of interest in the dissociation of $H_2CS$ and $C\ell_2CS$, respectively.

For $H_2SiS$, the geometry of the ground state was optimized, and the vertical excitation spectrum investigated.[2] Dipole moments and ionization potentials were also obtained.

The isomerisation and dissociation of HSiS, $HSiS^+$ and $HSiS^-$ was studied by MP2 geometry optimizations. In addition, ionization potentials and electron affinities of HSiS will be reported.[3]

1. M. Hachey, F. Grein and R. Steer, The $^1A_1$ electronic excited states of $H_2CS$: an ab initio MRD CI study. Chem. Phys. Letters, Vol. 183, 3,4, 204-208 (1991).
2. P.J. Bruna and F. Grein, Ab initio Study of the Vertical Spectrum and Ionization Potentials of Silanethione ($H_2SiS$), Journal of Physical Chemistry. In press.
3. P.J. Bruna and F. Grein, Theoretical Investigation of the Structures and Relative Energies of the Isomer Pairs HSiS/SiSH, $HSis^+/SiSH^+$ and $HSiS^-/SiSH^-$, Chemical Physics. In press.

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## COMPARISON OF LOCAL-DENSITY AND HARTREE-FOCK CALCULATIONS OF MOLECULAR POLARIZABILITIES AND HYPERPOLARIZABILITIES.

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Dipole moments, dipole polarizabilities, and first dipole hyperpolarizabilities have been calculated within both the Hartree-Fock approximation (HFA) and the Local Density Approximation (LDA) in order to assess the relative quality of these two approximations when finite basis sets of comparable quality are employed. In particular, comparisons are made using basis sets of roughly double or triple zeta quality with and without added field-induced polarization (FIP) functions for the 7 small molecules $H_2$, $N_2$, CO, $CH_4$, $NH_3$, $H_2O$, and HF using the HFA option in the program HONDO8 and the LDA options in the programs DMol and deMon.

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THE $^1A_1$ ELECTRONIC EXCITED STATES OF FORMALDEHYDE, AND COMPARISON TO ITS THIO ANALOGUE. AN AB INITIO MRD-CI STUDY

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Ab initio CI studies have been performed to determine the energies of the lowest six $^1A_1$ states of formaldehyde, $H_2CO$, as a function of the C-O distance in $C_{2v}$ symmetry. The vertical excitation energy of $^1(\pi,\pi^*)$ was found to be 9.52 eV, more than 1 eV below the ionization potential. It is thus unlikely that autoionization is the cause for the absence of experimental data as was previously suggested in the literature. Vertical excitation energies for the $n \rightarrow 3_{py}$ and $n \rightarrow 3d_{yz}$ Rydberg states were found to be within 0.2 eV of the experimental data. The geometry of the $^1(\pi,\pi^*)$ state was optimized. The molecule is found to be planar, with $R_{CO}$ = 2.92 Å. The $^1A_1$ state manifold of $H_2CO$ will be compared with that of its thio analogue, $H_2CS$.

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## Electronic Structure of Octahedral and Cubic Inorganic Clusters

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**Abstract:** Octahedral and cubic inorganic clusters containing π-donor ligands often exhibit a large range of different electron counts for the same geometrical arrangement and therefore do not follow the electron counting rules of the Polyhedral Skeletal Electron Pair Theory. The parameters responsible for this breakdown will be analyzed by means of extended Hückel and SCF-MS-Xα calculations. The differences between π-donor and π-acceptor ligands will be particularly highlighted by a comparison of related chloride and carbonyl clusters.

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THE EFFECT OF MANY CHAIN INTERACTIONS ON LATERAL MOTION IN POLYMER MELTS, Michael F. Herman and Ping Tong, Dept. of Chemistry, Tulane University, New Orleans, LA 70118, USA.--- A model is presented for the lateral motion of linear polymer chains in a monodisperse melt. Because each pair of neighboring chains in a melt are highly entangled, the lateral motion of each chain is taken to occur primarily along the contours of neighboring chains. This lateral motion is impeded by interactions with other nearby chains. Some obstacle chains constitute significant barriers to lateral motion, while others do not, depending on the local configuration of the chains. A model is developed for the fraction of barriers which constitute impassable barriers as a function of the length scale for chain motion. The cooperative motion of mutually impassable chains is considered in a model. A scaling analysis is applied to this model, leading to the prediction that the mean squared bead displacement scales as $t^{2/7}$. The corresponding terminal time scales with chain length as $N^{7/2}$. The center of mass diffusion constant, resulting from the correlated motion of all chains in a certain region, scales as $N^{-2.1}$.

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THEORETICAL ASSIGNMENT OF THE CORRELATION BANDS OBSERVED IN THE NEAR-THRESHOLD PHOTOELECTRON SPECTRA OF $N_2$,CO AND HCl

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Very recently, Comer and his coworkers studied the near-threshold photoelectron spectra of $N_2$, CO and HCl by using the synchrotron radiation. They succeeded in observing a series of the correlation bands above 20 eV. Some of them show the vibrational progressions, which may help to assign the final states of the photoelectron spectra. In the present study, we calculated the potential energy curves of the highly excited states of the ions, $N_2^+$, $CO^+$ and $HCl^+$ with the ab initio CI method, and then the Franck-Condon factors (FCF) from the neutral ground state are evaluated. In evaluating the FCF, a new code is developed, which is based on the Lanzcos recursive method. By comparing the experimental vibrational progression with the theoretical one, four observed bands of $N_2$ between 23 and 30 eV are unequivocally assigned, and the vibrational quantum numbers of the spectra are also identified.

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**FAST ELECTRON AND X-RAY SCATTERING FROM $B_2H_6$.**

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Cross-sections for the scattering of x-rays and fast electrons from $B_2H_6$ molecules are considered in the framework of the Waller-Hartree and Born theories. An extensive numerical study is made to investigate the influence of the target wave function quality on the scattering cross sections. A major finding is that diffuse basis functions, especially diffuse polarization functions on the peripheral atoms, are essential in obtaining converged results at the Hartree-Fock level of target wave function.

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**THE EVALUATION OF THE BOND DISSOCIATION ENERGY OF THE $FEF^+$ ION BY *ab initio* ECP-MCSCF CALCULATIONS AND FTICR-EXPERIMENTS**

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The title compound, $FeF^+$, has been generated *via* C-F activation of hexafluorobenzene in an ion-molecule reaction with bare $FeO^+$ in a Fourier-Transform-Ion-Cyclotron-Resonance mass spectrometer. By bracketing experiments the bond dissociation energy (BDE) of $FeF^+$ has been found to lie between 86 and 101 kcal/mol.

A modified pseudopotential parametrized on five low lying states of the neutral and cationic Fe together with a optimized basis *(6s3p8d/5s3p5d)* and the DZP *(9s5p1d/4s2p1d)* basis for fluorine is used for MC-SCF *ab initio* calculations with 501036 electronic configurations. The predicted BDE($FeF^+$) of 100.9 kcal/mol for the cationic ironfluoride is in good agreement with data from experimental techniques.

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## THE REACTION PATHWAY OF THE UNIMOLECULAR HF LOSS FROM PROTONATED FLUOROBENZENE. A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

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The potential energy surface for the unimolecular decomposition of protonated fluorobenzene is evaluated by *ab initio* MO calculations. Relative stabilities of various isomers as well as the barriers for the interconversion processes have been calculated at the MP2/6-31G*/HF/6-31G* level of theory.

The predicted reaction mechanism and the thermochemistry is in line with the experimental findings, as being derived from mass spectrometric kinetic energy release measurements and appropriate isotopic labeling studies.

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## THEORETICAL PHOTOABSORPTION SPECTRA OF ARGON CLUSTER IONS

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The photoabsorption spectra of argon cluster ions $Ar_n^+$ were calculated for n=3 to 24 with the DIM model. The thermal motions of the clusters were taken into account by the molecular dynamics simulation.

Two absorption bands are found in the UV and visible region of the spectrum of the trimer, which is in good agreement with experimental results. These absorption bands are assigned to $1^2\Sigma_u^+ \rightarrow 2^2\Sigma_u^+$ and $1^2\Sigma_u^+ \rightarrow 1^2\Sigma_g^+$. The shoulder is found in the red side of the visible band, which is assigned to $1^2\Sigma_u^+ \rightarrow 1^2\Pi_u$.

The larger clusters also exhibit two absorption bands. The peak of the visible absorption band is found to red-shift in two steps as the cluster size increases, which is also in good agreement with the experiment. The first red-shift is mostly explained in terms of the structure of the isomer, whereas the second one results from the change of the character of the photoexcited state.

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# GENERAL FORMULA EVALUATION OF ELECTRON-REPULSION-INTEGRALS AND THEIR DERIVATIVES. II.

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General formula method of paper I [J. Chem. Phys. 95, 5198 (1991)] can be improved. A rapid computer code can be obtained for a vector architecture. For example, a computation time is 300 ns per one [FF|FF] type of ERI for uncontracted GTOs. When the degree of contraction K=2 for the contracted GTOs, the computation time is 80 ns per one primitive (FF|FF) type of ERI. More rapid computations are performed for higher-order GTOs (per one ERI).

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# QUANTUM RATE OF REACTION OVER A DISSIPATIVE BARRIER

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**Abstract**

The quantum Langevin equation, in conjunction with the flux-position correlation function, is used to consider the solvent effect on barrier crossing. An analytical result is obtained for a harmonic barrier, which is a quantum version of Grote-Hynes theory. For a general barrier, a numerical approach is presented.

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## QUANTUM MECHANICS AS A FORM OF CLASSICAL MECHANICS.

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It is shown that an arbitrary quantum mechanical system is exactly equivalent to infinite classical system consisting of two parts: the classical analog of the original system and an infinite number of additional degrees of freedom. The time dependent variational principle allows one to limit the number of additional degrees of freedom, thereby converting the formalism into an approximate but practical computational scheme for simulating quantum dynamics by classical mechanics. The results of both numerical and formal studies suggest some interesting, new, purely classical, interpretations of such quantum phenomena as tunneling, wavepacket spreading, and the development of complex structure in the wavefunction. The possible benefits of this treatment for computations on systems of chemical interest are described.

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## A STATE-SELECTIVE MULTI-REFERENCE COUPLED-CLUSTER FORMALISM

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A Multi-Configurational Coupled-Cluster (MRCC) formalism for a single state is presented, and a comparison is made with a corresponding version of the Multi-Configurational Configuration Interaction (MRCI) method. In our approach the MRCC wave-function $|\Psi\rangle$ is obtained from the reference function $|\Psi_0\rangle$ with the usual exponential ansatz, i.e., $|\Psi\rangle = \exp(\hat{T})|\Psi_0\rangle$. The reference function $|\Psi_0\rangle$ is chosen as a linear combination belonging to a Complete Active Space (CAS)expansion . However, the coefficients of the CAS configurations are not kept fixed but are determined by the MRCC equations. A consequence of this choice is that the cluster operator $\hat{T}$ can be chosen in such a way that the exponential expansion terminates at a finite order, and no truncation is needed. Moreover the formalism is potentially exact, since the Full CI results are recovered if a complete expansion of $\hat{T}$ is used. The formalism is related to contracted MRCI approaches, and a similar contracted formulation of our method is possible. Redundancies which arise among the generators can be treated and eliminated in a similar way to what is done in contracted MRCI methods.

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ELECTRONIC STRUCTURE AND REACTIVITY OF METALS AND METAL-OXIDES BY DENSITY FUNCTIONAL METHOD

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Density functional program "deMon" and its extended version for the periodical systems were used to investigate the electronic structure of bulk and surfaces of Pd and MgO, and chemisorption of $H_2$ and $CH_4$ on them.

*Electronic Structure of Palladium Crystal.* The band structure of Pd fcc crystal was calculated. Convergence behavior of the cohesive energy and Fermi level was examined with respect to the truncation length of interactions. The calculation showed that the length more than 7 A was necessary to get convergence. The obtained cohesive energy (5.2 eV) was larger by ca. 1 eV than a experimental value (3.89 eV), and the Fermi energy (-5.2 eV) was closely agreed with a experimental value (-5.12 eV). The calculated band structure was compared with a result by Moruzzi et al., and the dispersion relation was well reproduced.

*Electronic Structure of MgO and Chemisorption of $H_2$ and $CH_4$.* The adsorption energies of $H_2$ and $CH_4$ were investigated using the $Mg_4O_4$ cubic cluster, and the results were compared with our previous Hartree-Fock(HF) and Moller-Plesset (MP) calculations. Although the DF method with local potential overestimated the binding, the inclusion of non-local potential considerably improved this overestimation. Calculation with the slab model is also in progress.

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**ACCURATE PROPERTIES OF $H_2$ AND $D_2$ FROM EXPLICITLY CORRELATED WAVE FUNCTIONS**

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Explicitly correlated Gaussian geminal wave functions of valence bond type are constructed for the ground electronic state of $H_2$ at 11 different bond lengths between $0.8a_0$ and $2.6a_0$. The variational potential energy curve is parallel to and about $0.08cm^{-1}$ above the exact one. These wave functions are used to calculate various properties as a function of bond length. The properties include multipole moments up to rank 10, the values of the electric field and its gradient at the nucleus, and the diamagnetic shielding constant. Rovibrational averages for selected states and thermal averages for selected temperatures are reported. The effects of isotopic substitution are also considered.

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THEORETICAL ASSIGNMENT OF RSS ANION AND INDOLE FREE RADICAL SPECTRA

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Iterative natural orbital FOCI calculations of the molecules $HSS^-$ and $CH_3SS^-$ are used to model the spectra of the $S\text{-}S^-$ bond. The first excitation energy is assigned to a band in the rhodanese enzyme and attributed to a $S\text{-}S^-$ bond at the enzyme active site. Double excitations from the multi-configuration reference is not required since reasonable agreement is obtained between the FOCI and multi-reference doubles CI excitation energies.

A peak at 570nm in oxidized cytochrome c peroxidase (CcP) has been attributed to an intermediate tryptophan free radical but the charge state has not been determined. FOCI calculations of the neutral and cationic free radicals of the indole side chain of tryptophan suggest that the absorption spectra of the neutral radical has been observed. This peak is calculated to shift substantially to the blue in water. Accurate calculation of the valence singlet and triplet excited states of benzene and the phenoxy radical also tests the FOCI procedure.

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# THEORY OF PULSES AND SPIN DYNAMICS IN NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

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Pulses in Nuclear Quadrupole Resonance (NQR) spectroscopy are selective and cause transitions between two pairs of levels $(\pm) \longrightarrow \pm(M+1)$, other transitions are not normally excited. The formulation of pulses in NQR is then described for any spin $I$ by two $2 \times 2$ rotation matrices. Calculations on resonance for spins with an axially symmetric nuclear quadrupole for up to three pulses are presented for spins $I = 1$ and $I = 3/2$. The formulation can be extended in a straightforward manner to axially asymmetric quadrupolar systems and those in the presence of a small magnetic field.

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# QUANTUM CANONICAL TRANSFORMATION TO ELIMINATE CORIOLIS AND CENTRIFUGAL TERMS COUPLING NEARLY DEGENERATE VIBRATIONAL STATES

by

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Effective rotational Hamiltonians for each vibrational state of a polyatomic molecule, obtained by applying standard perturbation theory to the Watson Hamiltonian, play a fundamental role in molecular spectroscopy. They cannot be obtained, however, when nearly degenerate states are coupled strongly by Coriolis and centrifugal terms. A canonical transformation technique due to Bogoliubov and Tyablikov is found to be useful for eliminating a few, but most important rovibrational coupling terms in the molecular Hamiltonian so that perturbation theory can still be applied and new effective Hamiltonians obtained. Formaldehyde and formic acid are treated as examples.

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*CIS-TRANS* RATIOS IN SUBSTITUTED PROLINES IN SOLUTION.

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We are studying the tripeptide pGlu-His-Pro-NH2, which is thyrotropin releasing hormone (TRH), and suspect the *cis-trans* isomerization of the His-Pro peptide bond to be at least part of the activation mechanism of TRH-receptor complex. A TRH-analog, in which Pro is substituted by 2,4-methano-proline (MePro) is known to be >95 % *trans* (1), in contrast to 85 % *trans* in TRH. This analog binds 11 000 times less avidly to the receptor than the native compound, but activates the receptor fully.This could mean that the receptor recognizes only the *cis* conformation.To characterize the *cis-trans* ratio as a possible explanation of the observed difference in binding affinities we studied the conformational properties of model compounds Ac-Pro-NH2 and Ac-MePro-NH2. In addition to the *cis* and *trans* forms with respect to ω(Ca'C'NCa), these compounds also have two rotamers about ψ(NCaCN''). All structures were optimized at HF/6-31G level, and final energies are calculated at MP2/6-31G* with ZPE and solvation corrections. Preliminary results indicate that the *trans*-Pro is lower in energy than either of the *cis*-forms, by 2.7 kcal/mol to ψ-cis and 5.0 kcal/mol to ψ-trans. The dipole moments are 2.4 D and 7.9 D, respectively, so it is expected that the *cis-trans* energy difference will be ~ 0 kcal/mol in solution. For MePro-TRH the ΔE(*cis-trans*) is 4.0 kcal/mol at HF-level, and the dipole moments are very similar, suggesting that solvation will not affect this difference. This can account for the rarity of *cis*-conformation in MeProTRH. The energetic and structural details of all four conformers of both compounds will be presented.

1) C. Mapelli, H. van Hallbeck, C. Stammer, Biopolymers 29 (1990) 407-422.

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ELECTRON TRANSFER IN METHANOL: THE ROLE OF HYDROGEN-BONDING. Branka M. Ladanyi and Teresa Fonseca*, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, U.S.A.

The study of dynamical effects of polar solvents on electron transfer reactions has been a very active area of research in the last few years. Low-barrier and barrierless photochemical reactions are particularly interesting since they are strongly influenced by solvent dynamics. Alcohols are frequently used as solvents for these reactions. One of the key questions still to be answered for electron transfer is: to what degree does the solvent hydrogen bond network affect the reactive event? To answer this question and to assess the importance of solvent dynamical effects in electron transfer reactions, we have performed molecular dynamics (MD) simulation studies of several exothermic barrierless and low-barrier electron transfer reactions in methanol. Reaction free energy surfaces were obtained by umbrella sampling and the reactant survival probabilities were then calculated by nonequilibrium MD simulation. We use our earlier MD results on solvation dynamics in methanol [1] to establish a connection between this phenomenon and the solvent's influence on electron transfer dynamics.

*Deceased, December 1991.

[1] T. Fonseca and B.M. Ladanyi, *J. Phys. Chem.* **95**, 2116 (1991).

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VIBRATIONAL PREDISSOCIATION OF $Ne_2Cl_2$ AND $He_2CL_2$ : A QUANTUM, TIME DEPENDENT APPROACH.

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A 3 degree of freedom model is used to investigate vibrational predissociation in $Ne_2Cl_2$ and $He_2Cl_2$. The rare gas atoms' distances to the center of mass of $Cl_2$ are represented on a grid while the $Cl_2$ vibration is described by a basis set. The time-dependent Schrödinger equation is solved with the Lanczos scheme, and observables are extracted from the wave packet. The rate constants for the breaking of one or both bonds are calculated, along with the $Cl_2$ vibrational product distributions. It is shown that the dynamics can generally be described in terms of only one resonance, and inspection of the time-dependent probability density yields a mechanistic picture of the different processes arising from the loss of one or two quanta of the $Cl_2$ vibration to the van der Waals bonds.

The 3D results agree fairly well with experimental data in the case of $Ne_2Cl_2$, while $He_2Cl_2$ is shown to require a higher dimensional treatment. Preliminary results of a 4D quantum time-dependent calculation for $He_2Cl_2$ are presented.

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# Development of a New Open-Shell Coupled-Cluster Method

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**Abstract**

Different forms of open-shell coupled-cluster theory are described and compared in order to determine the best compromise between accuracy and cost. All of the approaches considered here are based on a restricted Hartree-Fock reference function. The iterative coupled-cluster techniques include single and double excitations, or in other words the unknown parameters are limited to the $t_1$ and $t_2$ amplitudes. The effects of connected triple excitations are included via perturbation theory.

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# DISCRETE VARIABLE REPRESENTATION IN WAVE PACKET SCATTERING FROM SURFACES

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In order to treat the translational degrees of freedom in wave packet scattering from surfaces, we have applied both the widely used FFT algorithm and the Gauss-Chebychev quadrature scheme recently introduced by Muckerman. We provide a detailed comparison between the two approaches in function of the grid size, with and without the presence of symmetry in the diffractive scattering.

In the case of molecular scattering from corrugated surfaces, exact time-dependent studies have been restricted to basis set expansion methods. By means of a Gauss-Legendre-Fourier unitary transform we have developped a discrete variable representation on a two-dimensional fixed grid in terms of the angular coordinates. This new algorithm is unconditionally stable and favorably scales as $N^{3/2}$, where N denotes the number of rotational states. We report numerical tests which show that our new algorithm is more efficient than basis set expansion methods already at small N.

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## LONG TIME DYNAMICS OF REGULAR AND CHAOTIC SCATTERING BILLIARD SYSTEMS.

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The long time behaviour of classically chaotic scattering systems with two degrees of freedom are studied numerically. The bound systems exhibit classical chaos, namely positive Lyaponov exponent. For the scattering systems, hyperbolic dynamics exhibit exponential dwell time decay, whereas the mixed systems add a power law long time tail to the decay distribution. This power law is attributed to cantori bottlenecks to phase space flow, where the fractal island structures causes trajectories to "stick" for long times. A singular deflection function is shown to be fractal in nature on all scales. Product distributions for chaotic trajectories follow statistical theories for bimolecular reactions.

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## REGIOSELECTIVITY OF NUCLEOPHILIC ADDITIONS TO CYCLOPENTADIENYLIRON COMPLEXES OF SUBTITUTED BENZENES

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In this work, we compute the relative probabilities of different locations a model nucleophile may occupy on the molecular surfaces of cyclopentadienyliron complexes of a series of substituted benzenes. To this end, we construct a Boltzmann probability function evaluated at various positions along a formal molecular surface.

The results show that for the addition of a hydride ion to these organometallic complexes, the experimental product distribution (regioselectivity) is a function of the changes of the classical statistical probability of the nucleophile to contact different regions of the molecular surface.

A linear correlation is found between the experimental relative product yields and the theoretical relative Boltzmann probabilities of a nucleophile attacking a given position on the reactant. The results provide a quantitative description of regioselectivity of the nucleophilic additions, with electron-donating substituents favoring addition to the meta-position and electron-withdrawing substituents favoring ortho-additions.

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MOLECULAR G-TENSOR CALCULATIONS

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For a paramagnetic molecule, the g-tensor describes the anisotropic separation between different spin orientations of that molecule in an external magnetic field.

The SCF level calculations of g-tensor elements presented here differ from most previous calculations in that they include kinetic energy correction and gauge correction terms.

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GAS PHASE ION MOBILITIES OF $LI^+$ IN $N_2$ AND CO

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The fundamental quantity describing ion transport properties in dilute gases is the potential energy surface. The theory of ion mobility and diffusion coefficients of spherically symmetric ions in spherically symmetric gases is well understood. Calculation of these transport coefficients directly from their interaction potentials is now routine, and results that are calculated usually rival experimental measurements in accuracy. Ion-neutral systems that include internal degrees of freedom and anisotropy are much less understood, even though an excellent database of experimental measurements exists. Recent theoretical advances in kinetic theory and an ab initio calculation of the rigid rotor potential energy surfaces of $Li^+$-$N_2$ and $Li^+$-CO have been combined in order to calculate the ion transport properties of $Li^+$ in the gases $N_2$ and CO. Results of the transport calculations have shown that this new method can reproduce very accurate experimental data sets. It has been concluded from this agreement that both the kinetic theory and the potential energy surface approximate well the physics of ion-molecule drift tube experiments.

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## IMPROVED FEYNMAN PROPAGATORS ON A GRID AND NON-ADIABATIC CORRECTIONS WITHIN THE PATH INTEGRAL FRAMEWORK

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The idea of using a good representation as the zeroth order description of a problem, which is widely used in perturbation theory and in basis set calculations, is extended to the path integral formulation of quantum mechanics by constructing improved Feynman propagators. The best zeroth order propagators cannot be expressed in closed form in general, and are therefore constructed numerically and stored on one-dimensional grids. Use of improved propagators in discretized path integral calculations involves a trivial modification of Monte Carlo techniques and leads to convergence with fewer time slices. Application of a quasi-adiabatic propagator to a system coupled to a harmonic bath leads to a low-dimensional path integral with a non-local influence functional which incorporates the non-adiabatic corrections to the Born-Oppenheimer approximation and which (with parameters typical of chemical processes) can be evaluated by quadrature, providing an accurate method for investigating the real time quantum dynamics of system-bath Hamiltonians.

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## CALCULATIONS OF NMR SHIELDING CONSTANTS USING A COMBINATION OF PSEUDO-POTENTIAL AND IGLO METHODS.

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The pseudo-potential approach is one of the most effective methods for reducing the computation time for systems with a significant number of core electrons. However, a brute force combination of the CHF approach with a magnetic field independent nonlocal pseudo-potential is inappropriate. In this case the hamiltonian is not invariant with respect to a unitary transformation corresponding to a shift of the gauge origin of the vector potential of the external magnetic field. Therefore, we present here a more general type of pseudo-potential for a system in an external magnetic field. It cares for the invariance of the hamiltonian and has the correct limit in the absence of an external magnetic field.

Results of our calculations of carbon chemical shifts are in good agreement with data of all-electron calculations. Results for silicon chemical shifts are presented and problems concerning the non-transferability of the L-shell contribution are discussed.

One of authors (V.G.M.) is grateful to the Alexander von Humboldt Foundation for this research fellowship.

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MONTE CARLO SIMULATIONS OF DIPOLAR FLUIDS

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Monte Carlo calculations of fluctuations in the total dipole moment of a polar fluid were carried out in the canonical ensemble using biased sampling. Also determined were the configuration energy, dielectric constant, and distribution functions. Both hard and soft spheres with an embedded dipole were considered using both the minimum image and ewald sum conventions for the interaction. The results are compared over a range of dipole strengths and sensitivity to the system size is assessed.

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**GAUGE CONSIDERATIONS IN THE CALCULATION OF LASER-INDUCED RESONANCES IN THE PHOTODISSOCIATION OF $H_2^+$ IN AN ADIABATIC ELECTRONIC-FIELD REPRESENTATION.**

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Resonances induced by high-intensity laser fields in the photodissociation of $H_2^+$ are calculated in the radiation-field (RF) or velocity gauge within adiabatic and diabatic electronic-field dressed representations and they are compared to the corresponding ones obtained in the electric-field (EF) or length gauge. Gauge transformation within these calculations are also discussed.

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HYPERPOLARIZABILITY OF SOME 10- AND 18-ELECTRON SYSTEMS.

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First ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability values were obtained from finite-field self-consistent field and complete fourth-order many-body perturbation theory calculations for methane, ammonia, hydrogen fluoride, hydrogen chloride, hydrogen sulfide and hydrogen peroxide.

In addition, all the independent components of the multipole moment, linear and non-linear polarizability tensors up to the fourth rank of $Cl_2$, $P_2$, HBr and $CS_2$ were obtained from accurate self-consistent field wavefunctions.

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**THEORETICAL STUDY OF THE THERMAL AND PHOTOLYTICAL DECOMPOSITION OF GOLD-ALKYL COMPLEXES.**

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It's important to understand the mechanism of both thermal and photochemical decomposition of organometallic species in relation to their practical use in chemical vapor deposition of metals.

In this paper we present the results of an *ab initio* MRDCI//CASSCF study of the mechanism of both thermal and photolytic decomposition of gold-alkyl complexes. Geometrical structures, energy profiles, and vibrational analysis of the different critical points found will be presented.

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## AN AB INITIO STUDY OF FOUR-COORDINATE ORGANOALUMINUM-NITROGEN RING COMPOUNDS

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Neutral, chelated four-coordinate organoaluminum-nitrogen compounds have been investigated experimentally for some time. This paper reports on work done on several compounds of this class, $H_2AlNHCH_2CH_2NH_2$ and $Cl_2AlNHCH_2CH_2NH_2$, using ab initio techniques with basis sets of double-$\zeta$ quality and the self-consistent-field method. The two types of Al-N bonds in these molecules (covalent and dative) are characterized using analysis of the infrared frequencies and intensities, canonical molecular orbitals, atomic charges and bond orders of different conformers. The resemblances to related compounds which have been characterized experimentally are also reported.

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## GEOMETRICAL AND ELECTRONIC STRUCTURES OF ALUMINUM-SODIUM BIMETALLIC CLUSTERS

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The geometrical and electronic structures of several small aluminum-sodium mixed clusters, $Al_nNa_m$ (n=1-4, m=1; n=1-3, m=2; n=1-2, m=3), and their cationic clusters were examined with ab initio molecular orbital calculations. All the calculations were carried out at the restricted Hartree-Fock level of approximation for both closed and open shell systems. The low and high spin multiplicities of each cluster were examined. The structures of the most stable neutral and cationic clusters were fully optimized. The geometrical structure of the most stable state of the clusters keeps the frame of the Al cluster unchanged, and the Al-Al distances become shorter than in the corresponding Al clusters. The calculated ionization energies by the $\Delta$SCF method are qualitatively in agreement with the corresponding experimental values. The highest occupied molecular orbital of the neutral clusters suggests that an ionized electron is localized on the Al atoms, but the large orbital reorganization by ionization results in a substantial net positive charge on a sodium atom. The nature of chemical bond for the clusters is also examined.

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SOME TRENDS IN THE STABILIZED NITROGEN AND PHOSPHORUS YLIDES.

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An ylide is defined as a compound with opposite charges on adjacent, covalently bound atoms that both have an electronic octet. In this study, the geometries of the stabilized ylides, $(R^1{}_3X)R^2C\text{-}CR^3O$, where $R^1$=H,F; $R^2$=H,$CH_3$,$CF_3$; $R^3$=H,OH; and X=N,P were optimized using the 3-21G(*)basis set. For comparison, the two simplest ylides with $R^1=R^2=R^3$=H and X=N,P were also optimized using the large 6-31+G* basis set. The $NH_3$ ylides were influenced by hydrogen bond interactions to give a geometry with O and $NH_3$ on the same side of the C-C bond (cis). In the $NF_3$ ylides, the steric and electronic repulsions cause a trans geometry. The phosphorus ylides show a geometric dependence on $R^3$, being cis if $R^3$=H and trans if $R^3$=OH. Also, bond length trends and charges will be presented and discussed.

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**VARIATIONAL METHOD FOR THE VIBRATIONAL ENERGY LEVELS OF POLYATOMIC MOLECULES**

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In this work, a new method is developped to calculate the vibrational (J=0) energy levels of polyatomic molecules. The eigenvalues of an internal coordinate hamiltonian are found variationnally using the Lanczos algorithm to deal with a very large variational matrix. A Discrete Variable Representation (DVR) basis set is used to provide a good represention of the hamiltonian. It is easy to calculate the DVR of the kinetic energy without expanding it's coordinate dependence. The DVR provides with a very sparse matrix, a condition that is essential for an efficient use of the Lanczos algorithm for matrices too large for any computer's memory. The method developed here is applied to find the highly excited vibrational levels of formaldehyde, and the results are in good agreement with experiment and the calculations of other groups.

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DOES ELECTRONEGATIVITY HAVE A FUTURE?

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Pauling's original formulation of electronegativity was intended to be predictive. Given two atoms and their electronegativities, the ionic character of the resulting bond could be calculated. This work was extended by Mulliken to include orbital concepts. Others have extended electronegativity theory to predict the ionic energies of molecular bonds. However, as yet, total energies have not been predicted using electronegativity concepts alone. Moreover, there has recently been a shift towards the use of electronegativity as an analytical tool rather than as a predictive tool. L.C. Allen in particular has completely abandoned the traditional approaches to electronegativity in favour of a descriptive energy formulation that probably cannot be made predictive. The questions that thus arise are (a) can a predictive theory of electronegativity be found that is useful and (b) how useful is a descriptive theory of electronegativity? These questions will be examined. A theoretical attempt at finding a useful predictive theory will also be presented.

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# THE ELECTRONIC STRUCTURE OF $Li^{+}_{n}F^{-}_{m}$ CLUSTER IN IONIC CAGE

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The electronic band structure of LiF was investigated with cluster approach in which $Li^{+}_{n}F^{-}_{m}$ ions were embedded in the ionic crystal composed of point charges. The electronic structures were calculated by ab initio SCF and CI calculations. The band gap, band width of valence band, ionization threshold, electron affinity, and exciton band of the LiF crystal will be discussed.

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## APPROXIMATE TWO-MATRICES WHICH SATISFY THE CUSP CONDITION

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An ansatz which is based on one proposed by Valone[1] for obtaining the pair density from the density will be discussed. The two-electron density is constrained to reduce to the electron density when integrating over electron 2. Numerical results of the two-electron repulsion energies calculated from pair densities which satisfy the cusp condition will be compared with those obtained from similarly constructed pair densities which don't satisfy the cusp condition. The implications of the non-N-representability of the associated two-matrices and of the Colle-Salvetti two-matrix will be discussed.

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## QUADRATURE SCHEMES FOR INTEGRALS IN DENSITY FUNCTIONAL THEORY.

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The evaluation of integrals which arise in Density Functional Theory, as applied to molecules, is discussed. Becke's scheme for reducing them to a sum of integrals over atom based poltyhedra is used. Within each of these regions, quadratures for the spherical polars are examined; in particular we compare a Euler-Maclaurin based scheme with Gauss schemes. Upon specific investigations we find that the Euler-Maclaurin scheme is favoured for radial quadrature and Gauss-Legendre quadrature is preferred for theta. We investigate the number of points required for a given accuracy, and we demonstrateour favoured approach by calculations on a variety of molecules. We also present some applications of our approach.

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## A THEORETICAL STUDY ON CHEMICAL REACTIONS IN SOLUTION

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The stochastic path-integral technique suitable for chemical reaction dynamics was explored.[1)] It is shown that this technique enables the direct computaion of the transition amplitude with a finite space-time range, by generating a set of classical paths subject to simultaneous stochastic differential equations. The numerical values for a harmonic potential are in good agreement with previous analytical results.[2)] The flux-flux autocorrelation function is also evaluated for a colinear $H_3$ molecular system described by an Eckart potential and is found satisfactory in comparison with the previous results.[3)] In general, this method is easily extended in treating any multi-atomic systems if only some force field is available. Another two direct examples, i.e., full 3D $H_3$ molecular system and a model system in solvent, will be also demonstrated. In particular, in the latter example, the solvent dynamics is effectively desclibed as a frictional force by quantizing the corresponding Langevin equation as it is within the present formalism.

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## THEORETICAL STUDIES OF DYNAMIC PROCESSES IN HOST-GUEST COMPLEXES

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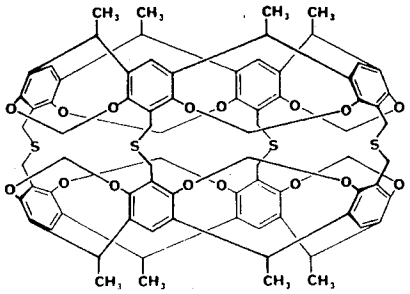
Many kinds of host molecules which incarcerate small molecules have been synthesized by Cram and coworkers.[1] We have studied dynamic process in one of these carceplexes in which **1** is a host molecule, and one or two acetonitriles are guests.[2] In the dynamic study using AMBER force field,[3] average orientation of the guest molecules in the cavity was examined and compared with experimental (NMR) results. The mechanism and pathways of the guest molecule escape process were also examined.



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### THEORETICAL STUDY OF THE PHOTOABSORPTION AND PHOTODISSOCIATION DYNAMICS OF FCO

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Potential energy surfaces for the electronic ground and excited states of the fluoroformyl radical, FCO, were calculated with the ab initio molecular orbital (MO) configuration interaction (CI) method. These potential surfaces are related to the experimentally observed photoabsorption spectrum between 340 and 220 nm. The transition dipole moment surfaces between these states were also calculated. The Franck-Condon factors between the zero point vibrational level in the ground state and 60 vibrational levels in the first excited states, $1^2A''$, are numerically evaluated, by solving the Schrödinger equation for the nuclear motion on the potential energy surfaces. While our result shows a long progression of the bending mode in the $1^2A''$ state between 340 and 280 nm, the experimentalists assigned the progression of the CO stretching mode. The calculated level spacing is 520 $cm^{-1}$, while the experimental one is 650 $cm^{-1}$.

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### VIBRATIONAL FORCE FIELDS AND STRUCTURE OF THE ANIONS OF $C_{60}$

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The study of fullerenes has attracted an increasing interest since the discovery of the high temperature superconductivity of the $C_{60}$ films doped with alcali atoms[1].

In this communication we present quantum chemical calculations of the structure and vibrational force field of the ground electronic state of the anions of $C_{60}$, performed by using an updated version of the QCFF/PI Hamiltonian[2]. When quasi-degeneracy is found among states of different spin multiplicity, the geometry and vibrational frequencies of the lowest electronic state of each multiplicity are obtained. The effect of vibronic coupling is analyzed in terms of the difference between diabatic and adiabatic force constants. The calculated vibrational frequencies are compared with the observed spectra, when available, and the effect of different amounts of negative charge on the equilibrium geometry and vibrational spectrum is discussed.

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**COMPARISON OF SOME KINETIC ENERGY DENSITY FUNCTIONALS.**

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Roothaan-Hartree-Fock self-consistent-field (SCF) kinetic energies are compared with kinetic energies obtained from various functionals applied to the SCF electron densities for a set of 77 molecules. The best functionals are much better than the first-order gradient expansion but need further improvement by an order of magnitude before they can considered reliable for practical applications to atoms and molecules. Some suggestions are made as to how such functionals might be found.

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**IMPROVED BASIS SETS FOR *AB INITIO* CALCULATIONS**

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A sequence of fully optimized atomic orbital basis sets with varying numbers of primitive Gaussian type orbitals (GTO's) and contracted GTO's (CGTO's) has been developed for the atoms H through Ne and for their stable singly charged positive and negative ions. Optimization of all exponents and contraction coefficients reduces the errors by about a factor of two relative to the standard basis sets of the same size, and completely eliminates the need for additional diffuse (+) basis functions for the description of negative ions. Nearly optimum molecular basis sets can be efficiently and systematically generated by atomic charge optimization (i.e. interpolation between the atom and ion basis sets). Atomic charge is a meaningful parameter to describe both the changes in the optimum AO basis functions and the basis set truncation error. Simple error correction schemes for both self consistent field (SCF) and correlation energies reduce errors in chemical energy differences by an additional order-of-magnitude.

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## ELECTRON PROPAGATOR INTERPRETATIONS OF BONDING AND SPECTRA

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Electron propagator theory (EPT) has served chiefly as an *ab initio* formalism for calculating vertical electron binding energies. The scope of applications has been increased recently by

- the development of methods to calculate total energy gradients and properties and
- the qualitative interpretation of Feynman-Dyson amplitudes.

The former aspect is illustrated through the accurate calculation of the geometries, vibrational frequencies and dipole moments of the ground and excited states of CaCN. Excited states of a given symmetry type are as easily treated as the lowest state. The latter aspect is demonstrated by the succinct one-electron picture of bonding in cluster models of polysilanes that is generated by EPT. In addition to producing quantitative predictions of photoelectron spectra, the calculations provide simple orbital explanations that relate conformational changes to spectral shifts. This work is supported by the National Science Foundation, the Petroleum Research Fund and the Pittsburgh Supercomputer Center.

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## MOLECULAR ORBITAL STUDY ON THE FORMATION REACTIONS OF THE INTERSTELLAR MOLECULES CONTAINING CARBONS

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In recent years, many unstable molecules are found in the interstellar space, especially in dark molecular cloud which is thought to be in the early stage of star formation. One of the most probable reaction mechanisms of the formation of these interstellar molecules is ion-molecule reaction. In the present theoretical study, we have investigated the possible reaction pathways in the ion-molecule reaction mechanisms of the growing process of carbon chain of hydrocarbons ( $C_nH$, n=1,2,3,... ) which was proposed by H. Suzuki. The molecular geometries and their energies were calculated with Hartree-Fock and MP2 methods.

In order to confirm that the chemical reaction in interstellar space is possible, the reaction has to be exothermic and there should be no energy barrier. The successive reactions with hydrogen molecules starting from carbon cation been formed by the irradiation of cosmic ray are calculated to be all exothermic up to $C_3H_3^+$ species. The results of the potential energy surfaces of each reaction pathway indicate that the stable intermediate molecules are observed in the most of the reaction stages, e.g., (reaction 1) $CH_2^+ + H_2 \rightarrow [CH_4^+] \rightarrow CH_3^+ + H$; (reaction 3) $CH + C^+ \rightarrow [CCH^+] \rightarrow C_2^+ + H$; (reaction 4) $C_2^+ + H_2 \rightarrow [H_2CC^+] \rightarrow C_2H^+ + H$; (reaction 5) $C_2H^+ + H_2 \rightarrow [C_2H_3^+] \rightarrow C_2H_2^+ + H$, etc.

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MOLECULAR DYNAMICS SIMULATIONS OF DNA WITH PRIMARY DAMAGE

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Molecular dynamics simulations have been conducted on a dodecamer of DNA d(CGCGAATTCGCG) with a primary radiation damage. The thymine in position seven, $T_7$, was replaced by a 5-hydroxy-6-thymidyl radical (TOH·), which is a primary damage to DNA. The geometry of the modified thymine, TOH, was optimized with a split-valence 6-31G basis set. The optimized geometry of TOH was used to construct the initial geometry of the damaged DNA dodecamer by replacing the native $T_7$ in the B-DNA structure of the undamaged DNA. Counterions were placed initially at positions bifurcating the O-P-O angle at a distance of 5.0 Å from the phosphorus. The solvent was simulated by an aqueous shell that extends to a distance of 9 Å from the DNA and represents 3–4 layers of water molecules. The structure thermally equilibrated at 300°K was used as the initial configuration for a 120 ps molecular dynamics simulation at constant temperature. After 80 ps the structure stabilized around an average. The average geometry of the DNA in the 80-120 ps interval shows that the radiation damaged DNA has a local kink induced by the structural changes in the damaged thymine. The methyl of the damaged thymine is distorted out of the plane of the base and is strongly repelled by the neighboring adenine, $A_6$, causing a disruption of the Watson-Crick hydrogen bonds between TOH and the complementary $A_{18}$ and in the $T_8$-$A_{17}$ base-pair. An unusual intrastrand hydrogen bond between the OH group of TOH and the $N_3$-H on the neighboring thymine, $T_8$, adds to the distortion and stabilizes $T_8$ in a position outside the helix. As a consequence of these structural changes, the AATT region with the damage shows considerably smaller mobility than the rest of the DNA. The structure of the radiation damaged DNA is bent and shortened by 15%. A possible biological consequence of such a damage could be related to the arrest of polymerase activity around the area of damage. The analysis of the molecular dynamics trajectories show that H-abstraction from a neighboring sugar, as a possible mechanism for strand break formation, is an unlikely result of such a lesion.*Supported by DOE grant DE-FG02-88ER60675*

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MODEL SYSTEMS FOR THE Cr INTERFACE WITH POLYIMIDE SURFACES

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Using the density functional method, calculations have been performed on chromium-acetone and chromium-phthalimide systems. These complexes are expected to be good models of the bonding of chromium to the polyimide (PMDA-ODA) surfaces. It has been found that chromium binds strongly to the carbonyl group with a binding energy of 3.2 eV. This is a high value compared to that of aluminum (2.4 eV) and of copper (1 eV). Chromium also has been found to bind to the phenyl ring. The competition between the two sites present in the phthalimide molecule is in favor of the phenyl ring by 2.4 eV.

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# ATOM-ATOM POTENTIAL ANALYSIS OF THE COMPLEXING CHARACTERISTICS OF CYCLODEXTRINS (HOST) WITH BENZENE AND *p*-DIHALOBENZENES (GUEST)

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Intermolecular interaction and modelling calculations on the complexes of α, β and γ-cyclodextrins (host) with benzene and *p*-dihalobenzenes (guest) were performed. The complex formation mechanism between the host and guest molecules was evaluated from three-dimensional potential maps generated by the atom-atom potential method, and the molecular packing of the complexed compounds was visualized by a space-fill representation. Stable inclusion complexes only form when both the host and guest molecules experience a significant decrease in the complexing potential.

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# DENSITY FUNCTIONAL STUDY OF $Ni(C_2H_4)_n$ COMPLEXES

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Density functional calculations have been performed to study the molecular and electronic structure of the $Ni(C_2H_4)_n$ series, with n=1, 2 and 3. The effect of the Ni basis set (all electron and model core potential) and the energy functional (local and nonlocal) on the calculated molecular properties of the $Ni(C_2H_4)$ complex is examined first. The singlet state is found to be the ground state in every case. The $D_{2d}$ (twisted) $Ni(C_2H_4)_2$ is energetically favoured over the $D_{2h}$ (planar) structure, and the binding energy of the second ligand is greater than the binding energy in $Ni(C_2H_4)$. These findings are rationalized within the framework of the MO formalism. IR vibrational spectrum has been simulated for $Ni(C_2H_4)_3$ which is compared to the experimental spectra recorded in petroleum ether solution at -50 °C. We found excellent agreement in the far infrared region (skeletal modes), however, there are a few discrepancies in the assignment of the ethylene internal modes.

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# VINYLIDENE AND THE HAMMOND POSTULATE

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*Contribution from the Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, CT 06459, and United Technologies Research Center, East Hartford, CT 06108.*

The potential energy barrier for the isomerization of vinylidene, :C=CH2, to acetylene, HC≡CH, has been calculated by the quadratic configuration interaction method using a 6s6p3d2f,4s2p1d basis of atomic pair natural orbitals with extrapolation to the complete basis set limit (CBS-QCI/[...3d2f] APNO model). The calculated barrier ($\Delta E^{\ddagger}_e$ = 2.2±0.5 kcal/mol) and energy change from vinylidene to acetylene ($\Delta E_o$ = -43.9±0.5 kcal/mol) are in excellent agreement with recent experimental values ($\Delta E^{\ddagger}e$ = 2 kcal/mol, and $\Delta E_o$ = -44.1±0.7 kcal/mol). In spite of the small barrier height for this strongly exothermic reaction, the transition state is located half way between the reactant and product in apparent violation of the Hammond postulate. The potential energy surface for the isomerization can best be understood by considering two distinct processes. The location of the transition state is determined by the hydrogen migration which has a significant barrier, whereas the exothermicity results from the conversion of the lone pair of vinylidene to a $\pi$ bond in acetylene. Each of these processes individually satisfies the Hammond postulate.

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# DETERMINATION OF THE POTENTIAL SURFACE FOR DIATOMICS USING THE DISCRETE VARIABLE REPRESENTATION.

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The Hamiltonian matrix for one vibrational degree of freedom and rotation is constructed with a tridiagonal Morse basis set. A unitary transformation is applied to the Hamiltonian in order to have a diagonal potential. This is the discrete variable representation for the interatomic distance coordinate. Then a non-linear least squares fitting procedure with experimental rotational-vibrational data, was performed to obtain the values of the vibrational potential at discrete positions. However some of the higher potential points have to be fixed due to lack of data, to enable finding a solution for the lower points parameters.

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## ON THE SCREENED-COULOMB EXCHANGE ENERGY IN THE KOHN - SHAM LSD SCHEME

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The expression for the LSD screened-Coulomb exchange energy density obtained in 1962 by J.E. Robinson et al. within a Thomas-Fermi screening model, and repeatidly cited afterwards, is rederived in a different way. It is shown that this expression does not account for the influence of the screening on the local Fermi wavevector. Explicit dependence of the LSD Fermi wavevector on the screening parameter $\alpha$ is obtained by reformulating the model in terms of a screened-exchange hole within the intracular-extracular coordinate representation. On this base, a new screened exchange energy density is derived. Its dependence on $\alpha$ is qualitatively different from the known one in the region of small and vanishing $\alpha$. The extension of this approach to a nonlocal level may shed light on the controversial long-range anomalies detected in the gradient expansion approximation for the Kohn-Sham exchange energy.

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## PHOTOTDISSOCIATION OF $Cl_2O_2$: IMPLICATIONS FOR OZONE DEPLETION.

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The depletion of stratospheric $O_3$ during the Antarctic Spring has received considerable scientific and media attention over the past few years. At this stage, a plausible depletion mechanism has been developed and is consistent with the observed characteristics of the depletion process. However, a number of features of the catalytic cycle proposed are poorly understood. The most important of these is the nature of the photolysis of $Cl_2O_2$ in the cycle.

The work reported here is a preliminary account of theoretical studies of the photolysis of $Cl_2O_2$ via CASSCF/CI methods with basis sets of DZP quality, including atomic natural orbital sets.

This work has been supported by NASA (Cooperative Agreement No. NCC1-55) and NSF (CHE-8913800). Computer resources have also been provided by the North Carolina Supercomputing Center.

# 105 SOLVENT EFFECTS ON HYPERPOLARIZABILITIES

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**Abstract**
In cases where comparison of gas-phase and solution-phase measurements of hyperpolarizabilities is possible, results indicate that solvent effects on the hyperpolarizability are not adequately modelled by the local field factors which are used in analysis of solution-phase experiments — 'molecular' values determined from gas-phase and solution-phase experiments can differ by a factor of 3. *Ab initio* methods which include electron correlation can give reasonably reliable results for gas-phase hyperpolarizabilities. However, the hyperpolarizabilities of many systems, and in particular those of experimental interest for device applications, can only be measured in solution. This highlights a requirement for understanding the solvent effect on hyperpolarizabilities. In this work we will investigate methods for calculating hyperpolarizabilities which can be directly compared to solution-phase measurements.

# 106 THE POTENTIAL ENERGY SURFACE OF THE $(H_2)_2$ DIMER

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An extended geminal model has been applied to calculate the potential energy surface of $(H_2)_2$ within the rigid rotor approximation. By adopting a [8s,4p,2d] uncontracted Gaussian type basis set and the numerical model EXRHF3, the total electronic energy has been calculated for 16 different internuclear distances from 3 to 12 a.u., and 7 relative orientations for each distance. An isotropic well depth of 98.3 μHartree is obtained. The most reliable experimental estimate of the well depth is 108 μHartree. An estimation of the errors due to basis set superposition error, truncation errors related to the electron correlation approach, adoption of an incomplete basis set, and the rigid rotor approximation, yields roughly 6 μHartree. It is argued that the residual difference, between the semi-experimental potentials and the ab initio potential is likely to have its origin in the regularising assumption used for the former.

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## WAVE PACKET PROPAGATION IN A DISCRETE VARIABLE REPRESENTATION USING THE SPLIT OPERATOR METHOD FOR MOLECULE-SURFACE SCATTERING CALCULATIONS.

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A wave packet propagation method in a discrete variable representation (DVR) is described in the context of a molecule-surface scattering problem. Both second and third order split operator methods are used for the propagation of an initial Gaussian wave packet. Calculations were performed for an $N_2$-flat surface scattering situation. S-matrix elements and transition probabilities were extracted from the final wave packet. The second and third order split operator propagators are compared for efficiency. We believe that the DVR-split-operator combination will be a method of choice for the treatment of more complex time-dependent problems.

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## AROMATICITY STUDIES USING THE SHAPE OF THE ELECTRON DENSITY

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Some organic compounds are stabilized by the formation of delocalized $\pi$ systems. In special cases, these $\pi$ systems meet a number of criteria that make them "aromatic". Aromaticity is an important concept related to the maximum degree of stabilization obtainable by $\pi$ delocalization. There has been several attempts at quantifying it in terms of energetic, geometric, diamagnetic, and electronic criteria. Interpretations using field-theoretical descriptions of phase transitions of $\sigma$-$\pi$ electrons have also been given.

In this communication, we propose a new approach which is based on the study of the different curvature properties of electronic isodensity contours for aromatic or nonaromatic compounds. A large series of organic cyclic molecules with different heteroatoms is explored.

## 113 ON A MOMENTUM-SPACE VERSION OF DISSIPATIVE WAVE MECHANICS

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In wave mechanics an appropriate description of a system under the influence of a linearly velocity dependent frictional force can be given by a nonlinear Schrödinger equation (NLSE) with logarithmic nonlinearity. However, the particular logarithmic form of the dissipative nonlinear frictional term in the NLSE is connected with the definition of the momentum- or velocity-operator in position-space. Therefore, in momentum-space this form of the NLSE is no longer correct to describe the same physical situation. This can be seen e.g. from the fact that, in contrast to the linear case, the Fourier transform of the solution of the NLSE in position-space does not fulfil anymore the logarithmic NLSE in momentum-space. It will be shown that, using results obtained from the theory in position-space, it is possible to find a form of the nonlinear dissipative frictional term which is valid in position- as well as in momentum-space. Using this form, the NLSE looks like a diffusion equation with complex diffusion coefficient, i.e. a combination of a diffusion and a Schrödinger equation. The solutions of this NLSE in momentum-space and connected time-dependent invariants will be discussed.

## 114 COMPARISON OF COUPLED CLUSTER RESULTS WITH A HYBRID OF HARTREE FOCK AND DENSITY FUNCTIONAL THEORY

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The performance of a hybrid of Hartree-Fock (HF) and density functional theory (DFT) is tested on a set of "pathological" quantum chemistry problems for which accurate coupled-cluster results are available. These involve, the classical barrier height and exothermicity of the $F + H_2 \rightarrow FH + H$ reaction, the activation energy of the "triple-whammy" dissociation of *s*-tetrazine, the spectroscopic constants of $Cr_2$, the equilibrium structure of $C_3^+$, and the electron affinity of the oxygen atom. The DFT results are obtained from large gaussian basis sets HF densities in conjuntion with Becke's gradient corrected exchange functional and Lee, Yang and Parr's correlation functional. The kinetic, electron-nuclear and classical electron-electron Coulomb terms are obtained from the HF procedure. In general, the predictions of this BLYP model are in qualitative good agreement with the more sophisticated coupled-cluster results.

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ACCURATE CALCULATION OF RELATIVISTIC EFFECTS ON MOLECULAR PROPERTIES OF $AU_2$

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All electron LDA calculations on $Al_2$ and $Au_2$ molecules have been carried out using numerical basisfunctions. In order to get accurate values of the total energy all approximations made for the calculation of the electronic potential have been taken into consideration. A very hight accuracy was achieved using a special transformation in elliptic hyperbolic coordinates for the calculation of the matrix elements. Some calculations were repeated using a Frozen Core approximation. The relativistic effects on molecular properties were studied very precisely. All results are in good agreement with other theoretical and experimental values.

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AVERAGE OF CONFIGURATION IONIZATION ENERGIES, ELECTRONEGATIVITIES AND HARDNESSES

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Neutral, acid and base electronegativities and acid and base hardnesses were calculated for the elements of the $2p^n$ and the $3d^n$ configuration from empirical Average of Configuration (AoC) data (1). Empirical AoC group electronegativities and hardnesses were computed using the SGOBE (2) and the LEGO (3) programme and the empirical AoC data. The results compared well with the Kostyk (4) theoretical AoC density functional results for the SPPP and the $sp^3$ states. The empirical AoC results were also comparable to the Todd (5) semi-empirical results except for elements containing lone pairs. A Grignard reaction was predicted from the empirical AoC hardnesses using the Hard-Acid Soft-Base theory.

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# INVESTIGATING HIGHLY EXCITED VIBRATIONAL STATES OF ACETYLENE

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The highly excited vibrational states of acetylene are variationally calculated using the surface of S. Carter *et al.*[1] The energy regime of interest is near the energy threshold for isomerization of acetylene to vinylidene. We have calculated Franck–Condon overlaps in order to simulate both the SEP experiments of Yamanouchi *et al.* on the highly excited states of acetylene[2] and the photodetachement experiments on the vinylidene anion of Ervin *et al.*[3]

We derive our Hamiltonian using the method of Kolos and Wolniewicz with the exception that we constrain the molecule to lie in a plane.[4] Our coordinates, which are similar to those of Holme *et al.*,[5] lead to an approximate separation between the stretching and bending degrees of freedom. We take advantage of this separation using an adiabatic representation. A fully coupled calculation in the adiabatic representation is then accomplished, allowing us to calculate vibrational wavefunctions and energies near the threshold of the acetylene–vinylidene isomerization.

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# MULTIMODE APPROACH TO HYDROGEN TUNNELING

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A procedure is developed to improve the quantitative evaluation of hydrogen transfer rates in polyatomic molecules and solids. The aim is to introduce a dynamical model that includes explicitly all vibrations participating in the transfer. This aim favors adoption of the Golden -rule approach, since it treats all vibrational modes equally. To simplify the resulting multidimensional transfer integrals, two basic assumptions are introduced: 1) adiabatic separability of the hydrogen modes directly involved in the tunneling from the other modes ("fast flip" approximation), and 2) negligible anharmonicity of these modes. The number of effectively participating modes can then be reduced drastically by transformation to an appropriate local representation which allows analytical integration over most of these other modes. Those that remain involve vibrations of the atoms between which the hydrogen is transferred. Their frequency, reduced mass and displacements are expressed in terms of the harmonic force field of the system before and after transfer and can be unambiguously evaluated if these force fields are available. These modes replace the empirical effective modes used previously. The theory is applied successfully to single hydrogen transfer in dimethylglyoxime and double hydrogen transfere in porphine.

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## COMBINING DYNAMICS WITH TRANSITION STATE THEORY; PROTON TRANSFER IN A MODEL OPIATE-RECEPTOR SYSTEM

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A unified approach to proton transfer (PT) is proposed based on combined TST corrected for tunneling (TC-TST) and dynamic Golden rule (GR) method. It is aimed at semi-quantitative analysis of the (tunneling) dynamics of proton transfer in real polyatomic systems. Input parameters of the method are spectroscopic and geometrical data about the initial and final products available from experiment or semiempirical quantum-chemical calculations (MNDO, AM1, MNDO/H) often being the only tool for analysis of such systems. The only adjustable parameter of the GR method, the value of the electronic coupling driving the transition, is reconstructed from the requirement that the results of the GR and TC-TST methods should match at thigh temperatures. The proposed approach also allows control and possible improvement of the barrier height results of the MNDO, AM1, MNDO/H methods, which are known to overestimate the reaction barrier height of hydrogen and proton transfer, and can distort the picture of the overall kinetics when applied to real systems of interest (e.g. photochemically or biologically active systems where PT is a common elementary step).

As an illustration, the method can be applied to estimate the relative ability of various compounds to activate μ-opiate receptors. Thus, for a model complex formed by protonated morphine (with equatorial N-methyl) and a μ-opiate receptor assumed to be a protein, the rate constant of PT is evaluated. According to our results, this process occurs with rate constant $\cong 10^8\ s^{-1}$, for an agonist such as morphine.

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## BROADENING FACTORS IN UNIMOLECULAR RATE THEORY

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The broadening factor representation of fall-off behavior of unimolecular rate coefficients as a function of pressure is essentially an expression of deviations from a referential strict Lindemann fall-off curve. There are advantages in expressing the broadening factor as a function of a variable u which is a bounded function of pressure. As a function of u, F has a relative minimum and is always concave upward. The important features of F(u) are therefore the location $u_{min}$ and the value $F(u_{min})$ of this minimum. Calculations of F were carried out for an extension of the Kassel model in the strong collision limit and in the weak collision case with the energy transfer probabilities being those of the exponential down model. Also in the strong collision limit, calculations based on standard RRKM theory and on flexible transition state RRKM theory were performed. In the strong collision limit the magnitudes of $u_{min}$ and $F(u_{min})$ and their temperature dependences are interpretable in terms of the energy dependences of transition state sums of states and reactant molecule densities of states. The effect of weak collisions is to shift $u_{min}$ in the positive direction and to decrease $F(u_{min})$.

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## MINDO/3 CYCLIC-CLUSTER CALCULATIONS OF THE RELATIVE STABILITY OF SILOXENE STRUCTURES

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Siloxene $(Si_6O_3H_6)_n$ is postulated to exist in planar, ring and chain structures. We have applied MINDO/3 in cyclic-cluster calculations to estimate the relative stability of these structures, and their electronic band structures. These are related to the luminescent properties of siloxene and porous silicon.

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## A THEORETICAL STUDY OF THE BONDING IN TRANSITION-METAL- LIGAND CATIONS

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The nature of the bonding of the first- and second- row transition metal ions to a variety of ligands is examined using a theoretical treatment that includes correlation energy. For both acetylene and ethylene ligands the ions on the left side of the row insert into the $\pi$ bond to form a three membered ring. On the right side of the row the bonding is electrostatic. The trends in the binding energies for both ligands are discussed. We also consider the interaction of one and two ammonia molecules to the first-row transition metal ions at the modified coupled pair functional (MCPF) level. While the bonding is predominantly electrostatic, other factors such as $4s4p$ or $4s3d\sigma$ hybridization and $4s$ to $3d$ promotion on the metal contribute to determining the ground state and the magnitude of the binding energy.

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ELECTRONIC STRUCTURE OF 1,3 DIPOLAR CYCLOADDITIONS USING THE LOCAL AND NONLOCAL SPIN DENSITY. Carlos Sosa and Jan Andzelm[+] Cray Research Inc., Eagan MN 55121, Jim Blake and Bert L. Chenard, Pfizer Inc., Groton CT 06340. Spin-polarized Local Density (LSD) methods have been applied to study 1,3 dipolar cycloadditions for fulminic acid plus acetylene, fulminic acid plus ethylene, fulminic acid plus nitroethylene, fulminic acid plus 1,3 butadiene and nitrone plus ethylene. Cartesian Gaussian DZP were used for all the calculations. Single point Non-local corrections have been applied using the LSD geometries to compute the relative energies of all reactants, transition structures and products. Vibrational frequencies were computed numerically by differentiating analytical first derivatives of the energy. It has been found that the NLSD approach brings significant improvements over the LSD barrier heights in most of the 1,3 dipolar cycloadditions investigated in this study.

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THE RELATIONSHIP BETWEEN THE HOMO ENERGIES AND THE EXPERIMENTAL pKa's IN BICYCLIC AZINES : AN AB INITIO STUDY.

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Basicities of nitrogenated compounds have played a prominent role in the development of the chemical reactivity in physical organic chemistry. For example, the N atom basicities, reflected in the experimentally pKa's values, have been used to interpret the chemical behaviour in azines.

In this work, an *ab initio* SCF-MO procedure have been used in order to interpret the origin of the basicities pattern observed in a series of bicyclic azines: I) Benzodiazine isomers (cinnoline 12BD, quinazoline 13BD, quinoxaline 14BD and pthalazine 23BD) and II) Naphthyridine isomers (15N, 16N, 17N, 17N, 18N, 26N and 27N), quinoline 1AN and isoquinoline 2AN.

We have found that exists a lineal relationship between the pKa's values and the energy of the High Occuppied Molecular orbital $\varepsilon$(HOMO), with correlation coefficient of 0.99 for molecules of group I and 0.97 for molecules of group II, respectivelly.

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PARALLEL FULL-POTENTIAL LINEARIZED AUGMENTED-PLANE-WAVE CALCULATIONS OF SILICA SODALITE. Mark S. Stave, Pacific Northwest Laboratory,* PO Box 999, Richland, WA 99352

An implementation of a total-energy full-potential linearized augmented-plane-wave method for bulk solids on parallel computers is described. Performance analysis in terms of the efficiency and the scalability of the algorithm will be provided for both clusters of work stations and massively parallel supercomputers such as the Intel Touchstone delta machine. The electronic structure and physical properties of silica sodalite, a prototypical zeolite, are examined and comparisons to periodic Hartree-Fock calculations are presented.

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## MOLECULAR PROBLEM: QFT APPROACH

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The problem of electron correlation energies in molecular systems usually has been treated through different approximation schemes within the Hamiltonian formalism. Here a different pathway is taken: a mean field many-body theory is presented which encompasses the QED framework and a functional integral approach, to render an alternative formulation. The coherent state partition function of a many-electron system represents the starting point of a quantum field theoretical development, which is shown to lead to a simple and physically transparent picture of correlation for a system of charged fermions in an external potential, or inhomogeneous electron gas subject to the nuclear Born-Oppenheimer field.

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## LARGE-$D$ LIMIT FOR CORRELATION METHODS IN ATOMS

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Insight into various correlation methods can be obtained by using models which exploit the simplicity of limits associated with the spatial dimension $D$. Particularly simple is the $D \to \infty$ limit for atoms, which can be treated analytically both with and without correlation for any atom or ion. We utilize a model based on this limit which yields correlation energies in good agreement with known values ($\pm 20\%$). For neutral atoms with $Z \leq 100$ we have so far computed full, IEPA and MP correlation energies, the latter through 7th order; these calculations make no reference to basis or configuration spaces. We find that IEPA overestimates the CE by 16–20% for $Z \geq 10$, while the MP series always converges in an oscillatory fashion. For two-electron atoms we have carried the analysis further to treat the MP, CI, and CC methods using minimal basis and configuration spaces. The dimensional limits tends to magnify, and thereby shed light on, certain problematic aspects of conventional correlation treatments. For example, many individual MP diagrams diverge as $D \to \infty$, and any finite CI yields a vanishing correlation energy as either $D \to \infty$ or $D \to 1$. However, the complete sum at each order of perturbation theory remains finite and realistic, as do certain infinite-order partial sums, such as the ladder sum. Finally, the CC approach is also severely limited by basis set trunctation, though a generalization of the concept of cluster operators suggested by the large-$D$ treatment removes this limitation.

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## ANGULAR DEPENDENCE OF HYDROGEN BOND STRENGTH IN SEVERAL COMPLEXES INVOLVING HYDROGEN FLUORIDE

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Angular dependence of hydrogen bond strength in $NH_3 \cdot\cdot HF$(1), $HF \cdot\cdot HF$(2), $H_2O \cdot\cdot HF$(3), $H_2CO \cdot\cdot HF$(4) and $H_2CO \cdot\cdot NH_3$(5) are calculated with 6–31 G** SCF method assuming linear hydrogen bond and fixed bond lengths. The range of hydrogen bond angle with respect to the main axis in the donor molecule is searched such that the hydrogen bond strength remains at least 70% as strong as that in the most stable conformation. 1 shows a narrow range of bond angle of $32^0$. 2 shows a wide angle range of $90^0$. 3 shows a wide angle range of $90^0$ along the plane bisecting $H_2O$ and a narrow angle range of $38^0$ in the plane of $H_2O$. Both 4 and 5 show an intermediate angle range of $70^0$. The implication of these results for structures of many hydrogen bonded clusters will be discussed.

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# INDUCED ROTATION BARRIER

# IN BENZOCYCLOBUTANECHROMIUM TRICARBONYL

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Rotation barriers in a series of centrally bound Benzocyclobutanechromium tricarbonyl systems are studied by extended Hückel method. The bond population difference (ΔBP) between the long C–C bonds and short ones in the distorted arene ring correlates well with the rotation barrier. Obviously, the ΔBP value measures directly the decrease in arene bonding capability with the chromium during $Cr(CO)_3$ rotation. Its magnitude is dependent on the extent of arene distortion and the strength of the antiaromaticity effect from the π bond of annelated four–membered rings.

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# FUNDEMENTAL WIGNER UNIT SUPEROPERATORS DEFINING $\mathcal{S}_n$-YAMANOUCHI $|(\tilde{i}_1-\tilde{i}_n)kqv>>$ BASES AS AN ASPECT OF $\delta_1$-BOSON PATTERN ALGEBRA OVER $\{\tilde{H}_v\}$ CARRIER SPACE DEMONSTRATING CO-OPERATIVE EFFECTS OVER LIOUVILLE SPACE FOR MQ-NMR CLUSTERS

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$\mathcal{S}_n$-scalar invariants over a field applied to the Liouville recoupling $v = \{.\}(k_1-k_n)$ term provide a route to demonstrate simple reducibility of the $\tilde{H}_v$ carrier subspaces pertaining to Liouvillian mapping, as a part of an augmented boson algebra which is itself an aspect of $\{\mathcal{J}_\pm, \mathcal{J}_0\}$ (superoperator) Heisenburg algebras; these are important for the way in which they characterise the structure of multiple-quantum NMR(MQ-NMR) spin clusters under SU2 × $\mathcal{S}_n$ and their coherence transfer networks, or associated spin dynamics.

Both the formulation of Liouvillian Yamanouchi bases in terms of fundemental Wigner unit superoperators over suitable pattern bases and the inherent nature of combinatorial number partitions, or p-tuples derived from specific recoupling v components, provide rather direct demonstrations of cooperativity for $D^k(\tilde{U}) \times \Gamma^{[\lambda]}(v)$ irreps under SU2 × $\mathcal{S}_n$ duality. Hence, the distinctive v recoupling aspect of Liouvillian mapping formalisms provides for the reduction of $\tilde{H}$ carrier space to $\{\tilde{H}v\}$ subsets, each component of which spans some simply-reducible set of irreps, $\{[\lambda]\}$- in part a consequence of inherent properties of v as a number partition having a specific $\{[\lambda]\}$ expansion.

The work reported here supplements discussions[1] of δ-boson quasi-particles over Liouville space, in context of refs.[2-3], and of expansion of inner tensor products over $\{[\lambda]\}$ and expansions of $\mathcal{S}_n$ number partitions as combinatorial p-tuples[4].

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**CHAIN LENGTH DEPENDENCE OF STATIC LONGITUDINAL POLARIZABILITIES AND HYPERPOLARIZABILITIES IN LINEAR POLYYNES.**

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Ab initio calculations of the static longitudinal dipole polarizability $\alpha_L$ and second dipole hyperpolarizability $\gamma_L$ are reported for the linear $C_{2n}H_2$ polyynes up to $C_{44}H_2$. A relatively small basis set that provides a reasonable description of these longitudinal properties, but not the corresponding transverse ones, is found. Basis set requirements are shown to diminish as the chain length increases. The values per acetylenic linkage, $\alpha_L/n$ and $\gamma_L/n$, converge very slowly with chain length; they are extrapolated to the infinite chain limit.

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PATH INTEGRAL CALCULATIONS WITH QUASI-ADIABATIC PROPAGATORS: EXACT QUANTUM DYNAMICS OF IVR IN MODEL HYDROCARBON CHAINS

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The quantum dynamics of CH relaxation in model linear hydrocarbon chains is studied using discretized path integrals with quasi-adiabatic propagators. The Hamiltonian in normal mode coordinates corresponds to a system coupled to a bath of harmonic oscillators. The time evolution operator is expressed as a path integral over the system coordinate with a one-dimensional propagator for a rescaled system Hamiltonian (which corresponds to dynamics along the adiabatic path) times a non-local influence functional which accounts for non-adiabatic effects. In this formulation, convergence of the discretized path integral is achieved with a very small number of time slices, and thus the path integral can be evaluated by quadrature using roughly 4 grid points for each node of the initial wavefunction. We report accurate quantum mechanical calculations of the survival probability for the v=5 and v=8 initial states of $HC_6$ and compare them to the results obtained from classical trajectory calculations.

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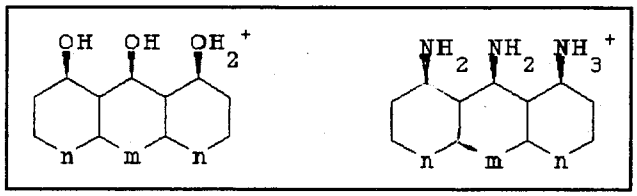
HYDROGEN BONDING AND PROTON TRANSFER IN POLYCYCLIC TRIOLS AND TRIAMINES. Carl Trindle and Felix Fernandez-Alsonso. University of Virginia, Charlottesville Virginia, USA 22903.




Channels permitting the passage of ions through hydrophobic media are of significance in a variety of biological processes. Proton transfer is probably aided by chains of hydrogen bonds. As a model of such chains identified in organic systems, we study the structure and vibrational modes of fused-ring systems (see sketch, at right) which display a variety of enforced geometries for hydrogen bonding and proton transfer. We follow the proton transfer through the reaction path, and estimate activation parameters. The computational model is MNDO, with occasional small-basis *ab initio* supplements.

# 134

PROTON ACCESSIBILITY AND ELECTRONIC STATES OF *p*-QUINONE DIANIONS

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The chemistry of two-electron reduced dianions of organic molecules has received increased attention in recent years from both theoreticians and experimentalists. The purpose of this paper is to get a deeper insight into the problem how active dianion species are as electron donors (proton acceptors), with the aid of both determining the formation constants of hydrogen-bonded complexes of *p*-quinone dianions ($PQ^{=}$) and investigating their electronic states.

Formation constants ($K^{=}$) of two-point hydrogen-bonded complexes of $PQ^{=}$ with $CH_3OH$ (1:2) have been successfully determined to be of the order of $10^4$ $dm^6$ $mol^{-2}$ by means of the nonaqueous electrochemical method. Partial geometry optimization calculations (HF/4-31G) of the hydrogen-bonded complexes show that the hydrogen-bond distance in the $PQ^{=}$ complex with $CH_3OH$ is much shorter than that in the PQ complex, and the atomic bond population is large enough to be considered as a value of a weak covalent bond. The formation energy of the $PQ^{=}$ complexes have been estimated as 33 kcal $mol^{-1}$ per hydrogen bond. These calculation has revealed that the bond of $PQ^{=}$ with $CH_3OH$ is remarkably strong compared to usual hydrogen bonds involving O···H-O, and clearly explains the origin of the quite large observed $K^{=}$ values, considering enthalpy driven stabilization of a hydrogen bonding. This might well explain that $PQ^{=}$ is easy to abstract protons *in vivo*, and further inspection of this model can give extensive insight into chemical reactions involving dianion intermediates.

# 135

## LCGTO-LDF CALCULATION OF TRANSITION STATES OF CHEMICAL REACTION : THE REACTION OF PENTACOORDINATE ALLYLSILICATE WITH ALDEHYDE

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Local density functional (LDF) calculations were done to locate some transition state structures of the reaction of allylsilicate with formaldehyde. In the previous study we performed ab initio Hartree-Fock calculations to determine the transition structures and showed that the cyclic form is preferable to the linear form as a transition structure of the reaction [1]. Here we have re-investigated the transition states by the LDF calculations. The transition structures and their energies will be presented with those obtained by ab initio Hartree-Fock method and second-order Møller-Plesset perturbation method.

1. M. Kira et al. Chem. Lett. 387-390 (1991)

# 136

## WAVEPACKET PROPAGATION TECHNIQUE FOR CALCULATING BOUND-STATE ENERGY LEVELS OF POLYATOMIC MOLECULES: ArHCl

Yeu Wang, Tucker Carrington Jr. and Gregory Corey, Department of Chemistry, Université de Montréal, C.P. 6128, succursale A, Montréal, Québec, Canada, H3C 3J7

A recently proposed Fourier resolution technique (Neuhauser J.C.P. 93, 2611 (1990)) is extended to multidimensions. By propagating an initial wavepacket in time and Fourier transforming from time to energy we obtain basis functions tailored to a given energy range. Using these special basis functions we are able to calculate accurate energy levels by diagonalising very small matrices. A Chebychev polynomial expansion is used to propagated the wavefunction on a two-dimensional grid on which the potential energy operator is diagonal. The action of the operators associated with the kinetic energy of the van der Waals stretch and the bend on the wavefunction are evaluated with an fast Fourier transform and a discrete-variable-representation based Gauss-Legendre transform, respectively. This method is tested on Hutson's H6 ArHCl potential, for $J=0$.

**137**

## THE DISCRETE VARIABLE REPRESENTATION OF A TRIATOMIC HAMILTONIAN IN BOND LENGTH - BOND ANGLE COORDINATES

Hua Wei and Tucker Carrington Jr., Department of Chemistry, Université de Montréal, C.P. 6128, succursale A, Montréal, Québec, Canada H3C 3J7

The discrete variable representation (DVR) is used to calculate vibrational energy levels of $H_2O$ and $SO_2$. The Hamiltonian is written in terms of bond length - bond angle coordinates and their conjugate momenta. It is shown that although these coordinates are not orthogonal and the appropriate kinetic energy operator is complicated the discrete variable representation is quite simple and facilitates the calculation of vibrational energy levels. The DVR enables one to use an internal coordinate Hamiltonian without expanding the coordinate dependence of the kinetic energy or evaluating matrix elements numerically. The accuracy of previous internal coordinate calculations is assessed.

**138**

## A MICROSCOPIC THEORY OF HIGH-PRESSURE PROCESSES: HOW DOES HIGH PRESSURE AFFECT A POTENTIAL ENERGY SURFACE?

Noham Weinberg* and Michael Basilevsky#, *Department of Chemistry and Biochemistry, Simon Fraser University, Burnaby, B.C. V5A 1S6, and #Karpov Institute of Physical Chemistry, Moscow , Russia

A new approach to the microscopic description of high-pressure processes has been formulated where the pressure influence on a chemical reaction system is represented by a pressure-dependent effective medium potential. The method has been applied to discuss reaction kinetics and chemical equilibria under pressures from 0 to 45 kbar. It was found that under pressures exceeding 50 kbar the deformation of an original potential energy surface caused by pressure can be so strong that the reaction becomes barrierless. It was also shown that at high pressures the reaction kinetics can demonstrate considerably non-equilibrium (not obeying transition state theory) behavior as a result of increased solvent viscosity.

**139**

## A NOVEL AND HIGHLY EFFICIENT ALGORITHM FOR THE THEORETICAL CONFORMATION ANALYSIS OF CYCLIC STRUCTURES

Noham Weinberg and Saul Wolfe, *Department of Chemistry and Biochemistry, Simon Fraser University, Burnaby, B.C. V5A 1S6*

A series of geometrical constraints has been devised which allows a search for the conformations of cyclic structures to be performed only over cyclic subspace of the conformational space of their acyclic parents. Additional constraints lead to an even smaller subspace represented by those cyclic conformations in which unfavorable nonbonded contacts are avoided. When these constraints are imposed, stochastic search procedures can rapidly identify those starting structures that lead, following energy minimization, to all significant low-lying energy minima, as well as the transition states that separate these minima. The strategy has been applied successfully to hydrocarbons, cyclic polyethers, lactones, cyclopeptides and other cyclic compounds.

**140**

THE DECOMPOSITION OF BI- AND TRI- CYCLIC TETRAZEPINONES: A MOLECULAR MECHANICS/SEMI-EMPIRICAL M.O.

C. I. Williams and M. A. Whitehead, Department of Chemistry, McGill University, 801 Sherbrooke Street, West, Montreal, P.Q. Canada H3A 2K6.

The decomposition behaviour of Bi- and Tri- cyclic tetrazepinones is being studied with both the PCMODEL molecular modeling package, and the AMI/AMPAC semi-empirical M.O. package. It is found experimentally that the decomposition is greatly influenced by substituents on the aromatic ring. In particular, electron withdrawing substituents give stable tetrazepinones, which decompose upon base catalysis to yield bicyclic imides, while electron donating substituents give unstable tetrazepinones, which spontaneously decompose to yield bicyclic triazenes. The following work correlates AMI/PCMODEL generated heats and free energies of formation, geometries, reaction intermediates and transition state barriers with experimental results. The results of this work will be used to predict the stability of tetrazepinones which so far have not been synthesized.

**141**

A DIVIDE-AND-CONQUER APPROACH TO LARGE MOLECULAR AND SOLID-STATE SYSTEMS. Weitao Yang, Department of Chemistry, Duke University.

A new density-functional approach for calculations of ground states of many-electron systems is presented. Without solving the Kohn-Sham orbital equations, the method divides a system into subsystems in physical space and determines the electron density for each subsystem. Various molecular and solid-state calculations have been carried out to demonstrate the accuracy of the method, and to show its promise for calculations of large systems.

**142**

APPLICATION OF THE FINITE ELEMENT METHOD TO SOLVE THE TIME DEPENDENT HARTREE-FOCK EQUATION IN AN INTENSE LASER FIELD

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A finite element approach is used to solve the time dependent Hartree-Fock equations for atoms in the presence of time dependent laser field. The method enables one to observe clearly the changes of the physical properties (energies, probabilities,dipole moments and so on) with time and to obtain the accurate ionization rates, harmonic generation and high order nonlinear optical polarizabilities $\chi_{2n+1}(0\leq n\leq 3)$ in a nonperturbative way. Furthermore, the method is easily adaptable to treat short time pulses and enables one to establish limits of perturbative approaches.

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**SUPPLEMENTAL POSTER LIST**
**(late registration and/or possible presentations)**

143. Gill, Peter M.W. — "An Exact Exchange Functional for the Hydrogen Atom"

144. Hamilton, Ian — "Energy Stepping Close to Dissociation for HF in a Moderate Laser Field"

145. Johnson, Benny G. — "The Performance of a Family of Density Functional Methods"

146. Seminario, Jorge M — "Comparison of Energies: DFT Versus Precise *Ab Initio*"

147. Sanchez, Mardonio — "Simulation of Liquid-Vapor Equilibrium"

148. Martínez-Magadán — "On the Importance of the $\sigma^{*2}$ Doubly-Excited State of $H_2$ in the M (Metal) + $H_2$ Reaction"

149. Zereg, Moussa — "Computation of Quantum Resonance Widths via Golden Rule Like Formula. Application to the Stark Effect"

150. Zamora, Mardonio — "Simulation of Liquid-Vapor Equilibrium"

151. Ulitsky, Alex — "Locally Enhanced Sampling with a Binary Collision Term: Application to Thermal and RElaxation Properties of Mono- and Diatomic Molecules in Rare-Gas Clusters"

152. Simmerling, Carlos — "Simulation of Protein Dynamics on the Secondary Structure Level"

153. Safont, V. S. — "Modeling Molecular Mechanisms in Active Centers of Enzymes"

154. Lim, Tiong-Koon — "Temperature Dependent Holl All Mixing Coefficient Method for Binary Mixed Electrolytes"

155. Jayatilaka, Dylan — "A New Open-Shell Perturbtion Theory"

156. Grigoras, Stelian — "Structure Elucidation of Polydiethynylsilane for NLO Applications, from Theoretical Simulation and Interpretation of Experimental Data"

157. Andrés, J. — "An Ab Initio Study of the Local Geometry of $M^{n+}$ ($V^{4+}$, $V^{5+}$, $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Mg^{2+}$, $Ca^{2+}$): $ZrSiO_4$, $ZrO_2$, $TiO_2$"

158. Singh, Sar Nath — "Electronic Structure of Cumulenes"

159. Nath Singh, S. — "Molecular Rydberg Excitations in Some Acids"

160. Seniuk, Andrew — "Degrees of Symmetry in Lattice Animals"

161. Jack, D. B. — "Localised H-atom Scattering in the HBr(ad)/LiF(001) + hν System"

162. Yuan, Jian-Yang — "Couette Flow in Colloidal Suspensions"

143 AN EXACT EXCHANGE FUNCTIONAL FOR THE HYDROGEN ATOM

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We have constructed a gradient-corrected exchange functional which, when used in a self-consistent Kohn-Sham procedure, gives the exact Schrödinger energy and density for the hydrogen atom. Surprisingly, our functional bears little resemblence to any of the commonly used exchange functionals. In particular, its asymptotic behaviour is NOT consistent with the 1988 functional of Becke implying, thereby, that Becke's derivation is flawed.

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ENERGY STEPPING CLOSE TO DISSOCIATION FOR HF IN A MODERATE LASER FIELD

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For this system, although the coupling of HF to the laser field is small and continuous, the compensated energy of HF does not simply drift. Instead, the compensated energy changes in a stepping fashion and there are time intervals in which $E_c(t)$ is essentially constant.

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THE PERFORMANCE OF A FAMILY OF DENSITY FUNCTIONAL METHODS

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The performance of six local and gradient-corrected density functional methods is examined for a set of 32 small neutral molecular systems. The LCAO Kohn-Sham orbitals were obtained using the 6-31G* basis set, without employing any auxiliary fitting procedures. Equilibrium geometries, dipole moments, harmonic vibrational frequencies, and atomization energies were calculated by each density functional method, as well as by Hartree-Fock, MP2, and QCISD using the same basis. Comparisons are made with experimental results for each method.

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# COMPARISON OF ENERGIES: DFT VERSUS PRECISE *AB INITIO*

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## Abstract

We have calculated absolute energies for a large number of molecules by density functional theory in the local approximation (LDA) as implemented in the procedures *DMol*[1] and *deMon*[2]; and in the nonlocal (NL) density approximation as implemented in the procedure *deMon*. All those energies have been compared to very precise *ab initio* calculations obtained by the Gaussian 2 (G2) procedure[3]. We have found that the local approximation yields very poor energies but their errors follow a linear trend with respect to the total energies. Therefore, the correction of local energies is straightforward. However, the non local calculations yield acceptable energies but their deviations from the almost exact values do not follow the linear trend of the local approximation errors. The linear behavior of the local errors makes possible their correction and allows the use of the local methods, which are less demanding in terms of computational resources, to study large molecular systems that cannot presently be treated by *ab initio* methods at a high level of theory. In addition, we have calculated relative energies (atomization, and dissociation) and compared them to the very precise G2 and experimental energies. The reproduction of experimental energies by the corrected local energies is strong indication that exchange-correlation contribution is treated well in the local procedures, except for a substantial but linear correction needed in the density functional. This correction would eliminate most of the overestimation of the binding energies that has been observed in the local methods[4]. Errors in the dissociation energies using the local approximation average to 51.2 Kcal/mol using *DMol*, 21.0 Kcal/mol using *deMon* (disqualifying both local procedures to be used as tools of chemical prediction) and 5.3 using one of the non-local functionals of *deMon* procedure. However, after the linear correction is made to the absolute energies of the local procedures, the average errors are 4.8 and 5.3 Kcal/mol for *DMol* and *deMon* respectively. The G2 reference energies used for calibration have an average error of 1.1 Kcal/mol with respect to precise experimental values.

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[2] D. R. Salahub, R. Fournier, P. Mlynarski, I. Papai, A. St-Amant and J. Ushio, in *Density Functional Methods in Chemistry*, edited by J. K. Labanowski and J. W. Andzelm (Springer, New York, 1991)
[3] L. A. Curtiss, K.Raghavachari,G. W. Trucks and J. A. Pople, J. Chem. Phys 94, 7221 (1991)
[4] J. M. Seminario, M. C. Concha and P. Politzer, ...

147 | SIMULATION OF LIQUID-VAPOR EQUILIBRIUM

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In this work we present liquid-vapor equilibrium curves for atomic and molecular systems calculated by means of Molecular Dynamics and Monte Carlo Methods. For both simulation models, a pairwise interaction potentials was used and in the case of molecular systems the intramolecular interaction was explicitly taken into account. The Molecular Dynamics studies consider an inhomogeneous system in which liquid and vapour coexist and form a well defined interphase. Taking advantage of this, we calculated some properties in the interphase (i.e. surface tension). This method has been applied to small hydrocarbons (methane and ethane) and water, obtaining good agreement with experimental results for liquid and vapor densities.On the other hand, due to the theoretical interest, Canonical and Gibbs ensemble Monte Carlo methods were used to study orthobaric densities of square well fluids for one and two components systems.

148 | ON THE IMPORTANCE OF THE $\sigma^{*2}$ DOUBLY-EXCITED STATE OF $H_2$ IN THE M (METAL)+ $H_2$ REACTION.

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The potential energy surfaces of the M ($Ga^+$, Zn, Ru) + $H_2$ reactions with M in its ground state were obtained through large MRCI + MP2 calculations using double-{ (Zn,Ru) and triple - { ($Ga^+$) gaussian basis sets. For all cases a stable linear H-M-H complex is found (after overcoming a potential energy barrier)which is diabatically related with the M + $H_2$ ($\sigma^{*2}$) fragments. The reaction pathways are discussed in the light of a model previously proposed by us.

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# COMPUTATION OF QUANTUM RESONANCE WIDTHS VIA GOLDEN RULE LIKE FORMULA. APPLICATION TO THE STARK EFFECT

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It is shown that the standard fermi-like golden rules used for calculating the widths of quantum resonances can be derived from various linear approximations of a cumulative distribution function. The simplest one is $\Gamma \sim (\Delta E)^2/W$. This expression involves the dispersion in energy $\Delta E$ of the resonance and the width W of an effective continuum. The above expression gives accurate results when it is applied to the Stark effect of the ground state of the hydrogen atom. The variation of $\Gamma$ as a function of the electric field is understood in terms of the variation of $(\Delta E)^2$. In the whole range of the values of the electric field investigated, from 0.001 to 0.1 atomic units, the width W can be considered as constant.

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# SIMULATION OF LIQUID-VAPOR EQUILIBRIUM

Mardonio ZAMORA

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## LOCALLY ENHANCED SAMPLING WITH A BINARY COLLISION TERM: APPLICATION TO THERMAL AND RELAXATION PROPERTIES OF MONO- AND DIATOMIC MOLECULES IN RARE-GAS CLUSTERS.

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The Locally Enhanced Sampling (LES) which is based on the trajectory bundles [1-2] and the Time Dependent Hartree approximation suggests an efficient way to explore phase space in molecular simulations. Basically, the computational effort is growing linearly (rather than exponentially) with the number of degrees of freedom [3].

In LES we focus our interest on a small part of the system which is of prime interest. At each time step, a number of configurations (say N) is generated for the small part while only one configuration is kept for the rest much larger system [4,5].

It can be shown that within LES approximation the effective temperature [6] and the virials [7] for the enhanced part are N times larger than the rest of the system [6,7]. This violation of the generalized equipartition theorem may have profound effects on the calculations of structural and dynamic properties. In the present study we introduce a variant of LES in which the partition of the density to a product is modified during the dynamics. The coordinate sets assumed separate are reevaluated each time step taking into consideration the presence of hard collisions [7]. Better description of collisional events is therefore obtained.

The LES approximation with the correction for collisions was examined analytically and numerically. The following properties were computed: spatial correlation function, temperature and virials, translational and vibrational (for diatomic) energy relaxation. These properties were examined in Ar clusters, in $I_2$/Ar and in I-Cl/Xe(Kr). Exact, LES and corrected LES results are compared. The spatial correlation function and equilibrium properties such as temperature and virials are better described in the new protocol.

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## SIMULATION OF PROTEIN DYNAMICS ON THE SECONDARY STRUCTURE LEVEL

152

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When visualizing protein structures it is customary to reduce the atomic detail picture to a less comprehensive but clearer picture of secondary structure elements, e.g. helices. A program was initiated to develop simulation methodology for proteins as a collection of effectively rigid helices. The potential of mean force for interactions of helices was calculated for myohemerythrin in [1]. Here we present a stochastic algorithm that makes it possible to simulate the motion of the helices directly. It is based on the SHAKE algorithm and the fact that any rigid body can be fully characterized by at least three point masses with distance constraints (we used four point masses). Hence, in the proposed simulation methodology, each helix is represented by four particles instead of ~400 hundreds atoms, a major reduction in the problem dimensionality. Furthermore, the effective masses are considerably heavier than atomic masses which enables us to use a much larger time step, i.e. in usual MD simulations a 1fs time step is employed, while we are employing 50fs for a time step.

In the poster the algorithm will be discussed in detail and a computational example of the dynamics will be provided for the protein myohemerythrin modeled as a bundle of four helices.

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[2] J.P. Ryckaert, G. Ciccotti and H.J.C. Berendsen, J. Comput. Phys. 23,327 (1977)

153 MODELING MOLECULAR MECHANISMS IN ACTIVE CENTERS OF ENZYMES

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An overview on theoretical studies of reaction mechanisms in active centers of enzymes is presented. In particular, the transition state structures are analyzed and discussed in this context. Selected examples are studied: LADH, Formate Dehydrogenase, Biotine and Rubisco.

154 TEMPERATURE DEPENDENT HOLL ALL MIXING COEFFICIENT METHOD FOR BINARY MIXED ELECTROLYTES

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A temperature dependent Higher Order Limiting Laws (HOLL) All Mixing Coefficient method is developed for the calculation of the activity coefficients of binary mixed electrolytes. The method is simpler and more accurate.

# A New Open-Shell Perturbation Theory

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**Abstract**

A new open shell perturbation theory is described. The method is based on the spatial orbitals from an open-shell restricted Hartree-Fock (RHF) wavefunction, but differs from other approaches in the spin part of the singly occupied orbitals, which has the form

$$\sigma_+ = \frac{1}{\sqrt{2}}(\alpha + \beta)$$

The number of independent parameters in this symmetric spin orbital perturbation theory is much less than in any other theory, leading to significant computational savings. Geometries and frequencies using the method will be presented for selected molecules.

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# STRUCTURE ELUCIDATION OF POLYDIETHYNYLSILANE FOR NLO APPLICATIONS, FROM THEORETICAL SIMULATION AND INTERPRETATION OF EXPERIMENTAL DATA.

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Recently, a novel π - conjugated polymer, polydiethynylsilane (PDES), with excellent nonlinear optical properties has been reported. The structure of several isomeric forms for PDES have been characterized theoretically. The results show that the 4-membered ring structure is the most plausible and some dialkyl,ethynylsilane groups may insert in the backbone of PDES as sequential copolymers. These results were obtained using molecular orbital method at ab initio level (3-21G* modified) and molecular mechanics method with potentials derived from ab initio calculations. Second order polarizability calculations indicate what polymeric structures might provide materials with improved Chi-3 values.

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## AN AB INITIO STUDY OF THE LOCAL GEOMETRY OF $M^{n+}$ ($V^{4+}$, $V^{5+}$, $Fe^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Mg^{2+}$, $Ca^{2+}$): $ZrSiO_4$, $ZrO_2$, $TiO_2$.

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The computation of the electronic structures and equilibrium geometry of an impurity center, $V^{4+}$, $V^{5+}$, $Cr^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Mg^{2+}$, $Ca^{2+}$, in different crystal structures, $ZrSiO_4$, $ZrO_2$, $TiO_2$, is carried out using an extension of the ab initio Perturbed Ion (aiPI) method.

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## ELECTRONIC STRUCTURE OF CUMULENES

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The molecular spectra of cumulenes-hydrazoic acid, isocyanic acid, Keten, diazomethane, carbon dioxide, nitrous oxide, allene, dimethyl cyanamide, ethyl isocyanate, and carbon suboxide have been calculated by the semi empirical RINDO/S method following a C-I procedure. The most prominent valence and Rydberg states as well as the admixture of valence and Rydberg states so calculated have been discussed. In addition, the paper is provided with ionization potentials, S-S and S-T energies, S-T splittings, effect of cumulated double bonds along with their experimental correlations.

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## MOLECULAR RYDBERG EXCITATIONS IN SOME ACIDS

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Rydberg states in some acids like fulminic acid,acetic acid,nitric acid,isocyanic acid and methyl formate calculated under semi-empirical SCF-MO-R INDO/S scheme are presented. The most prominent Rydberg states as well as the admixture of valence and Rydberg states,thus calculated have been discussed. In addition,the paper is provided with experimental correlations for these states.

## DEGREES OF SYMMETRY IN LATTICE ANIMALS

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Andrew SENIUK

A very general lattice (the *Hypercubic Transcendental Lattice*, or HTC) is constructed, for which the nodes are finite subsets of $Z^\infty$ and two such subsets are assosiated by an edge whenever they differ by the presence/absence of a single *cell*. (A cell is simply one vector in $Z^\infty$.)

A sublattice of square-cell *animals* is then extracted from the HTL by removing all nodes whose third or higher component is non-zero, and also removing all remaining nodes which are not animals. (A general animal A can be defined as a set of cells, every pair of which can be interconverted by successive unit changes in their vector coördinates, one component at a time, such that at every step the coördinates still belong to the original set A.)

Finally, a degree-of-symmetry measure for animals is devised, based on the minimum number of lattice edges traversed in reaching the "nearest" animal which contains the desired symmetry element. This may find application in analysing symmetry properties of smooth shapes, since such shapes can be approximated to any degree of accuracy by embedding them in a lattice of appropriate dimensions, and lattice animals lend themselves to comparatively fast computations. Furthermore, it is hoped that a useful measure of the degree of *similarity* of two smooth shapes may be obtained by comparing their composite measures of symmetry.

161 **Localised H-atom scattering in the HBr(ad)/LiF(001) +hν system.** V.J. Barclay, D.B. Jack, J.C. Polanyi, and Y. Zeiri, Dept. of Chemistry, University of Toronto, Toronto M5S 1A1, Canada.
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The angular and energy distributions of 1.1 and 2.6 eV H-atom scattering from a LiF(001) surface are compared for two different sources of hot H-atoms: (1) localised H-atoms produced by the photolysis of HBr molecules adsorbed on the LiF(001) surface; and (2) H-atoms from a beam at the same energy and angle of approach to the LiF(001) surface as in (1). These distributions are the results of classical stochastic trajectories. The calculated angular distributions are compared with experimental distributions [E. B. D. Bourdon *et al.*, J. Chem. Phys., **95**, 1361 (1991)]. The computed effects of changing H-atom energy and surface temperature are also examined; localised scattering becomes increasingly non-specular at lower photon-energies, and broader at higher surface temperatures.

162 Couette Flow in Colloidal Suspensions.

Jian-Yang YUAN , McGill U., dept of Chemistry

We show that in a Couette flow in colloidal crystals formed from suspensions of highly charged and poorly screened spheres the usual Taylor instability is suppressed and two different types of instabilities emerge.

# 11th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

# 11e SYMPOSIUM CANADIEN SUR LA CHIMIE THÉORIQUE

## INTERNATIONAL CONFERENCE INTERNATIONALE

**August 2-7, 1992** **Montréal, Québec**


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# *WELCOME TO MONTREAL*

1) ***The reception on Sunday, August 2, 1992 is on the patio of the Otto Maass Chemistry Building (corner of Sherbrooke and University) from 7:00 P.M. to about 11:00 P.M. Present the ticket for a complimentary drink.***

2) ***Please check and correct your name on the Participants' List. Copies will be available for you on Wednesday.***

3) ***If you are giving a poster, the number in the Conference Book corresponds to the number on the board.***

***I hope the symposium is interesting and stimulating for you and that your stay in Montreal is a pleasant one.***

***Bryan Sanctuary***

***Dennis Salahub***

1. Coed Residences
2. Royal Victoria College
3. Montreal Neurological Inst.
4. Molson Stadium
5. Currie Gymnasium (Athletics)
6. Lyman Duff (Microbiology)
7. Strathcona (Anatomy & Dentistry)
8. Ernest Rutherford (Physics)
9. Foster Laboratory (Physics)
10. James (Administration)
11. Wilson Hall (Social Sciences)
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13. Moyse Hall (Theatre)
14. McConnell (Engineering)
15. MacDonald (Engineering)
16. Frank Dawson Adams
17. McDonald Stewart (Library)
18. Burnside Hall (Math & Computer Sciences)
19. Otto Maas (Chemistry)
20. Strathcona, Pollack (Music)
21. McCord Museum
22. McLennan Library
23. Samuel Bronfman (Management)
24. Redpath Library
25. Redpath Hall
26. Redpath Museum
27. Union (Student Clubs)
28. Bookstore
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30. Stewart (Biology)
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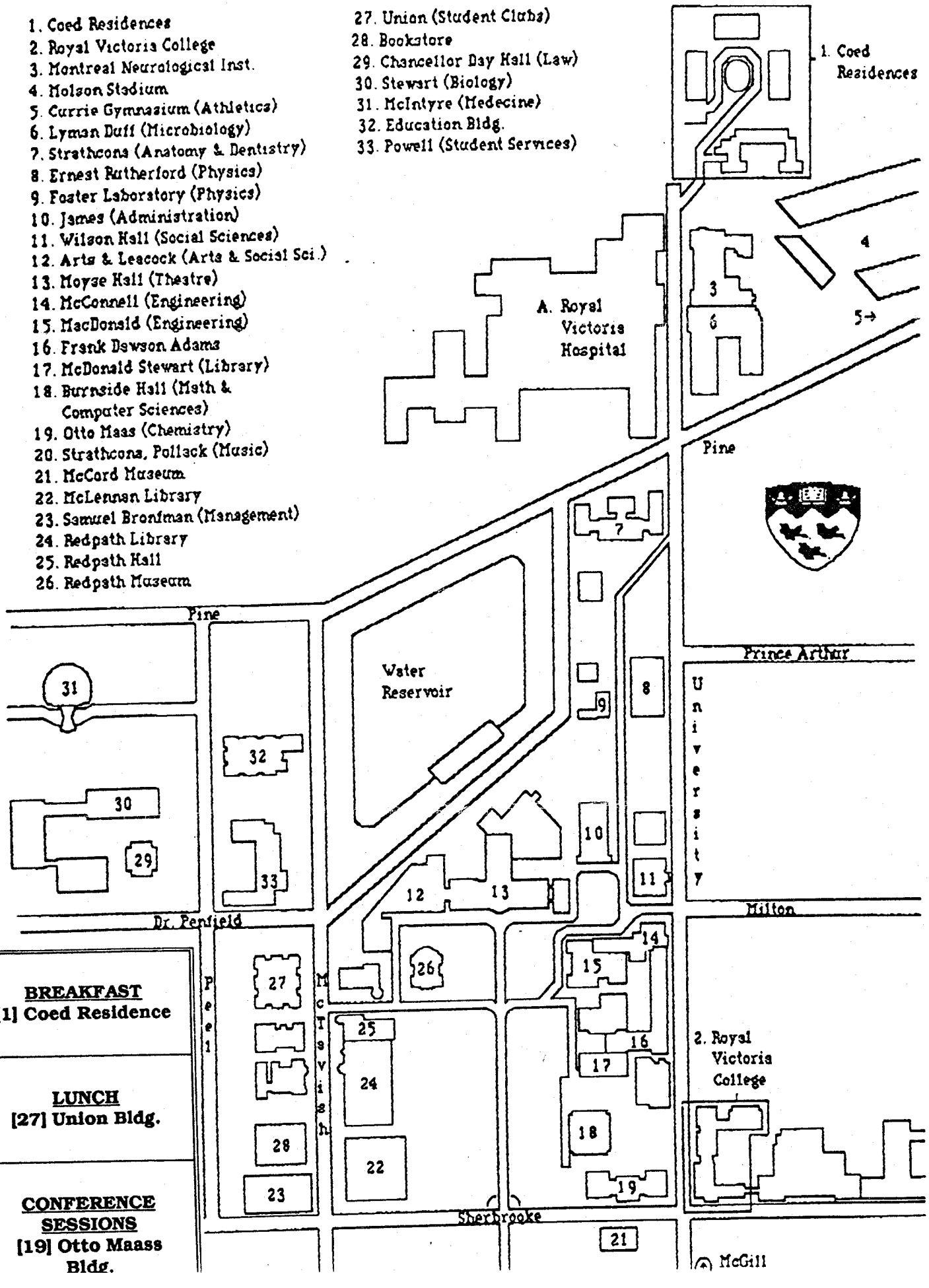


**BREAKFAST**
**[1] Coed Residence**

**LUNCH**
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**CONFERENCE SESSIONS**
**[19] Otto Maass Bldg.**