9th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY
9e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE
INTERNATIONAL CONFERENCE INTERNATIONALE
1986 June 23 - 27 juin
Toronto, Ont.

GENERAL CONFERENCE INFORMATION

The 9th Canadian Symposium on Theoretical Chemistry will be held on June 23-27th, 1986, at Trinity College, University of Toronto.

CONTRIBUTED PAPERS

Contributed papers will be welcome from all areas of theoretical chemistry. All contributed papers will be presented in poster format. Abstracts should be typed on the enclosed sheet in accordance with the instructions given there.

REGISTRATION

The registration fee includes full participation in the conference, the book of abstracts, complementary coffee breaks, and the conference banquet on Thursday evening.

The registration desk will be open from 2:00 p.m. to 6:30 p.m. on Sunday June 22nd, in the front hall of St. Hilda's residence (see enclosed campus map). On Monday, June 23rd, and for the remainder of the week, the registration desk will be open from 8:30 a.m. to 4:00 p.m. just outside the lecture hall (George Ignatieff Theatre).

ACCOMMODATION

University residence, St. Hilda's, Trinity College

If you have requested University accommodation you should go directly to the St. Hilda's College residence, 44 Devonshire Place and go to the Porter's desk at the front entrance. He will then give you the key to your room. A $5.00 deposit is required, which will be refunded when you return the key at the end of the conference.

Park Plaza

The Park Plaza Hotel is situated at 4 Avenue Road (north west corner of Bloor and Avenue Road). Register in the normal way. Room rate is $78.00 single/double.

Co-Chairmen/Co-présidents:

R. Kapral
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University of Toronto
Toronto, Ontario, Canada
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TRAVEL

By Air

Toronto is served by most major airlines and is easy to reach by direct flights from Europe and the United States.

Transportation from the airport is readily available. Airport buses provide a regular direct service to the downtown area. The best bus is the Gray Coach from the Departure level to Yorkdale Station, then take the subway south to Museum, which is close to both the Park Plaza and Trinity College (see map). Cost $4.00. There are always limousines waiting at the Departure level. The cost to the downtown area is approximately $24.00.

By Train

If you are travelling by train to Union Station, it is a short subway ride from there to Museum Station. A single subway fare is $1.00 but it is best to purchase token, 5 for $4.00.

The University of Toronto is located in the heart of the city and is accessible by subway and surface transportation from most parts of the city.

By Car

Travellers who will be driving to Toronto require a driver's licence from any country, which is valid for 3 months. If driving a borrowed car, bring a letter from the owner, and if you are driving a rented car, a copy of the rental contract. Parking is available at the University in the St. George Street parking lot behind St. Hilda's College at the rate of $4.00 per day.

CUSTOMS REGULATIONS

For customs regulations as they apply to visitors entering Canada please consult the nearest Consulate or Embassy of Canada, or write to: Customs and Excise Branch, Revenue Canada, Connaught Building, Mackenzie Avenue, Ottawa, Ontario K1A 0L5.

INSURANCE

Visitors are strongly advised to check that they have complied with all requirements both for entry into Canada and for their return journey.

Visitors are not covered by Canadian Health Insurance Plans. It is therefore recommended that participants arrange their own personal health and accident insurance. This can generally be done in the home country but those wishing to do so may obtain information and application forms for visitor's insurance from Ontario Blue Cross, 150 Ferrand Drive, Don Mills, Ontario M3C 1H6 or by telephone at (416) 429-2661. The rate is $3.00 for single coverage per day and $6.00 for family coverage per day.

General

No responsibility can be assumed for personal accidents, sickness, theft or property damage on behalf of delegates. Delegates are advised to take out insurance as they consider necessary.

PASSPORTS AND VISAS

Participants are strongly advised to determine their individual requirements with respect to entering Canada. Citizens of some countries require non-immigrant visas in addition to passports. Persons from outside the U.S.A. wishing to enter the U.S.A. from Canada should make arrangements before leaving their home country. Multiple entry visas are required if entering Canada and/or the U.S.A. more than once. U.S. citizens do not require passports or visas to enter Canada, but may be asked to prove their citizenship; a birth certificate or voter's registration card is adequate. Registered aliens residing in the United States must have their Alien Registration Cards.

SOCIAL PROGRAMME

There will be a Wine and Cheese Reception on Sunday, June 22nd from 6:30 p.m. to 8:30 p.m. in Seeley Hall, Trinity College, with a cash bar (2 free drinks will be provided by the Symposium).

There will be a free afternoon on Wednesday, June 25th and following tours have been arranged:

- an afternoon excursion to McMichael Art Gallery in Kleinburg, Ontario
- an afternoon excursion to Niagara Falls and Niagara on the Lake
- an evening boat excursion on Lake Ontario with dinner at Captain John's (a boat restaurant moored in Toronto Harbour)

Please indicate on the attached form if you will be attending any of these excursions.

The Symposium Banquet will be held in Stratchan Hall, Trinity College at 7:30 p.m. on Thursday, June 26th and will be preceded by a reception (cash bar) in Seeley Hall at 6:30 p.m. After the banquet there will be a slide show presented by the famous Canadian photographer, Mr. Budd Watson entitled "The Seasons - Georgian Bay".

INFORMATION ON LOCAL CUISINE

Toronto abounds with many excellent restaurants of every kind and description and there is a great selection surrounding University campus, especially for lunches. Dundas Street and Spadina Avenue are in China Town and within easy walking distance of Trinity College if you feel like Chinese food. Bloor Street, Yorkville Avenue and Cumberland Avenue have endless cafes and restaurants and there are also cafeterias on campus if you do not feel like walking. Mrs. McClelland will have a full list of all the restaurants within the area.

SCIENTIFIC PROGRAMME

Invited lectures will be given each morning and afternoon. A detailed scientific programme will be sent to you at a later date. A list of the invited speakers and the titles of their talks is given below:

INVITED SPEAKERS	SUBJECT
R.J. Bartlett	"Analytical Derivative Techniques in Coupled Cluster Approach"
C.W. Bauschlicher	"The Importance of Electron Correlation on Transition Metal Bonding"
E.R. Davidson	"Comparison of Experimental and Theoretical Determinations of Electron Density"
G.W.F. Drake	"Relativistic and QED Effects in Two-Electron Atom and Ions - Comparison of Theory and Experiment"
K.F. Freed	"Renormalization Group Theory of Polymers"
H.Fukutome	"Charactization of Localized Broken Symmetry Solutions, Solitons, Polarons and Breathers in the Time Dependent HF Equation of a One-Dimensional System and their Significance in the Lattice Dynamics and Electron Correlation in Polyenes and Polyacetylene"
L. Glass	"Birfurcation and Chaos in the Hearts of Chickens and Men"
E.J. Heller	"Spectroscopy with Photons and Particles: Correlation Functions and Semiclassical Nonlinear Dynamics"
J.T. Hynes	"Along the Reaction Coordinate in Solution"
J. Koutecky	"General Rules on the Structure of Small sp Metal Clusters"
R.D. Levine	"Algebraic Methods for Molecular Structure and Dynamics"
J. Oddershede	"The Polarization Propagator Method and Its Applications"
G. Patey	"Recent Advances in the Integral Equation Theory of Liquids and Solutions"
I. Procaccia	"Infinity of Scenarios for the Onset of Chaos in Lorenz-like Flows"

J. Ross	"Experiments and Theory on Chemical Instabilities"
P.J. Rossky	"Quantum Simulation of Aqueous Systems"
D.R. Salahub	"Metal Clusters Interacting with Adsorbates - The Local (Spin) Density Description"
M. Shapiro	"Coherent Control of Chemical Reactions"
H.J. Silverstone	"Beneath the Surface of Quantum-Mechanical Perturbation Theory: Diverence, Borel-Based Summability, Exponentially Small Subseries, and the Quasi-Semiclassical Method, with Theoretical and Practical Application to the LoSurdo-Stark Effect, the Hydrogen Molecule-Ion, and the JWKB Method"
H. Swinney	"Chemical Chaos and Intermittency"
A.J. Thakkar	"Quantum Chemistry in Momentum Space: An Overview"
D.R. Truax	"Supersymmetry"
J.P. Valleau	"Monte Carlo Study of a Model of a Fexible Polyelectrolyte"
A. van der Avoird	"A Quantum Chemical Approach to the Properties of Molecular Crystals"
P. Wolynes	"Beyond the Golden Rule: From Proteins in Semiconductors"
M.C. Zerner	"Characterizing Potential Energy Surfaces: Art and Science"

Contributed papers, from all areas of theoretical chemistry are welcome. The poster sessions will be scheduled in the afternoon. The attached abstract form should be consulted for additional information.

9th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

9e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE

June 23 - 27, 1986

University of Toronto, Trinity College

Toronto, Ontario, Canada.

WE THANK THE NATURAL SCIENCES AND ENGINEERING RESEARCH COUNCIL OF CANADA AND FLOATING POINT SYSTEMS, INC, FOR FINANCIAL SUPPORT GIVEN TO THIS SYMPOSIUM.

SCHEDULE OF INVITED LECTURERS AND POSTER SESSIONS

MONDAY		TUESDAY		WEDNESDAY	THURSDAY	FRIDAY
8:30 - 8:50 a.m.	WELCOME					
Chairmen	B.C. Eu		B.L. Clarke	W.J. Meath	W.G. Laidlaw	R.J. LeRoy
8:50 - 9:40 a.m.	L. Glass	8:30 - 9:20 a.m.	J. Ross	H.J. Silverstone	P.J. Rossky	G.W.F. Drake
9:40 - 10:30 a.m.	H. Swinney	9:20 - 10:10 a.m.	I. Procaccia	A. Thakkar	J.P. Valleau	E.R. Davidson
10:30 - 10:50 a.m.	COFFEE BREAK	10:10 - 10:30 a.m.		COFFEE BREAK		
Chairmen	M.A. Whitehead		V.H. Smith	S.G. Whittington	W. Siebrand	R.F. Snider
10:50 - 11:40 a.m.	R.J. Bartlett	10:30 - 11:20 a.m.	R.D. Levine	K. Freed	A. van der Avoird	G. Patey
11:40 - 12:30 p.m.	J. Oddershede	11:20 - 12:10 p.m.	D.R. Traux		H. Fukutome	M. Pettitt
12:30 - 2:00 p.m.	LUNCH	12:10 - 2:00 p.m.		LUNCH	12:30 p.m. BUSINESS MEETING 1:00 p.m. LUNCH	SYMPOSIUM ENDS
Chairmen	P.W. Brumer		P.G. Mezey		A.D. Brandrauk	
2:00 - 2:50 p.m.	J.T. Hynes	2:00 - 2:50 p.m.	C.W. Bauschlicher	FREE AFTERNOON	M. Shapiro	
2:50 - 3:40 p.m.	E.J. Heller	2:50 - 3:40 p.m.	M. Zerner		O. Atabek	
3:40 - 4:00 p.m.	COFFEE BREAK	3:40 - 4:00 p.m.			COFFEE BREAK	
Chairmen	R.F.W. Bader		POSTER SESSION		POSTER SESSION	
4:00 - 4:50 p.m.	J. Koutecky		Mostly Dynamics		Mostly Structure	
4:50 - 5:35 p.m.	D.R. Salahub					
					6:30 p.m. RECEPTION (Combination Room)	
					7:30 p.m. BANQUET (Stratchan Hall)	

INVITED SPEAKERS	SUBJECT
O. Atabek	"Bound And Dissociative Spectroscopies of Ozone"
R.J. Bartlett	"Analytical Derivative Methods in Coupled Cluster Theory"
C.W. Bauschlicher	"The Importance of Electron Correlation on Transition Metal Bonding"
E.R. Davidson	"Experimental and Theoretical Determination of Electron Density"
G.W.F. Drake	"Relativistic and Ouantum Electrodynamic Effects in Two-Electron Atoms and Ions- Comparison of Theory and Experiment"
K.F. Freed	"Renormalization Group Theory of Polymers"
H. Fukutome	"Broken Symmetry Solutions in the UHF Equation of Polyacetylene and their Physical Significances.
L. Glass	"Universal Bifurcations, Chaos and Cardiac Arrhythmais
E.J. Heller	"Spectroscopy with Photons and Particles: Correlation Functions and Semiclassical Nonlinear Dynamics"
J.T. Hynes	"Along the Reaction Coordinate in Solution"
J. Koutecky	"General Rules on the Structure of Small SP Metal Clusters"
R.D. Levine	"Algebraic Methods for Molecular Structure and Dynamics"
J. Oddershede	"The Polarization Propagator Method and Its Applications"
G. Patey	"Recent Advances in the Integral Equation Theory of Liquids and Solutions"
B.M. Pettitt	"Molecular Configurations and Conformations in Solution"
I. Procaccia	"The Onset of Chaos in Simple Flows: A Tale of Richness and Complexity"
J. Ross	"Experiments and Theory Studies in Chemical Instabilities"
P.J. Rossky	"Ouantum Simulation of Aqueous Systems"

D.R. Salahub	"Metal Clusters Interacting with Adsorbates - The Local (SPIN) Density Description"
M. Shapiro	"Coherent Control of Unimolecular Reactions"
H.J. Silverstone	"Beneath the Surface of Quantum-Mechanical Perturbation Theory: Diverence, Borel-Based Summability, Exponentially Small Subseries, and the Quasi-Semiclassical Method, with Theoretical and Practical Application to the LoSurdo-Stark Effect, the Hydrogen Molecule-Ion, and the JWKB Method, and the meaning of Asymptotic Expansions"
H. Swinney	"Chemical Chaos and Intermittency"
A.J. Thakkar	"Quantum Chemistry in Momentum Space: An Overview"
D.R. Truax	"Supersymmetry"
J.P. Valleau	"Monte Carlo Study of a Model of a Flexible Polyelectrolyte"
A. van der Avoird	"A Quantum Chemical Approach to the Properties of Molecular Crystals"
M.C. Zerner	"Characterizing Potential Energy Surfaces: Art and Science"

INVITED SPEAKERS' ABSTRACTS

M1

UNIVERSAL BIFURCATIONS, CHAOS AND CARDIAC ARRHYTHMIAS, Leon Glass, Michael R. Guevara, Alvin Shrier, Department of Physiology, McGill University, Montreal, Quebec, Canada

During periodic stimulation of cardiac tissue, as the amplitude and frequency of the stimulation are varied, a large number of different coupling patterns are observed. These changes in qualitative features of the dynamics (bifurcations) can be predicted from an analysis of associated finite-difference equations. Aperiodic, "chaotic" dynamics are also theoretically predicted and experimentally observed. The rhythms observed in experimental and theoretical models are analogous to several cardiac arrhythmias observed clinically, and thus a partial classification of cardiac arrhythmias is possible based on the theory of bifurcations of finite-difference equations.

M2 CHEMICAL CHAOS AND INTERMITTENCY. Harry L. Swinney, Department of Physics, University of Texas, Austin, Texas 78712 U.S.A.

Experiments on the Belousov-Zhabotinskii reaction in a stirred flow reactor reveal a transition to chaos through a period doubling sequence. The chaotic behavior is characterized in phase space by strange attractors that have been constructed from the laboratory data. These attractors have low fractal dimension (between 2 and 3), which indicates that the observed nonperiodic behavior can be described by low dimensional deterministic models. Within the chaotic regime there are many parameter intervals corresponding to complex periodic states, and these periodic states occur in a universal order given by a one-dimensional map. In other concentration and flow rate regimes we observe three distinct routes to chaos that involve intermittency. These three forms of intermittency were predicted by Pomeau and Manneville in a study of a one-dimensional map. Thus, even though the Belousov-Zhabotinskii reaction involves more than 30 chemical species, one-dimensional map models provide a remarkably good description of the dynamics in some parameter ranges we have studied.

M3

CANADIAN THEORETICAL CHEMISTRY CONFERENCE: ANALYTICAL DERIVATIVE METHODS IN COUPLED-CLUSTER THEORY. Rodney J. Bartlett, Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida 32611 U.S.A.

The coupled-cluster approach has been extended to include triple excitations partially, defining our CCSDT-1 model. This method is shown to reproduce the energies from a series of full CI results (using as many as 28 million determinants) performed at NASA Ames on the CRAY-2 to within a fraction of a kcal/mol at equilibrium geometries; and even subject to an RHF reference function to within ~3 kcal/mol at highly stretched geometries, where the reference is inappropriate.

The theory for analytical derivatives in CC theory is summarized, with the primary result being that instead of potentially 3N equations for gradients, only one "complementary" equation which is very similar to the CC equation themselves, requires solution. Hence CC gradients can be obtained with about twice the effort required for a CC calculation of the energy.

Analytical second-derivatives, at the simplest level of calculation, MBPT(2), have been implemented and results compared to SCF theory and experiment for a series of interesting systems including CH_3NO_2 and SiC_2.

M4

THE POLARIZATION PROPAGATOR METHOD AND ITS APPLICATIONS. Jens Oddershede, Department of Chemistry, Odense University, DK-5230 Odense M, Denmark.

The polarization propagator will be introduced as the linear response of a system to an external perturbation. Also non-linear response functions will be derived. The physical contents of these propagators as well as their equations-of-motion will be discussed.

Various approximate propagator methods will be reviewed with the main emphasis been put on a newly developed method which combines some of the virtues of the propagator method and the coupled cluster expansion of the ground state. Applications of both the coupled cluster and other propagator methods will be presented, including calculations of excitation energies, oscillator strengths and coupling constants for CH^+, CO and C_2H_2.

M5 ALONG THE REACTION COORDINATE IN SOLUTION. James T. Hynes, Dept. of Chemistry, University of Colorado, Boulder, CO 80309 USA

Although many reactions of interest in chemistry occur in solution, the influence of a solvent on the rate of reactions is not well understood at the molecular level. We will describe the results of Molecular Dynamics computer simulations of atom transfers $A+BC \longrightarrow AB+C$ in inert solvents and a model S_N2 reaction $Cl^- + CH_3Cl \longrightarrow ClCH_3 + Cl^-$ in H_2O designed to probe these questions. The comparison of the results to analytic theory will also be presented. These simulations were carried out in collaboration with the K. Wilson group at UC, San Diego.

M6 SPECTROSCOPY WITH PHOTONS AND PARTICLES: CORRELATION FUNCTIONS AND SEMICLASSICAL NONLINEAR DYNAMICS. Eric J. Heller, Department of Chemistry, University of Washington, Seattle, Washington 98195 U.S.A.

Traditional spectroscopy such as electronic and resonance Raman scattering, infrared absorption and emission, and microwave spectroscopy have a basis in correlation functions which may be interpreted semiclassically. The same is true of spectroscopies involving particles, such as neutron inelastic scattering and atom-surface time-of-flight spectroscopy. The use of correlation functions, with an underlying classical or semiclassical picture of their meaning, is especially well motivated for large molecules and systems with many degrees of freedom. Traditionally, only those correlation functions which have a direct classical analog when written in the Heisenberg Picture of Quantum Mechanics have been treated classically. However, using wavepacket techniques in the Schrodinger Picture, one can treat a variety of correlation functions (such as electronic and resonance Raman scattering, or surface time-of-flight scattering) which have no direct Heisenberg classical analog. Once it is understood how the appropriate correlation functions can be interpreted classically, the fascinating phenomenology of classical and semiclassical nonlinear dynamics and its spectral manifestations arises.

M 7 GENERAL RULES ON THE STRUCTURE OF SMALL sp METAL CLUSTERS, J. Koutecky, Freie Universität Berlin, Institut f. Physikalische Chemie, Berlin, West Germany.

The electronic and geometric structure of alkaline metal clusters can be understood and interpreted using simple concepts of quantum chemistry. Three factors play an important role: (1) the compactness of the cluster; (2) the nodal properties of the molecular orbitals (or, more generally, of natural orbitals), and (3) the energy stabilization due to polerization functions (metal orbitals). The transition from planar geometries of small alkaline metal clusters (4-6 atoms) to the cluster shapes with 5-fold symmetry and, further, to the tetrahedral structures is explained. The connection with the results of other methods and models will be reported. The electronic and geometric structure of IIa clusters and mixed Ia-IIa clusters is explained. The factors important for the electronic structure of IIIa-IVa clusters will also be mentioned,

M8 METAL CLUSTERS INTERACTING WITH ADSORBATES - THE LOCAL (SPIN) DENSITY DESCRIPTION. Dennis R. Salahub, Département de chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3V1.

The Local - (Spin) - Density methods incorporate exchange and correlation effects through a local correlated electron gas potential. The LCGTO variant of the method allows the accurate calculation of the electronic structure, geometries, and vibrational properties of medium sized transition metal clusters interacting with adsorbates. A compact, orbital, description of the bonding is obtained. Following a brief description of the method, I will discuss recent results on transition metal dimers and clusters and on their interactions with adsorbates.

T1

EXPERIMENTAL AND THEORETICAL STUDIES IN CHEMICAL INSTABILITIES. John Ross, Department of Chemistry, Stanford University, Stanford, CA 94305, U.S.A.

We report a variety of new experimental results on reaction ($CH_3CHO + O_2$) to external periodic perturbations of one and both fluxes of reactants in a continuous stirred tank reactor.

A theoretical study of proton pumps predicts variation in efficiency of the pump with oscillatory ATP flux, including the possibility of an increase in efficiency compared to steady flux.

T2 THE ONSET OF CHAOS IN SIMPLE FLOWS: A TALE OF RICHNESS AND COMPLEXITY.

Itamar Procaccia, The Weizmann Institute, Rehovot, ISRAEL

The scenarios for the onset of chaos in macroscopic physical systems are conveniently put in a few classes, like period doubling, quasiperiodicity and intermittency. It will be shown that once one examines the onset of chaos in simple flows (of the class of the Lorenz model), this convenient simplicity loses its meaning. In such systems there exists an infinity of scenarios for the onset of chaos, each of which is characterized by its own metric universality and its own renormalization group. The reason for this richness will be explained, and the nature of the phase diagrams (which display fascinating self-similarity) will be discussed. A new approach to the renormalization of dynamical systems will be outlined, stressing that all these scenarios can be dealt with in a unified fashion.

T3 ALGEBRAIC METHODS FOR MOLECULAR STRUCTURE AND DYNAMICS. R.D. Levine, The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel.

Algebraic methods are a natural tool when the interest is in observables and, in particular, in their time evolution. The link with bound states is through symmetry, and specifically dynamical symmetry (which contains the familiar discrete operations giving rise to the degeneracy group as a special case). Recent work has demonstrated that algebraic methods are by no means limited to systems with harmonic-like spectrum. After some simple applications to one dimensional problems and a brief review of bound excited states of triatomic molecules we shall discuss scattering theory in an algebraic framework. Throughout the emphasis will be on proceeding in a systematic fashion from the Hamiltonian as given in geometrical coordinates to its algebraic form.

T4

SUPERSYMMETRY. D. Rodney Truax, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.

Supersymmetry has its origins in particle physics. There it is used as a vehicle for the unification of gravity with the three other fundamental forces: electromagnetism, the weak force, and the strong force. In this context, a supersymmetry transformation transforms bosons into fermions or bosonic degrees of freedom into fermionic degrees of freedom or vice verse. Such transformations can be treated in a manner analogous to space-time symmetries or internal symmetries such as spin for example. However, there is a difference between ordinary symmetry and supersymmetry. Generators of space-time symmetries satisfy commutation relations while the generators of supersymmetry operations obey commutation or anticommutation relations. The former form Lie algebras; the later a graded algebra or a superalgebra, as it is now called. Superalgebras have a wider application than in particle physics. The simplest superalgebra yields supersymmetric quantum mechanics. Although supersymmetry has been around since the early 1970's, its use in other areas of physics really only dates from 1981. The burgeoning literature on this topic will be reviewed and applications in chemical physics outlined.

T5 THE IMPORTANCE OF ELECTRON CORRELATION ON TRANSITION METAL BONDING.

Charles W. Bauschlicher, Jr. and Stephen R. Langhoff, NASA Ames Research Center, Moffett Field, California 94035 U.S.A. and Stephen P. Walch, Eloret Institute, Sunnyvale, California 94087 U.S.A.

A systematic overview of the bonding in transition metal systems will be given. The mixing of the low-lying atomic states ($3d^n4s^2$, $3d^{n+1}4s^1$, and $3d^{n+2}$) in the transition metal hydrides is shown to depend strongly on the level of theory, and that the dipole moment is a sensitive measure of this mixing. The bonding in the transition metal oxides and sulfides is more complex due to the double and triple bond character in the wave function. The bonding in the transition metal dimers and trimers, as well as the bonding in such organometallics as $Ni(CO)_4$, $Fe_2(CO)_9$ and $CR(NO)_4$ will also be discussed.

T6

CHARACTERIZING POTENTIONAL ENERGY SURFACES; ART AND SCIENCE. Michael C. Zerner, Quantum Theory Project, University of Florida, Gainesville, Florida 32611 U.S.A.

One of the most dramatic advances of quantum chemistry in the last decade has centered around the ways in which molecular geometries and reaction transition states can be explored through computation. In this lecture we review the various ways in which these searches along molecular potential energy surfaces are made; both the "art" and the science. A particular line search strategy will be discussed, as will a method for quickly obtaining an approximate Hessian (second derivative) matrix accurate enough even to search for transition states. Examples will be given where these techniques have been used to examine some unusual structures which can be generated from a nearly arbitrary starting arrangement of atoms.

W1 BENEATH THE SURFACE OF QUANTUM-MECHANICAL PERTURBATION THEORY: DIVERGENCE, BOREL-BASED SUMMABILITY, EXPONENTIALLY SMALL SUBSERIES, AND THE QUASI-SEMICLASSICAL METHOD, WITH THOERETICAL AND PRACTICAL APPLICATION TO THE LoSURDO-STARK EFFECT, THE HYDROGEN MOLECULE-ION, THE JWKB METHOD, AND THE MEANING OF ASYMPTOTIC EXPANSIONS. Harris J. Silverstone, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218 U.S.A.

Ordinary Rayleigh-Schrödinger perturbation theory (RSPT) diverges for certain familiar, prototype problems: hydrogen in an electric field (LoSurdo-Stark effect); hydrogen in the field of a proton (H_2^+); and the harmonic oscillator perturbed by a quartic anharmonic term. Associated with these problems are also exponentially small subseries. The field-induced ionization rate of the hydrogen atom has a series of form exp(-k/F) times a power series in the electric field strength F. The energy levels of H_2^+ occur in pairs; the separation between two paired levels has a series of form exp(-kR) times a power series in 1/R, where R is the internuclear distance. Further, the rate of divergence of RSPT is quantified by the growth of the perturbed energy coefficients, which schematically is $E^{(N)} \sim N! \times [1 + a/N + b/N(N-1) + \cdots]$. The "Bender-Wu" correction coefficients, a, b, ..., turn out to be coefficients in an exponentially small subseries. Thus arise the questions, how does one "sum" these divergent series, and how does one calculate exponentially small subseries not visible by RSPT. The method to be sketched here for calculating the series is quasisemiclassical — related to the semiclassical JWKB method. It involves asymptotic expansions of Airy and confluent hypergeometric functions, which are summable via Borel's method. Borel-based summability is also a numerical tool, as is illustrated. The Borel-based sums of series that occur in the above mentioned problems are complex, even though the series are formally real. This observation has important consequences for understanding asymptotic expansions and for the JWKB method.

W2

QUANTUM CHEMISTRY IN MOMENTUM SPACE: AN OVERVIEW. Ajit J. Thakkar, Department of Chemistry, University of New Brunswick, Fredericton, NB, E3B 6E2, Canada.

The momentum representation of quantum mechanical state vectors for bound states is very much underutilized in theoretical chemistry in comparison with the position or co-ordinate representation. Current quantum chemical activity in momentum space can be classified into three categories: 1) development of methods for the approximate solution of the Schrödinger equation in momentum space as well as use of momentum space techniques to facilitate the calculation of integrals arising in conventional electronic structure theory; 2) calculation of momentum densities, from the Fourier-Dirac transforms of position space wavefunctions, for comparison with and prediction of experimental results obtained by Compton scattering, high energy electron impact and binary (e,2e) spectroscopy; and 3) attempts to find, from electron momentum distributions, novel insights into the nature and genesis of chemical bonding which both complement and supplement the conventional ones. An overview of some of the most interesting results obtained in each of these three categories will be presented with an emphasis on chemical interpretation of momentum space information.

W3

RENORMALIZATION GROUP THEORY OF POLYMERS. Karl F. Freed, James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637 U.S.A.

The connectivity of a polymer chain leads to the presence of long-range correlations in a polymer and consequently to the applicability of renormalization group methods for describing large length scale polymer properties which are insensitive to microscopic molecular details apart from that contained in a few phenomenological parameters.[1] The polymer is modelled as a self-interacting continuous random walk, and this leads to a path integral representation of the configurational statistics of polymers in solution. The chain space renormalization group theory of polymers is briefly introduced, and then comparisons of predictions for equilibrium and dynamical polymer properties are made with experimental data and with results of Monte Carlo simulations.

[1] K.F. Freed, "Renormalization Group Theory of Macromolecules", Wiley, in press.

9th Canadian Symposium on Theoretical Chemistry

Th 1

QUANTUM SIMULATIONS OF AQUEOUS SYSTEMS

P.J. Rossky
Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

ABSTRACT

With the implementation of path integral simulation methods, it has become possible to study fundamentally quantum mechanical equilibrium phenomena in complex many-body systems. The technique and the results obtained for two aqueous systems will be described. The first is that of bulk liquid water, in which each molecule is treated quantum mechanically. We focus on the impact of quantization of intermolecular degrees of freedom. We examine the structural ramifications of the resultant increased amplitude for hydrogen bond distortions, and the reflection of this in the structural differences between isotopic waters. The second example is the structure of a hydrated excess electron, a system incorporating a highly quantum mechanical solute. Aspects of the electron-solvent interaction will be discussed, and results for solute and solvation structure will be presented and compared to that observed in simple ionic solutions.

Th 2 MONTE CARLO STUDY OF A MODEL OF A FLEXIBLE POLYELECTROLYTE. John P. Valleau, Chemical Physics Theory Group, University of Toronto, Toronto, Ontario M5S 1A1.

This is a preliminary account of an attempt to study by Monte Carlo simulation the behaviour of a flexible polyelectrolyte in the presence of supporting electrolyte. A very simple model of the polyelectrolyte has been used, and a primitive-model supporting electrolyte; even so only rather short chains can be studied, of course. The conformational behaviour is examined, and it is compared to the behaviour of chains described by a screened-coulomb model. The structure of the surrounding electrolyte is also studied, and compared to that near a rod-like polyelectrolyte.

Th 3 A QUANTUM CHEMICAL APPROACH TO THE PROPERTIES OF MOLECULAR CRYSTALS.

Ad van der Avoird, Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

It is well known that quantum chemical calculations can yield detailed anisotropic intermolecular potentials between small molecules. These intermolecular potentials determine the structure and the properties of molecular solids, but in order to evaluate these properties explicitly one has to perform lattice dynamics calculations. Inspired by quantum chemical methods, we have developed a new method to make such calculations. This method holds also in those cases where the standard harmonic method breaks down, i.e. for lattice vibrations with large amplitudes which occur especially near phase transitions and in the so-called plastic phases. The properties calculated via ab initio potentials are very accurate indeed. This will be illustrated on various modifications of solid nitrogen and oxygen. Particularly solid oxygen is interesting, because it is a magnetic material. The ab initio calculations have yielded information on the spin-dependent potential between the triplet O_2 molecules which appeared, via lattice dynamics and spin-wave calculations, to solve several open problems.

Th 4

BROKEN SYMMETRY SOLUTIONS IN THE UHF EQUATION OF POLYACETYLENE AND THEIR PHYSICAL SIGNIFICANCES. Hideo Fukutome, Department of Physics, Kyoto University, Kyoto 606, Japan.

The UHF equation in the PPP model of polyacetylene has broken symmetry solutions of many kinds, periodic and localized ones. The simplest periodic broken symmetry solutions are the density waves of charge, spin, bond order or spin bond order with the period of two. The simplest localized broken symmetry solutions are solitons and polarons. We show the structures of these solutions and how they are affected and stabilized by the electron-electron Coulomb interaction. We discuss the relationships of the localized soliton and polaron solutions to the periodic density wave solutions. We mention also about more complicated broken symmetry solutions such as soliton arrays and breathers. We discuss how the characteristic features of these broken symmetry solutions, which are produced by the Coulomb interaction, affect physical properties of polyacetylene. We show that the Coulomb interaction has serious effects on physical properties of polyacetylene such as the bond alternation, band gap, ESR, ^{14}C-NMR, C1s-XPS, optical absorption and electric conductivity.

Th 5 COHERENT CONTROL OF UNIMOLECULAR REACTIONS, Moshe Shapiro*and Paul Brumer†,
*Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, 76100 ISREAL
†Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1 CANADA.

A method of controlling branching unimolecular reactions, using the coherence of lasers is presented. It is shown that pre-selected chemical products may be obtained, in preference to others, by utilizing the interference between naturally occuring processes, via the dissociation of a superposition state. Control is attained by manipulating the relative intensities and phases of two coherent beams. Enhanced yields of chemical products of interest are shown to result. Theoretical limits of coherent control, in direct and resonant processes are derived. Computatuinal results on the I*/I branching ratios in the photodissociation of FI and CH3I, including the effects of quantum state of a given reaction product, resulting in population inversion with respect to all higher energetic levels, is shown to be attainable. Proposals of possible experiments designed to demonstrate coherent control are outlined.

Th 6 BOUND AND DISSOCIATIVE SPECTROSCOPIES OF OZONE. O. Atabek, Laboratoire de Photophysique Moleculaire du CNRS, Bat. 213 Universite de Paris 91405 Orsay - FRANCE

The photochemistry of ozone is a fastly growing area of the physics of the upper atmosphere. For a complete theoretical description precise informations concerning the various potential surfaces which are involved as well as dynamical methods which relates them to observed vibrational-rotational levels and cross sections are needed. This work is concerned by the calculation of IR frequencies of the ground X $^1A_1$ state as well as the $1\ ^1B_2$ X $^1A_1$ absorption and fluorescence (resonant Raman) cross sections.

The close-coupled equations of molecular scattering theory formulated in a body fixed reference frame are worked out for the evaluation of vibrational energy levels of the ground state with zero total angular momentum. A judicious choice for a local basis optimizes the number of equations and the Fox-Goodwin propagator associated with an iterative matching procedure is used achieving an accuracy of a few wavelengths in an energy range of 2000 cm^{-1}. This method provides not only an efficient alternative to variational and so-called spectral methods but its generalisation to the calculation of resonances occuring in dissociation processes is possible.

Dissociative spectroscopy deals with the absorption and fluorescence cross sections. Due to the symmetry of ozone the coupled equations formulation can not be reduced to but one fragmentation channel (competition between O_3 $O+O_2$ and O_3 O_2+O). A simple Franck-Condon analysis provides a much more easier way for the solution. In the vicinity of the equilibrium geometry of O_3, the ground state may be described in terms of its three normal modes with appropriate harmonic oscillators. The excited state presents a saddle point at the vertical of the minimum of the ground state and may locally be described in terms of reaction coordinates as a sum of two harmonic oscillators and a parabolic barrier. Within this model complete analytical expressions for the line shape and for the fluorescene spectrum are derived. The results for the line shape of the Hartley band and its temperature dependance and constitute fairly good reproduction of experimental data. Concerning the fluorescence spectrum, even if the model calculations do not always completely agree with the observed spectrum, the main features of it are explained.

F1

RELATIVISTIC AND QUANTUM ELECTRODYNAMIC EFFECTS IN TWO-ELECTRON ATOMS AND IONS - COMPARISON OF THEORY AND EXPERIMENT. G. W. F. Drake, Department of Physics, University of Windsor, Windsor, Ont. N9B 3P4.

Two-electron atoms and ions provide the simplest non-trivial testing ground for our understanding of the basic interactions which enter into more complex atomic and molecular systems. Recent high precision measurements of transition energies in helium and helium-like ions are sensitive not only to relativistic corrections, but also to one- and two-electron quantum electrodynamic (QED) effects analagous to the Lamb shift in hydrogen. The aims of the paper are to present a summary of the types of effects which must be considered, and to discuss theoretical techniques for calculating them. A detailed comparison with high precision measurements will be made.

F2

EXPERIMENTAL AND THEORETICAL DETERMINATION OF ELECTRON DENSITY.

Ernest R. Davidson, Department of Chemistry, Indiana University, Bloomington, Indiana, U.S.A. 47405

Comparison will be made between calculations and experiment for (e,2e), EPR, and field gradients. Chemical insights to be gained from these comparisons will be emphasized. Sources of error in the theoretical values will be discussed.

F3 RECENT ADVANCES IN THE INTEGRAL EQUATION THEORY OF LIQUIDS AND SOLUTIONS.

G. Patey, University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, British Columbia CANADA V6T 1Y6

General Methods which allow the hypernetted-chain and Percus-Yevick integral equation theories to be solved for fluids of non-sperical particles will be discussed. These methods can be readily applied to both "hard" and "soft particles of arbitrary shape. Numerical results which illustrate the range of application of these theories will be given, including calculations for water, aqueous electrolytes and simple model liquid crystals.

F4

MOLECULAR CONFIGURATIONS AND CONFORMATIONS IN SOLUTION. B.M. Pettitt, Department of Chemistry, University of Houston-University Park, Houston TEXAS 77004 U.S.A.

Recently developed integral equation methods for the evaluation of intermolecular and intramolecular interactions in polar solvent media can now be solved for a wide range of applications. Examples include the solvent modification of interionic interactions between atomic or molecular ions in water and the liquid environment induced shifts in conformational equilibria for both polar and non polar flexible molecules in water. By using simple atom centered interaction site potentials many features of solvation phenomena can be traced specifically to the molecularity of the solvent and hence cannot be adequately reproduced by simple continuum dielectric solvent representations.

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ABSTRACTS FOR POSTER SESSION A

Tuesday, June 24th, 1986

A1

Nonlinear Transport Processes and Fluid Dynamics: Effects of Thermoviscous Coupling and Nonlinear Transport Coefficients on Plane Couette Flow of Lennard-Jones Fluids, D.K.BHATTACHARYA and BYUNG CHAN EU, McGill University, Montreal, Canada

To examine the effects of nonlinear transport processes on the flow properties of a real fluid, we study the plane Couette flow under a temperature gradient in a Lennard-Jones fluid over a range of gas pressure. The analysis is based on the nonlinear transport coefficients derived in the modified moment method. The linear transport coefficients appearing in the theory are those constructed by Ashurst and Hoover from the nonequilibrium molecular dynamic simulations, while for the equation of state for the Lennard-Jones fluid we use the empirical form proposed by Ree. Examples for the flow characteristics at two extreme conditions when either the gas is very dilute, or when it is very dense, are presented. It is shown that the temperature and velocity profiles for nonlinear transport processes are significantly different from the ones obtained with the linear transport coefficients. In the dilute gas limit, slip boundary conditions are used which are derived by applying the Langmuir theory of gas-surface interaction. Flow profiles show pronounced boundary layer structures near the wall when the product of the Knudsen number and the Mach number is sufficiently large.

A2 NOISE-INDUCED TRANSITIONS IN MODEL CHEMICAL SYSTEMS. Edward A. Celarier and Raymond Kapral, Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada.

Nonlinear, dissipative dynamical systems provide models for reacting chemical systems far from thermodynamic equilibrium, as well as for a wide variety of phenomena in laser physics, population biology, cardiology, biological regulation, etc. These systems display a wide variety of exotic dynamical behaviors (period-doubling, chaos, etc.) Of course, natural systems are often subject to appreciable coupling to a "noisy" environment. The addition of noise to the deterministic equations of motion can alter or destroy some of these dynamical states, or even call new states into existence.

We discuss a number of noise-induced transition phenomena found in numerical simulations based on physical systems. In particular, we explore noise-induced switching between bistable states of a model "chemical" oscillator, and identify the mechanism whereby it occurs. We also compare the effectiveness of different noise statistics in promoting the switching.

We apply the same analysis to noise-induced switching in a model of an optical bistable device, and discuss the connection between noisy continuous-time flows and noisy discrete-time mappings. The structure of the boundaries between dynamical basins of attraction is an important determinant of the system's response to external fluctuations.

A3 LINEAR AND BRANCHED POLYMERS IN CONFINED GEOMETRIES. Merk-Na Chee, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

The behaviors of confined linear and uniform star polymers, modelled by self-avoiding walks on the square and cubic lattices are compared and contrasted. For the 2-dimensional square lattice, the growth constant of a uniform star polymer confined between two lines is found, from exact enumerations, to be smaller than that for the corresponding linear polymer. In addition, we are able to determine exactly the growth constant of a 3-arm star polymer confined between two lines unit distance apart. For the 3-dimensional cubic lattice, the growth constant of the polymer confined between two parallel planes is proven to be independent of its functionality.

A4 CLOSE-COUPLING CALCULATIONS OF COLLISIONS OF NO($X^2\Pi$) WITH A Ag(III) SURFACE. G. C. Corey, J. E. Smedley, and M. H. Alexander, Department of Chemistry, University of Maryland, College Park, Maryland 20742.

Quantum calculations of inelastic transition probabilities in collisions of NO($X^2\Pi$) with a Ag(III) surface will be discussed. The silver surface is assumed to be flat and rigid; diffraction and phonon effects are neglected. The open-shell character of the NO molecule is explicitly described in an intermediate Hund's coupling case. This allows us to examine the fine-structure and Λ-doublet effects in the scattering process. The average of the relevant A' and A" NO-Ag potentials was described by a modification of a recent potential surface due to Tully. A chemical model for the difference potential was developed. The results of exact close-coupling calculations are compared with transition probabilities predicted within the coordinate-representation sudden approximation as well as with previous experimental studies.

A5 **DYNAMICAL THEORY OF STATISTICAL UNIMOLECULAR DECAY.** Randall S. Dumont and Paul Brumer, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1 CANADA

Statistical unimolecular decay is formally derived through explicit use of molecular dynamics assumptions based upon ergodic theory. Both statistical lifetime and product distributions are considered and effects due to direct dissociation, relaxation of the initial distribution and similar heuristic notions are rigorously included. The result is a new model which shows exponential decay with a rate which depends upon both phase space volumes and relaxation time τ. The decay rate predicted by this new model is generally larger than the RRKM value, k_s, approaching it only in the limit of rapid relaxation ($\tau \ll k_s^{-1}$). Results of numerical calculations supporting this new 'delayed lifetime gap model' are also given. Furthermore, statisticality of any product distribution $\Pi(j)$ is shown to require that the mean gap times associated with products j must be equal for all j. This requirement is also shown, for the case of multiple chemical product channels, to be implicit in the traditional rate equation approach to unimolecular dissociation.

A6 INTERACTIONS BETWEEN BENDING VIBRATIONS AND MOLECULAR ROTATIONS: A MODEL STUDY. Gregory S. Ezra, Department of Chemistry, Cornell University, Ithaca, New York 14853 U.S.A.

The classical mechanics of the interaction between bending vibration and three-dimensional molecular rotation is studied for a simple rigid bender model of a nonlinear triatomic. In this model, coupling between rotation and vibration occurs only through the dependence of moments of inertia on the bending angle. Use of the one-dimensional representation of rotational motion due to Augustin and Miller enables surfaces of section to be constructed for the fully coupled system. The rotation-vibration phase space is explored as a function of energy and angular momentum. Near-separable quasiperiodic, resonant and chaotic motions are identified, and can be related to characteristic patterns of rotation-vibration energy flow. Long-time correlations are found in the dynamics of apparently chaotic trajectories, and are possibly associated with the existence of bottlenecks in phase space.

Supported by NSF Grant CHE-8410865

A7 MASTER EQUATION AND THE RELAXATION OF THE MOMENTS. G. Gidiotis and W. Forst, Department of Chemistry and CRAM, Laval University, Quebec Canada GK 7P4.

We address in general terms the problem of energy transfer in weak-collision thermal systems. The master equation describing the temporal evolution of a gaseous system in contact with a heat bath is transformed into a system of linear, constant-coefficient first-order differential equations of moments of the population distribution. The relaxation of the moments is examined in some detail and is shown to depend on the properties of a characteristic matrix in both the discrete and continuous cases. In general, the relaxation is non-exponential, but for any transition probability function there exists a condition which is sufficient, but not necessary, for the relaxation to be exponential. We also show that for any transition probability function with discrete eigenvalues there are quite generally always N linear combinations of the moments which will all relax exponentially.

Discrete Models of Growth and Dynamical Percolation in Chemistry

by Simon J. Fraser

Department of Chemistry and Scarborough College

University of Toronto, Toronto, Ontario M5S 1A1

AB

Abstract

Space-time lattice (cellular automaton) models of pattern formation and growth are described. Suitable local rules for automaton evolution represent the spreading of wavefronts of activity in an excitable medium. A random distribution of seeds produces expanding rings which fuse and annihilate. The seeding density, p_A, is used as a scaling parameter to give a unique, reduced dynamics in arbitrary dimension d. For d=2, in this (continuum) picture, the rings fuse globally (percolate) at a critical instant, $\hat{t}_c = .45$. For the unscaled time evolution dynamical percolation is examined in the p_A X t plane. A swath of these spanning states is found. On the "explosion" boundary of this swath the percolation cluster just forms; on the "implosion" boundary it breaks up. Using a small-sample method the fractal dimension of the critical cluster is estimated to be 1.9 (±.01). The structure of the critical cluster is discussed in detail. Also percolation for continuously emitting seeds, which produce "discs" of activity, is related to ring evolution.

A9

FLUORESCENCE: A PROBE FOR INTRAMOLECULAR DYNAMICS?

Daniel Gruner and Paul Brumer, Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada.

The controversial question of exactly what can one learn about the dynamics of an isolated molecule from its fluorescence emission is examined. We have made a comparison of the time evolution and fluorescence characteristics of two similarly excited systems, in the small molecule limit, which have well defined classical dynamical behaviour: one regular (quasiperiodic) and the other ergodic and mixing. The quantum dynamics of these systems were found to be remarkably similar. Fluorescence studies also fail to show any behaviour which discriminates between the two systems, whose wavefunctions differ significantly. Our results suggest the inability to experimentally identify "quantum chaos" in pure state quantum dynamics, as we were unable to detect any observable property which would characterize such behaviour in one of the most likely systems to display it - the stadium billiard.

A10

POTENTIAL ENERGY DETERMINATION BY INVERSE PERTURBATION ANALYSIS WITH LOCAL CORRECTION FUNCTIONS.

I. P. Hamilton and J. C. Light, The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Inverse first order perturbation analysis is used to iteratively correct a potential energy surface; with local Gaussian correction functions the analysis is shown to be accurate, flexible, and rapidly convergent for both one and two dimensional examples. The analysis is employed to obtain an improved two dimensional potential energy surface for the twist-pucker motion in cyclopentene.

A II

MODE SPECIFICITY IN THE MODEL UNIMOLECULAR REACTION H-C-C → H + C=C.

W. L. Hase and K. N. Swamy, Department of Chemistry, Wayne State University, Detroit, Michigan 48202; B. C. Garrett, Chemical Dynamics Corporation, Columbus, Ohio 43220; C. W. McCurdy, Department of Chemistry, Ohio State University, Columbus, Ohio 43210; J. F. McNutt, Shell Development Company, Houston, Texas 77057 U.S.A.

Semiclassical and quantum mechanical studies of bound and resonance states for a model H-C-C → H + C=C Hamiltonian are compared. Excellent agreement is found between the semiclassical and quantum mechanical bound state eigenvalues and resonance positions. The close-coupling and stabilization graph with analytic continuation methodologies are used for the quantum calculations, and they give resonance positions and widths which are in good agreement. Resonance lifetimes vary by five orders of magnitude within a 1 kcal/mol energy interval. A correspondence between quasiperiodic/chaotic classical motion and regular/irregular quantum states is found for both bound and resonance states.

A12 THE SENSITIVITY OF IVR IN BENZENE TO POTENTIAL ENERGY SURFACE PROPERTIES.

William L. Hase and Da-hong Lu, Department of Chemistry, Wayne State University, Detroit, Michigan 48202; Ralph J. Wolf, Department of Chemistry, University of Arkansas at Little Rock, Little Rock, Arkansas 72204 U.S.A.

Quasiclassical trajectory calculations have been performed to study intramolecular vibrational energy redistribution (IVR) from CH overtone states in benzene. The rate and extent of this redistribution is sensitive to details of the potential energy surface. A particularly important potential energy surface property is attenuation of the HCC bending force upon CH stretch excitation. This property gives rise to non-irreversible IVR when the CH stretch is highly excited. An analogue to quantum beats is observed in phase averaged quasiclassical trajectories.

A13 REACTION PATH AND VARIATIONAL TRANSITION STATE THEORY RATE CONSTANT FOR $Li^+ + (CH_3)_2O \rightarrow Li^+[(CH_3)_2O]$ ASSOCIATION. Scott Vande Linde, Sandra L. Mondro, and William L. Hase, Department of Chemistry, Wayne State University, Detroit, Michigan, 48202 U.S.A.

Canonical variational transition state theory rate constants are calculated for the $Li^+ + (CH_3)_2O$ recombination reaction. To calculate the variational transition state theory rate constant, the reaction path and frequencies orthogonal to the reaction path are required. The temperature dependent transition states are determined by finding the maxima in the free energy along the reaction path. Only one maximum is found at each temperature. The $Li^+ - (CH_3)_2O$ rocking motions are treated as free rotors, as harmonic oscillators and as a two-dimensional hindered rotor. The latter two treatments result in the same values for the free energy, while the free rotor treatment results in a lower value of the free energy.

A14

Three-Dimensional Quantum Mechanical Reaction Coordinates: Infinite Mass

N.M. Witriol and G.H. Herling, Louisiana Tech University, Ruston, LA 71272,USA, and Naval Research Laboratory, Washington, DC 20375-5000 USA

The rigorous, collinear, canonical point transformation method[1] is extended to three dimensions in the infinite central mass limit. With B as the central atom in the ABC system, the first transformation performed is $(x_A, y_A, z_A, x_B, y_B, z_B) \rightarrow (r, R, \theta, \phi, \psi, \tau)$, where r and R are the AB and BC interatomic distances, the Euler angles are (θ, ϕ, ψ) and τ is the angle between $\vec{r}_{AB}$ and $\vec{r}_{BC}$. The second transformation performed is $(r, R, \theta, \phi, \psi, \tau) \rightarrow (\xi, \eta, \theta, \phi, \psi, \tau)$, where ξ is the reaction coordinate which mimics the reaction path and η is the vibrational coordinate of the system. The effective metric tensor g_{ij} and the coordinate dependent potential W have been calculated with the use of the symbolic algebraic manipulation code SMP, and the Hamiltonian of the system has been obtained in the transformed reaction coordinate space. This transformed space is a one-one mapping from the original space, and therefore does not have any three-one regions. The transformed Hamiltonian is Hermitian, and the method is ready for numerical implementation.

1. N.M. Witriol, J. D. Stettler, M.A.Ratner, J.R. Sabin and S. B. Trickey, J. Chem. Phys. 66, 1141 (1977)

A15

Time Reversal and Unitarity in the Frozen Gaussian Approximation for Semiclassical Dynamics

Michael F. Herman, Department of Chemistry and The Quantum Theory Group
Tulane University, New Orleans, LA 70118

The time reversal and unitarity properties of the frozen gaussian approximation (FGA) are considered. The FGA is a semiclassical approximation for time-dependent wavepacket dynamics. It approximates the evolution of a quantum wavefunction by expanding it in gaussian functions and propagating each gaussian along a classical trajectory. The width of the gaussian functions is not allowed to change as a function of time. We show that, for a particular FGA formulation, the unitarity and time reversal properties of the exact quantum propagation hold. The unitarity property is proven within the stationary phase approximation for integrations, which is consistent with the semiclassical nature of the FGA. The time reversal property can be demonstrated without invoking the stationary phase approximation. We also discuss why the unitarity property will not hold for some other common variants of the FGA.

A16 ELECTROMAGNETIC WAVICLES: THE QUANTA OF ACTION. Geoffrey Hunter and Robert L.P. Wadlinger, Department of Chemistry, York University, 4700 Keele Street, North York (Toronto), Ontario, Canada M3J 1P3.

Elementary particles (wavicles) are considered to be space-time rotational states of the electromagnetic field within a local domain, the motion being governed by Maxwell's equations. The size and shape of the domain is determined by the principle that events within the domain are causally related; i.e. separated by time--like intervals. Maxwell's equations have been solved for a wavicle moving at the speed of light. The solutions are eigenstates of the intrinsic angular momentum (i.e. spin) with integer, or half-integer, eigenvalues $kh/2\pi$. The light-speed-limited domain is a circular ellipsoid, of length λ, the wavelength, and circumference $k\lambda$. The solutions possess helicity, which for $k = 1$ correspond to left-, right-, or non-circularly polarized light.

In quantum mechanics particles are regarded having both position and momentum, with the minimum errors in position and momentum being related by the uncertainty principle. In contrast, the theory presented here regards an elementary particle as electromagnetic energy contained within a finite domain. Hence its position is essentially uncertain within the linear size of the domain. This leads to the idea that the minimum quantum of action arises because the particle cannot convey its energy in less time than it takes to traverse the length of its own domain; its minimum action is the product of its length and its momentum. To emphasize its finite nature we refer to this kind of particle by Eddington's name wavicle. This finite photon model is consistent with several experimental properties of electromagnetic radiation.

A17 THE DYNAMICS OF QUANTUM-CLASSICAL CORRESPONDENCE. Sheldon Kanfer and Paul Brumer, Chemical Physics Theory Group, University of Toronto, Toronto, Ontario M5S 1A1, Canada

We have undertaken a study of the factors which influence the timescale for agreement of quantum-mechanically and classically propagated dynamical variables. Beginning with a quantum mechanical superposition state in a one-dimensional dissociative potential well (and its associated phase space density) the quantum-classical agreement has been assessed with respect to number and density of levels in the packet. The number of levels in the packet far outweighs their density in controlling correspondence, with ever higher numbers exhibiting better quantum-classical agreement, albeit for shorter periods of time. The effect of increasing level density is ambiguous, sometimes improving, sometimes impairing the correspondence.

A18 SELF-CONSISTENT ADIABATICALLY REDUCED DYNAMICS.

Stephen J. Klippenstein, Gregory A. Voth, and R. A. Marcus, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125 U. S. A.

An iterative procedure is applied to the adiabatically reduced coupled equations derived by Voth and Marcus [J. Chem. Phys. 84, 2254 (1986)]. The result is a self-consistent adiabatic procedure for determining an approximate quantum mechanical solution to the dynamics of nonstationary states. The eigenfrequencies and dynamics thus obtained are seen to be more accurate. The first order equations have a similar form to the zeroth order equations and as such require comparable computational effort.

A19

ADIABATICALLY REDUCED COUPLED EQUATIONS FOR INTRAMOLECULAR DYNAMICS CALCULATIONS. Gregory A. Voth, Arthur Amos Noyes Laboratory of Chemical Physics, MC 127-72, California Institute of Technology, Pasadena, California 91125 U.S.A.

The adiabatically reduced coupled equations approach to intramolecular dynamics calculations [J. Chem. Phys. 84, 2254 (1986)] will be discussed and some recent applications of the method will be presented. These applications include a description of the dynamics of local mode states in H_2O and an approximate approach for calculating state-to-state multiphoton transition probabilities in molecules.

A20 A SPHERICAL TENSOR APPROACH TO THE FREE INDUCTION DECAY PROBLEM IN NMR

Mangala S.Krishnan and B.C.Sanctuary, Department of Chemistry, McGill University, 801 Sherbrooke West, Montreal PQ H3A 2K6

The Free Induction Decay (FID) of magnetisation in solids following the application of a radio-frequency pulse has been of considerable interest for a long time. Both experimental and theoretical investigations on this have been mainly due to I.J.Lowe, R.E.Norberg and co-workers. We have proposed an alternative formalism based on Spherical Tensors irreducible under the rotation group SO(3), the group of the Hamiltonian. A basis set of multispin Irreducible Tensor Operators (ITO), obtained by Clebsch-Gordan coupling of suitably chosen single spin ITO's has been used for this purpose. The density matrix is expanded in terms of these operators and their associated observables, which describe correlations among various spins. Application of Wigner-Eckart theorem to the quantum Liouville equation then leads to a hierarchy of equations that describes the evolution of these correlations as due to the coupling among lower and higher spins. A truncation procedure is being developed to express the decay of magnetisation in terms of a relatively small number of higher tensor rank correlations, thereby elucidating the statistical mechanical aspects of the many-body problem of dipolar interactions in a crystal both formally and explicitly.

A21 THEORETICAL RESULTS FOR AQUEOUS ELECTROLYTE SOLUTIONS. Peter G. Kusalik, Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6 CANADA

In traditional theories for electrolyte solutions the solvent is treated only as a dielectric continum which acts to moderate the coulombic interactions between the ions. The theory of Debye and Hückel adopts this primitive model approach. A more complete theoretical picture of electrolyte solutions can be obtained by including the solvent as a true molecular species. We will report results obtained using integral equation methods for model electrolyte solutions which explicitly include a water-like molecular solvent. The structural, dielectric, and thermodynamic properties of these systems will be examined. We use the general formalisms developed by Kirkwood and Buff to derive expressions relating the microscopic correlation functions and the thermodynamic properties of electrolyte solutions without restricting the nature of the solvent. Then knowing the functional dependence of these microscopic correlation functions on ionic concentration in the low concentration limit, we obtain exact limiting laws for many thermodynamic quantities, including the mean activity coefficient and partial molar volumes. These analytical relationships and numerical results for model electrolyte solutions will be compared with experiment. The validity of Debye-Hückel theory will also be examined.

A22

MODELLING DISPLACEMENT OF FLUIDS IN POROUS MEDIA. W.G. Laidlaw, R. Maier, Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, N. Wardlaw, Department of Geology and Geophysics, University of Calgary, Calgary, Alberta T2N 1N4 and Li Yu, Nanhai Western Oil Company, Zhanjiang, People's Republic of China.

Networks of pores and their interconnecting throats can be used to model porous media displacement of one fluid by another in this network depends on pore size, connectivity, interfacial tension, wettability, fluid viscosity, external forces, and the availability of sources and sinks for the fluids concerned. At any given time the distribution of fluids in the network can be assessed by computer algorithms. Such distributions can then be related to macroscopic porous media displacement properties such as relative permeability, saturations and ultimately to oil recovery percentages. The stability of these results to external forces is a particular focus of our work.

A23

Modelling of Phenylene Ring Motion in 2-2 Diphenyl Propane.

B. Laskowski, Analatom, Inc., 253 Humboldt Court, Sunnyvale, CA 94089, R. Jaffe, NASA-Ames Research Center, Moffett Field, CA 94036, and A. Komornicki, Polyatomics Research Institute, 1101 San Antonio Road, Suite 420, Mountain View, CA 94043.

2-2 Diphenyl Propane can be thought of as being a model for part of the repeating unit of polycarbonate and polysulfone polymers. They are representatives of an important class of polymers which are comprised, in part, of 1,4-substituted phenylene groups.

To make an unambiguous connection between the macroscoppic mechanical properties of these polymers and the microscopic molecular motions from which such properties derive, the amplitudes of the various phenylene ring and main chain motions must be specified. The large amplitude phenylene torsional motion is believed to play a large role in determining physical properties such as toughness and crystalinity of these polymers. To assess the phenylene ring motion the Ab Initio Self Consistent Field (SCF) molecular orbital and gradient methods are used to determine the conformational properties and torsional potential functions. In particular, a study of the monomer, dimer and trimer fragments will be described to categorize the geometries and rotational barriers.

A24

SPECTROSCOPIC OBSERVATION OF PHASE TRANSITIONS IN SF_6-Ar_n CLUSTERS.

Dieter Eichenauer and Robert J. Le Roy, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

In infrared photo-depletion spectroscopy of molecular beams of SF_6-Ar_n clusters, the ν_3 band of the SF_6 chromophore has been found to have widths and frequency shifts which varied with the size of the cluster[1] and with the method of formation.[2] A model for explaining these spectral changes in terms of the dependence of the Ar-SF_6 pair potential on the vibrational distortion of the SF_6, has been developed. The main contribution to the shift appears to arise from the vibrational dependence of the electrostatic field due to the oscillating dipole moment associated with the ν_3 mode of the SF_6 molecule. A Monte Carlo simulation based on this instantaneous dipole-induced dipole model qualitatively explains the observed data. Moreover, it suggests that a sharp peak in the dependence of the observed spectral line width on source pressure is due to the fluid-solid phase transition in these clusters.

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[1] T.E. Gough, D.G. Knight and G. Scoles, Chem.Phys.Lett. **97,** 155 (1983)
[2] T.E. Gough, M. Mengel, P.A. Rowntree and G. Scoles, J.Chem.Phys. **83,** 4958 (1985)

A25

EFFECTIVE DEPHASING THEORY OF QUANTUM TRANSPORT IN DISORDERED CONDENSED PHASE SYSTEMS. Roger F. Loring and Shaul Mukamel, Department of Chemistry, University of Rochester, Rochester, N.Y. 14627 U.S.A.

A novel theory[1] of the transport of quantum mechanical entities such as conduction electrons, molecular vibrations, or electronic excited states in disordered systems is presented. The theory is based on the Effective Dephasing Approximation (EDA), in which the configuration averaged Liouville-space propagator of the excitation is mapped onto the propagator for an ordered lattice with an effective, frequency dependent dephasing rate. This dephasing rate is determined self-consistently. The approach is applicable to strongly disordered systems and can be used to describe a "metal-insulator" phase transition between localized and delocalized excitations (the Anderson transition). In agreement with scaling theory, we predict the existence of such a transition for a dimensionality greater than two. We apply the EDA to the calculation of the signal in a four-wave-mixing experiment on a molecular crystal with an inhomogeneously broadened absorption spectrum.

1. Roger F. Loring and Shaul Mukamel, Phys. Rev. **B33** (1986).

A 26

A QUASICLASSICAL TRAJECTORY STUDY OF MOLECULAR ENERGY TRANSFER IN H_2 + H COLLISIONS. John E. Dove and Margot E. Mandy, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

Energy transfer of highly excited simple molecules is important in nonequilibrium chemical systems, including laser induced chemical reactions and high temperature dissociation. However the factors which govern the energy transfer behaviour of highly excited molecules are not well understood. We have examined molecular energy transfer in exchange and nonexchange collisions of H_2 with H, using quasiclassical trajectory calculations on an accurate ab initio potential energy surface. Except for the (v,J) state and translational energy, all initial parameters were Monte Carlo selected. Over 150,000 trajectories were calculated for 18 different (v,J) levels of para-H_2 at translational energies of 3 to 200 kcal/mol. Energy transfer in H_2 + H nonexchange collisions is qualitatively similar to that in H_2 + He where the main process at low internal energies is rotation-translation transfer and at high internal energies is rotation-vibration interchange with little net change in translation. However there are striking differences between nonexchange and exchange collisions in H_2 + H. In the exchange collisions, the final distribution is not strongly dependent on the initial state; there is substantial rotation-vibration interconversion at low translational energies, while at higher energies there is, in addition, rotational excitation at the expense of translation, and product states of high J and low v tend to be favoured regardless of initial state.

A27 EVOLUTION OF SPATIAL STRUCTURES IN CHEMICAL SYSTEMS. Gian-Luca Oppo and Raymond Kapral, Chemical Physics Theory Group, University of Toronto, Toronto, Ontario M5S 1A1 Canada.

Pattern development in spatially extended chemical systems is usually modelled by reaction-diffusion equations. Solutions of these equations are difficult and preclude a complete analysis of possible phenomena, especially those aspects related to the calculation of time-dependent statistical quantities. Discrete models exhibit similar behaviour to their continuous analogs in some regions of parameter space, and are computationally and analytically much more tractable. The evolution and competition between spatial structures is studied for a system possessing coexisting steady states. An analysis of critical behaviour, nucleation and spinodal decomposition is carried out. The effects of fluctuations on the pattern formation process are also investigated. A chemical system possessing some of these features is the iodate oxidation of arseneous acid, which can serve as a testing ground for the theoretical predictions.

A28

STATISTICAL BIAS IN DIFFUSION MONTE CARLO SIMULATIONS: AN EMPIRICAL STUDY.

Stuart M. Rothstein, Narayan Patil, and Jan Vrbik, Departments of Chemistry and Mathematics, Brock University, St. Catharines, Ontario, Canada L2S 3A1.

Diffusion Monte Carlo (DMC) is a random walk computational method for solving and ground-state Schrodinger equation for atoms or molecules. One obtains a biased estimate of the exact energy, where the bias increases with the time step used in the simulation. We present six new DMC algorithms, all of which have the same theoretical justification. Yet, when applied to the LiH and H_2 molecules, the algorithms gave results with markedly different error. Furthermore, algorithms which exhibit a small error when applied to one molecule show significantly greater error for the other. The explanation for these results relates to sampling of configuration space in the neighborhood of the nuclei. We discuss how best to sample the nuclear regions, to aid in the design of new DMC algorithms.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

A29 RADIO FREQUENCY PULSED OPTICAL NUCLEAR POLARIZATION. J. Rowat and J.P. Colpa, Department of Chemistry, Queen's University, Kingston, Ontario CANADA K7L 3N6

The technique of optical nuclear polarization (ONP) generates nuclear spin polarization from electron spin polarization of excited triplet states. Near the level crossing (LC) point of the triplet spin levels hyperfine coupling between electron and nuclear spins transfers electron spin polarization to the nuclei. If radio frequency pulses of varying duration are applied to spin sub-levels near the LC point, the resulting nuclear spin polarizations are large and are found to beat at the Rabi using a master equation will be presented.

A 30

Electrostatic Interact Solvated Macromolecules of General Shape

P. B. Shaw

Department of Phythe Pennsylvania State University, Universi
Park, PA 16802

A solvated necule of general shape is modeled as a char
bearing cavity oielectric constant in a high dielectric medi
A unit point chaed within the cavity induces a polarization
charge density ovity surface which is determined by a linear
inhomogeneous inquation. This surface polarization charge d
in turn determinoisson Green function, which plays the role
the Coulomb pote the presence of a dielectric interface. Wh
the point chargeiciently close to the cavity surface, the in
equation can be n terms of local surface geometry. This limi
solution is alsoroughout a spherical cavity in a conducting
medium. For a avity, the approximation can be improved thro
the introductiosi images." Electrostatic pK shifts are calc
for a cavity shmodels the geometry of an enzyme with a large
indented active

A 31

ROTATIONAL DECOUPLING: CAN INTRAMOLECULAR VIBRATIONAL ENERGY FLOW BE INHIBITED BY ROTATIONAL EXCITATION? Randall B. Shirts, Department of Chemistry, University of Utah, Salt Lake City, UT 84112 U.S.A.

There has been a great deal of recent theoretical and experimental interest in intramolecular vibrational dynamics due to its importance in infrared multiple photon processes and unimolecular reactions. Almost all theoretical studies have neglected rotational motion. It is commonly assumed that the additional coupling provided by rovibrational terms in the molecular Hamiltonian will increase the rate of energy flow, lower the threshold for the quasicontinuum and increase the extent of classically chaotic motion. In model studies, we have observed this behavior. However, it is also possible for rotational excitation to decrease the amount of vibrational energy flow. A model for the stretching motions of H_2O serves as an example of this phenomenon. The explanation for rotational decoupling will be described using classical and quantum studies, and the search for real molecules exhibiting the phenomenon reported. The significance of rotational decoupling in mode specific infrared multiple photon experiments will also be discussed.

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CHARACTER TABLES AND SYMMETRY EIGENVECTORS FOR TWO-ROTOR MOLECULAR SYSTEMS.

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Abstract

In an early paper (Y.G. Smeyers and M.N. Bellido, Int. J. Quantum Chem., **19**, 553 (1981)), we have studied the internal dynamics of acetone by solving the Schrödinger equation for two equivalent C_{3v} rotors rotating in a C_{2v} frame. For this purpose, Group Theory for non-rigid molecules was widely used. In particular, the symmetry eigenvectors which diagonalize in boxes the hamiltonian matrix were deduced by using the well known character table of the G_{36} group for acetone-like molecules. The procedure was applied to study the internal dynamics of acetone and xylene molecules.

In order to generalize this study to other two C_{3v} rotor molecules, of higher or lower internal symmetries than acetone, the corresponding character tables need to be known. In the present work, these character tables are deduced into the frame work of the Altmann Group Theory for non-rigid molecules, and from them the symmetry eigenvectors are determined. The symmetries considered are those of para-xylene, dimethylamine, N-methylethylidenamine, trans-1,2-dimethylcyclopropane, and a completely asymmetrical dimethyl molecule.

A33 MODEL DEPENDENCE OF COLLISION EFFICIENCIES FOR THERMAL UNIMOLECULAR REACTIONS. Neil Snider, Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6.

Formulas for collision efficiency factors for one and two channel unimolecular reactions were derived for several simple models. It was found that the efficiency factors are determined to within about 5% by the model's $\langle \Delta\varepsilon \rangle$, the mean energy transferred per collision, and its $\langle (\Delta\varepsilon)^2 \rangle$, the mean square energy transferred per collision. At fixed $\langle \Delta\varepsilon \rangle$ the collision efficiency factor for a single channel reaction increases with decreasing $\langle (\Delta\varepsilon)^2 \rangle$. This result is explainable in terms of the collider's producing an energy flow such as to maintain the reactant molecule energy distribution more nearly equal to the Boltzmann distribution. The just mentioned results do not apply to the efficiency factor related to the branching fraction for a two channel reaction if $|\langle \Delta\varepsilon \rangle|$ is less than or equal to the difference between the channel threshold energies. In this case it is the large, negative $\Delta\varepsilon$ part of the energy transfer distribution which determines the collision efficiency.

A34 S_n-ADAPTED TENSOR BASES IN THE QUANTUM-LIOUVILLE FORMULATION OF NMR SPIN DYNAMICS OF $[A]_n$ and $[AX]_n$ SPIN SYSTEMS. F.P. Temme and B.C. Sanctuary, McGill University Montreal, Quebec, CANADA

The spin dynamics and relaxation of multispin systems, involving clusters of like spins, utilizes S_n-adapted inner coupled tensors, whose primitives arise from combinatorial views of intermediate $_{1h}$ angular momenta coupling schemes as "trees". S_n-adaptation of these equal I_i multispin bases proceeds via either, (a) the projection super-operator, ρ_μ approach, or else (for specific cases) by the use of (b) automorphisms within a scheme that treats the primitive intermediate $_{1h}$ couplings in a democratic manner. Both lead to partitioning of the basis into subdomains with dimensionalities $n_\mu = \text{tr}\ \rho_\mu$ for $[A]_n$ systems. The second approach under S_3 provides eigenvalues λ for the $[A]_3$ system that are specific μ-th characteristics; this ensures that $T^{kg\pm}\ ^{\lambda}(\bar{k}\bar{k}\bar{k})$ and $T^{kg}(S_3)\ (\bar{k}\bar{k}\bar{k})$ are equivalent. For $[AX]_n$ spin systems partitioning is governed by the direct product Liouville projector, and its associated invarience properties, over the double spin tensors, $[T^k \times F^k]^{kg}$.

A35 HIGHER ORDER ADIABATIC SEPARATION OF STRONGLY COUPLED SYSTEMS.

T. Tung Nguyen-Dang, Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

A systematic search method for obtaining higher-order adiabatic representations of coupled systems is developped, starting from the phase corrected adiabatic approximation recently proposed by Maréchal. The method is illustrated by its application to three simple, exactly soluble, two-body systems: the free hydrogen atom, the linearly forced hydrogen atom and the system of two harmonically coupled oscillators. Interesting results and problems, associated with the higher-order adiabatic separation of nuclear and electronic motions in a molecule are presented and discussed.

A 36 RELAXATION THEORY FOR ANISOTROPIC MUONIUM WITH RANDOM HYPERFINE DISTORTIONS. Ralph Eric Turner, Department of Chemistry, University of British Columbia, Vancouver, B.C. V6T 1Y6

The spin dynamics associated with random hyperfine distortions of an ensemble of muons, which have thermalized as muonium atoms in solids, is approximated with the motion generated by averaging the spin evolution of a single isolated muonium atom over a product of continuous hyperfine frequency distributions. The hyperfine tensor includes an isotropic Fermi contact term and a symmetric traceless dipole-dipole term. Relaxation functions are calculated for both the zero and high field limits and fit to the available f used quartz data.

A37

SEMICLASSICAL TREATMENT OF THE VIBRATIONAL SPECTROSCOPY OF THE OCS MOLECULE. Eric E. Aubanel and David M. Wardlaw, Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6.

A longstanding goal in theoretical chemistry is the development of practical semiclassical methods for the treatment of nuclear motion in molecules. In addition to providing useful conceptual advantages, such methods offer the possibility of complementing quantum matrix element and matrix diagonalization calculations with less tedious, more flexible, and less time-consuming computations. To this end vibrational energy levels (up to ~7500 cm^{-1} with respect to the ground state), transition intensities, and mean dipole moments for OCS have been determined semiclassically via classical trajectories with suitable classical actions. The 'quantized' trajectories are obtained by the adiabatic switching method. A model potential energy function, determined by Foord, Smith and Whiffen by fitting to spectroscopic data, is employed. The accuracy of the semiclassical results is established by comparison to the corresponding full quantum calculation. Several high energy eigenvalues have been obtained semiclassically for the first time and are compared to experimental results. Advantages and extensions of the present method are discussed.

A38 IMPURITY EFFECTS ON CHEMISORPTION. T. Zhang[1] and W.-K. Liu, Department of Physics and the Guelph-Waterloo Program for Graduate Work in Physics, University of Waterloo, Ontario CANADA N2L 3G1. [1]Physics Department, Henan Normal University, Xinxiang, Henan, CHINA.

The influence of a substitutional impurity atom on the chemisorption properties of an atom adsorbed on the (100) surface of a simple cubic substrate is investigated using the Green's function method. The pure solid substrate is approximated by the tight-binding scheme and the impurity is described by the Koster-Slater model. The interaction energy is calculated as a function of the band filling, the effective adatom level, the hopping potential between the adatom and the nearest surface atom, the impurity level and the relative adatom-impurity separation. The occurrence of localized states lying outside the band is also studied as a function of the various system parameters.

A 39 CONTROL OF PRODUCT YIELDS FOR ATOMS AND IONS IN THE PHOTODISSOCIATION OF LITHIUM FLOURIDE. Catherine Asaro and Paul Brumer, Chemical Physics Theory Group, Dept. of Chemistry, University of Toronto, Toronto, Ontario, M5S-1A1, Canada and Moshe Shapiro, Dept. of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel

The single-frequency vacuum-UV photodissociation of lithium flouride (Asaro and Dalgarno 1986) produces both ions and neutral atoms. We develop a theoretical model that uses multiple-frequency coherent radiation to obtain control over the fragments produced by dissociation out of the two lowest sigma states of LiF. The anisotropy in the states differs at low energies, so the yield of atoms versus ions also varies with scattering angle. The nature of the curve-crossing for the two states leads to separability of the excitation and dissociation events, which precludes application of the coherent theory to the total yields for the process. However, control may be obtained at a fixed scattering angle as a function of the elliptical polarization of a single laser. It is thus possible to separate the products by fixing the angle of observation and varying the polarization of the laser or by fixing the polarization and varying the detection angle.

Catherine Asaro and A. Dalgarno, 1986 in preparation

EXPONENTIAL APPROXIMATION TO ONE PARTICLE DENSITY MATRIX AND THE WIGNER'S DISTRIBUTION. Max Berkowitz, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514 U.S.A.

It is shown that the earlier proposed thermodynamic-like description of the ground state of a many-electron system, which demands an introduction of local quantities, such as temperature, entropy, etc. is equivalent to a well defined approximation for the density matrix and therefore for the Wigner's distribution. This approximation has been successfully applied to calculation of Compton profiles and exchange energy functional in a framework of density functional theory.

ABSTRACTS FOR POSTER SESSION B

Thursday, June 26th, 1986

B1 **The Electronic and Geometric Structure of the Lowest $^5\Sigma^+$ and $^5\Pi$ States of $CrCl^+$.**

A.E. Alvarado-Swaisgood and J.F. Harrison, Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322

Recent experimental work[1] suggests that $CrCl^+$ reacts (exothermically) with alkanes (activating the C-H and C-C bonds) while Cr^+ does not. A mechanism for the enhanced reactivity of $CrCl^+$ has been suggested by Mandich[1] *et al.* and involves the $^5\Pi$ state of $CrCl^+$. In this talk we will present MCSCF and MCSCF+1+2 calculations of the properties of the $^5\Sigma^+$ and $^5\Pi$ states of $CrCl^+$ and discuss their relevance to the proposed mechanism.

[1]M.L. Mandich, M.L. Steigerwald and W.D. Reents, Jr., private communication.

B2

ANIONS IN THE LOCAL SPIN DENSITY METHOD.

Jan Andzelm and Dennis R. Salahub,
Département de chimie, Université de Montréal,
Montréal, Québec, H3C 3J7, Canada.

A perturbational approach to self interaction corrections (SIC) in the Local Spin Density (LSD) method is introduced and tested in atomic and molecular calculations. This correction is shown to be of major importance for electron affinities. The direct SIC-LSD terms (calculated with the LSD density), are the most important and the inclusion of the deformation of the LSD density in first order brings about very good agreement with experimental electron affinities. The errors are ~0.1 eV for C^-, O^- and F^-. Because of the non-linearity of the exchange correlation potential, SIC calculations for degenerate orbitals, which use average densities, are in error and independent calculation for each spin orbital is necessary. Application of this technique for molecules will be discussed.

Even without the SIC, LSD calculations can provide a useful (though less accurate) description of atomic and molecular anions, provided that LCAO, rather than numerical or scattered-waves, techniques are employed. LCAO-LSD calculations yield stable negative ions in many cases where bound numerical solutions do not exist. This is because the limited (but not small) basis set acts as a barrier which confines the electrons around the atom, effectively cutting off the incorrect tail of the LSD potential. Results at this level for several inorganic and metallic molecular anions will be presented.

B3 ELECTRON CORRELATION: COULOMB SHIFTS AND COULOMB HOLES. K.E. Banyard, Department of Physics, University of Leicester, Leicester, England.

Electron correlation goes beyond the traditional Hartree-Fock (HF) treatment by introducing electron-electron repulsions. Naturally, correlated wavefunctions produce greatest change, measured relative to the HF description, in the probability density for the inter-particle separation. This occurs in both position- and momentum- space coordinates. Such changes give rise to the Coulomb hole, $\Delta f(r_{12})$ vs. r_{12}, in position space and the Coulomb shift, $\Delta f(p_{12})$ vs. p_{12}, in momentum space. Partial Coulomb holes and shifts, which illustrate how correlation effects vary around a test electron located in different regions of space, are particularly useful in highlighting changes in the relative importance of the radial and angular components of correlation. In this context, angular 'holes' and 'shifts' have also proved helpful in the understanding of trends in correlation characteristics. Hence, the strengths and weaknesses within a given correlated wavefunction can be ascertained. As examples, results are presented and analysed for some low-lying excited states of He and Li and comparisons are made with the ground states.

B4

SINGLE EXCITATIONS ON MULTIREFERENCE CI WAVE FUNCTIONS : A TREATMENT OF THE LEFT-RIGHT CORRELATION IN MULTIPLE METAL-METAL BONDS

Marc BENARD, Roland WIEST and Alain STRICH
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67000 STRASBOURG (FRANCE)

It is shown that imposition of a proper dissociation of a multiple metal-metal bond (by means of CI or CASSCF treatments) does not provide a complete description of the left-right correlation between metal atoms. A limited CI treatment is proposed to account for the remaining part of the left-right correlation, based on a CI expansion restricted to single excitations from a properly selected multireference basis. Applications to Cr_2H_6 (triple Cr-Cr bond) and $Cr_2(O_2CH)_4$ (quadruple bond) will be displayed.

B5

Why do aluminum trihalides dimerise? : A Multiple-Scattering analysis, E. M. Berksoy, M. A. Whitehead, Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6 ; and B. McMaster, Department of Physics, McGill University, Montreal, PQ, Canada H3A 2T8

Aluminum trihalide monomers and dimers were studied using the Multiple Scattering method with X-alpha exchange and Vosko-Wilk-Nusair exchange-correlation potentials.

Different percent overlaps were required for each monomer-dimer halide to give the experimental dimerization energy; with this parametrization of overlap, the ionization potentials for the monomers and dimers were predicted in good agreement with experiment for both potentials.

Dimerization occured because aluminum comtributed less electrons to the bonding in the dimer than in the monomer compared to the halides. The contour plots gave no evidence of a metal-metal bond or any significant aluminum-bridge halide bonds but strong aluminum-terminal halide bonds. The aluminum apparently sits in the bridge halide density cloud; it is closer to the free Al atom density in the dimer than the monomer, which perhaps drives the dimerization.

B6 ON THE DIRECT DETERMINATION OF CONSTRAINED PURE STATE ONE-ELECTRON DENSITY MATRICES : A NEW THEORETICAL METHOD AND ITS APPLICATIONS. P.KHAN, K.K.DAS AND S.P.BHATTACHARYYA, Theory Group, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, INDIA.

An algorithm proposed recently by us for the determination of pure state constrained one electron density matrices has been remodelled (Pramana J. Phys. 25, 281 (1985); Chem. Phys. Letters. 125, 225 (1986). The remodelled algorithm is applied to the construction of ground state potential energy curve of Lithium hydride molecule using the experimental dipole moment function as the external constraint. The equilibrium internuclear distance (r_e) is seen to be unaffected by the "dipole moment constraint". The "force-constant" however, improves remarkably. The constrained density and the corresponding "natural" orbitals are analysed thoroughly revealing interesting features of the "rearranged density" under the influence of the constraint.

MRD-CI STUDY OF THE ISOMERS HSiO, SiOH AND THEIR NEGATIVE IONS $HSiO^-$, $SiOH^-$

B7

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E3B 6E2

ABSTRACT

The equilibrium geometries were obtained after MRD-CI (NO's) calculations using a DZP AO basis augmented by semidiffuse p and d functions. SiOH is more stable than HSiO by about 13 kcal/mol and with a D_o(SiO-H) of 29.1 kcal/mol. HSiO is a σ radical, with the 10 a' MO spread out on all centers while SiOH has a π-structure being such MO almost localized on Si. The first excited $^2A''$ (3a") (SiOH) has a bent equilibrium geometry, in variance with Walsh's rules. Additional calculations for the $^2A''$ and $2^2A'$ (HSiO) states for bent structures (α = 95°) and SiO elongations show similar features as reported for the HCO radical. The vibrational frequencies and the dipole moment functions with respect to the internal coordinates have also been studied. Calculations carried out for SiO, OH and SiH indicate a good agreement for μ(R) when compared with other ab initio results using extended AO basis. The μ of H_2SiO and t-HSiOH are also studied. The geometrical parameters, ν, μ and SiO-bond strengths in HSiO/H_2SiO as well as between SiOH/HSiOH are very close. The IP(ad) of SiOH (6.52 eV, without ZPE) is 2 eV smaller than for HSiO and thus increasing the relative $SiOH^+/HSiO^+$ stability to 64 kcal/mol. The proton affinity (O-site) of 8.10 eV agrees with a value 8.1 ± 0.7 eV (exp.). The results for $HSiO^-$ and $SiOH^-$ are interesting. The $X^1A'(10a'^2)$ $HSiO^-$ state is most stable by 10 - 15 kcal/mol than $X^3A''(10a'\ 3a'')$ $SiOH^-$. The EA (HSiO) is also rather large (about 1.75 eV) when compared with an EA (HCO) of 0.313 eV (exp.). The $^3A''$ state for both $HSiO^-$ and $SiOH^-$ is placed 0.2 - 0.3 eV below the corresponding neutral state while $^1A'(SiOH^-)$ is less stable than X^2A' SiOH.

B8 THE ACCURACY OF THE PERMANENT MULTIPOLE VALUE FOR THE FIRST ORDER COULOMB ENERGY AS A FUNCTION OF ORIENTATIONS, DISTANCES AND BASIS FUNCTION TYPES. D. Belford and E.S. Campbell, Department of Chemistry, New York University, New York, NY 10003 USA

The electrostatic (first order Coulomb) energies of the isolated molecule charge densities of small molecules which form H-bonds (HF, H_2O, NH_3) will be compared with energies calculated by both single center and multicenter permanent multipole expansions. Calculations will be presented for distances $\geq$ those in their condensed phases and for different attractive and repulsive orientations. Comparisons will be made between results from basis sets with and without polarization functions. Limited results showing the effect of an increase in the number and diffuseness of polarization functions will be included. Our work will be continued for other types of small molecules.

B9 AB INITIO MCSCF AND MRD-CI CALCULATIONS OF THE TORSIONAL POTENTIAL ENERGY SURFACE ABOUT THE N--N BOND IN FORMALDAZINE (2,3-DIAZA-1,3-BUTADIENE).

Vera M. Kolb, Maria M. Szczesniak, Cary F. Chabalowski, Abbott Laboratories, Department 47E, Abbott Park North Chicago, Illinois, U.S.A. 60064

Certain opiates agonists and antagonists containing the azine moiety have been shown to exhibit lasting activity, which has generated further interest in exploring the structure of formaldazine, especially the torsion angle about the N--N bond. Ab initio MCSCF and CI calculations at several basis set sizes were performed in this study on formaldazine to produce a potential energy surface for the twisting about the N--N bond. The calculations show that the ground state wavefunction consists of at least two main configuration-state-functions at every torsion angle studied. This offers an explanation for the failure of other theoretical studies to find a shallow, local minimum in the curve predicted by experiment to be at a torsion angle of approximately 60° (with trans planar being 180°).

B 10 POINT GROUP SYMMETRY-ADAPTATION IN CLIFFORD ALGEBRA UNITARY GROUP APPROACH (CAUGA). Joe Paldus, Jin-Quan Chen*, and Mei-Juan Gao*, Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

The symmetry adaptation procedure for the UGA (Chen et al. Scientia Sinica 23 (1980)1116), which can account for the invariance properties of the Hamiltonian with respect to any finite point group G, is both modified and adapted to the CAUGA.

Starting from a symmetry-adapted one-electron (MO) basis $|\mu_i\kappa_i>$, with μ_i labeling the n_i-dimensional irrep of G, we first construct the pure configuration many-electron basis $^i|\nu_i\mu_i\kappa_i>$, adapted to the chain $U(n_i) \supset G \supset G(s)$, in terms of the $U(n_i)$ Gelfand-Tsetlin (GT) basis $|\nu_i W_i>$, since the n_i basis vectors of the μ_i-th irrep of G span the defining representation of $U(n_i)$. Here W_i is the appropriate Weyl tableau and G(s) designate a subgroup chain of G. The pure configuration basis $|\nu_i\mu_i\kappa_i>$, $i = 1,\ldots,m$, are then consecutively coupled to the desired G-adapted states by using the CG coefficients of G, and to the $U(n_1) \subset U(n_1 + n_2) \subset \ldots \subset U(n)$ basis by using the permutation group induction coefficients. This basis can be expressed in terms of the U(n) Gelfand basis by using the unitary group subduction coefficients (SDC). The SDC are particularly simple for the highest weight state (HWS), which can be in turn represented through the $U(2^n)$ two-box Weyl tableaux of CAGUA. The non HWS's are obtained by applying the $U(n_i)$, $i = 1,\ldots,m$ lowering generators to the HWS. In this way, we obtain the CAUGA G-adapted basis.

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B 11

Electronic Structure of the P_b Defect at the $Si(111)/SiO_2$ Interface.

Michael COOK and Carter T. WHITE, Code 6129, U.S. Naval Research Laboratory, Washington, D.C. 20375 USA

A sequence of cluster models for the amphoteric P_b dangling-bond defect ($Si_3{\equiv}Si\cdot$) have been studied by all-electron SCF calculations using the spin-polarized multiple-scattering Xα method. The largest system we consider is the 73-atom C_{3v}-symmetry cluster $(Si_{22}H_{21})/(Si_6O_{18}H_6)$, a model for an isolated P_b center at the $Si(111)/SiO_2$ interface. The Si side of the junction is represented by a roughly hemispherical fragment of crystalline silicon. The silica phase is a puckered ditrigonal ring of six SiO_4 tetrahedra, bonded to a hexagon of Si(111) surface atoms surrounding the central P_b defect. Similar six-membered rings occur naturally in the tridymite and cristobalite phases of silica. The surface of the model cluster is saturated by hydrogen atoms.

One-electron energies and one-electron properties are calculated from the molecular wavefunction and comparisons are made with available experimental data. The dependence of the properties of the trivalent silicon defect on cluster size is investigated by similar calculations on the sequence of model systems SiH_3, Si_4H_9, $Si_{13}H_{27}$, and $Si_{22}H_{27}$, which represent an isolated P_b center on the pristine Si(111) surface.

B12 FIFTH ORDER CONSTANT DENOMINATOR PERTURBATION THEORY WITHIN THE LOCALIZED BOND MODEL. J. M. CULLEN, Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, W. N. LIPSCOMB, Department of Chemistry, Harvard University, Cambridge, MA 02138, M. C. ZERNER, Department of Chemistry, University of Florida, Gainesville, FL 32611 and Guelph Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1.

A complete fifth order constant denominator perturbation treatment is derived for the localized bond model of Malrieu, Diner and Claverie [J. P. Malrieu, in Modern Theoretical Chemistry, Vol. 7, Semiempirical Methods of Electronic Structure Calculations, Plenum Press, New York 1977]. Energy and wave function are expressed directly in terms of antisymmetrized molecular integrals through the use of the linked cluster diagrammatic representation. The result is a method which executes as rapidly as third and fourth order and which is proportional to N^3, where N is the number of bonds present. Calculations are performed for model cases where the starting zero order reference wave function poorly describes the system. These include strongly delocalized systems such as the annulenes and highly polarized molecules such as methyl isocyanide. Molecules containing atoms having multiple lone pairs where the hybridization becomes nonunique are also investigated. Results are computed at the PPP and CNDO/2 semiempirical levels where comparisons can be economically made to full CI solutions.

B 13

QUANTUM MECHANICAL CALCULATIONS ON THE EXCITED STATES OF OXAZIRIDINE. Cynthia Darling, Joe BelBruno, and Robert Ditchfield, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755 U.S.A.

Ab initio molecular orbital calculations with basis sets ranging from minimal to split-valence plus polarization have been employed to study the equilibrium geometry of oxaziridine and several methyl-substituted oxaziridines. Ionization potentials were calculated at several levels and compared with experiment where possible. First order configuration interaction was used to calculate singlet and triplet excited state energies, dipole transition moments, and oscillator strengths relative to a single reference ground state determinant. To describe Rydberg states, the basis sets were extended by the addition of very diffuse functions. The calculated relative orderings of valence and Rydberg excited states in substituted oxaziridines have been used to facilitate an interpretation of the MPI spectrum of N-isopropyl dimethyl oxaziridine. In addition, an analysis of the calculated electronic structures for low-lying excited states has been used in an attempt to gain insight into the nature of the two dissociation channels which BelBruno et al. observed when N-isopropyl dimethyl oxaziridine is photolysed.

B 14 MAXIMALLY ORTHOGONAL BOND DIRECTED HYBRID ATOMIC ORBITALS AS AN AID IN THE VISUALIZATION OF MOLECULAR ORBITALS. John Downing, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 U.S.A.

The form of the molecular orbitals produced by calculations using minimal basis sets is strongly dependent on the orientation of the molecule with respect to the Cartesian coordinate system in which the molecular geometry is specified. This leads to difficulty and uncertainty in the interpretation of the results in qualitative terms, particularly in the absence of molecular symmetry which provides a "natural" choice for the coordinate system. For example, even the classification of molecular orbitals as having pi or sigma symmetry in ethylene can be an arduous task if the C=C bond does not lie in a coordinate plane. This problem can be alleviated by expressing the molecular orbitals in terms of hybrid atomic orbitals on each atom which conform to the local symmetry at that atom. Such hybrids are typically directed, for example, along bonds, perpendicular to bond planes, or along pyramid axes. Although these hybrids cannot in general be made strictly orthogonal, their non-orthogonality can be minimized by a suitable choice of the s-orbital fraction for each hybrid. An algorithm for the automatic construction of such hybrids given only the minimal basis set overlap matrix, molecular orbitals in terms of the minimal basis set, and the molecular geometry is presented along with several examples of the result of its application.

B15 FORMYL QUANTUM CHEMISTRY: GEOMETRIES, VIBRATIONAL FREQUENCIES, ELECTRONIC DISTRIBUTIONS, AND UNIMOLECULAR REACTIONS OF HCOX (X = -CCH, -CN, -NC).

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

Ab initio quantum chemical calculations have been employed in a detailed examination of several formyl compounds: propynal, HCOCCH; formylcyanide, HCOCN; and formylisocyanide, HCONC. HF/3-21G, HF/6-31G* and MP3/6-31G* geometries have been optimized. The results for propynal are compared with experiment and empirical schemes for the scaling of rotational constants to yield better predictions for use by microwave spectroscopists are examined. The predicted rotational constants for ground state formylcyanide and formylisocyanide should aid in the detection of these as yet uncharacterized species. Vibrational frequencies at the 3-21G SCF and 6-31G* SCF computational levels were also determined. In contrast to many molecules, certain vibrational modes in propynal, and by inference forymlcyanide and formylisocyanide are significantly better described by the 6-31G* basis as opposed to the 3-21G set. Dipole moments, Mulliken analyses, and electron density contour plots provide information on the electronic distributions in this series of molecules. Preliminary studies of the ground state unimolecular dissociations will also be presented.

MULTICONFIGURATIONAL SPIN TENSOR ELECTRON PROPAGATOR (MCSTEP) IONIZATION POTENTIALS FOR GENERAL OPEN SHELL SYSTEMS

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B16

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We have developed a multiconfigurational spin tensor electron propagator (MCSTEP) technique for the theoretical determination of ionization potentials (IP) for general open shell and highly correlated atomic and molecular systems. In order to achieve this, we have used and extended the generalized spin tensor methods of Rowe and Ngo-Trong from nuclear physics. To properly account for correlation effects, we have additionally included tensor coupled ionization potential and electron affinity operators analogous to the state transfer operators necessary in multiconfigurational linear response. These MCSTEP results are extremely encouraging for both principal and shake-up IPs. MCSTEP ionization potentials and ionization process probabilities have been evaluated for F_2, O_2, and NH_2 and have been used to carry out detailed examination and interpretation of the respective PES or ESCA spectra. For F_2 and NH_2, the MCSTEP ionization potential results are compared to other large scale theoretical methods using the same basis set and at the same geometry. In addition, the PES of F_2 below 30 eV and of NH_2 below 16 eV were not previously well characterized experimentally except for a few of the lowest principal peaks. Apparently no reliable spectra have been reported for higher energies. We report and characterize several IPs in F_2 and NH_2 between 0-40 eV including several IPs that have not as yet been assigned experimentally.

B 17

Theoretical Studies of the Electronic and Geometric Structure of Small Polyatomic Cations Containing Sc.

A.E. Alvarado-Swaisgood, A. Mavridis, and J.F. Harrison, Department of Chemistry, Michigan State University, E. Lansing, MI 48824-1322.

Recent theoretical results on the interaction of Sc^+ with H, CH, CH_2, CH_3 and CO will be presented. In particular the electronic and geometric structure and the nature of the transition element-main group element bond, as predicted by MCSCF and MCSCF+1+2 calculations will be discussed and compared to available experimental data and previous calculations.

B 18 STRUCTURE AND ENERGETICS OF $SiH_nF_m^+$ (n + m = 1-4). E. W. Ignacio and H. Bernhard Schlegel, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

The equilibrium geometries of $SiH_nF_m^+$ (n + m = 1-4) were determined at the HF/3-21G and HF/6-31G* levels. The structures of Si $H_nF_m^+$ (n + m = 1-3) resemble the neutral molecules, but SiH_4^+, SiH_3F^+, $SiH_2F_2^+$, and $SiHF_3^+$ are characterized by a very long SiH bond. These are best described as complexes between hydrogen atom and $SiH_nF_m^+$, n + m = 3. The vertical and adiabatic ionization energies were calculated at the MP4/6-31G** level. Correlation corrections are relatively unimportant for the ionization potentials of the radicals, but make a significant contribution to the ionization potentials of the closed shell species, SiH_nF_m, n + m = 2,4.

B 19 CONFIGURATION INTERACTION STUDIES OF ATMOSPHERIC COMPLEX $HClO_2$. Jawed A. Jafri, Old Dominion University Research Foundation, Norfolk, Virginia 23508, and Donald H. Phillips, NASA Langley Research Center, Hampton, Virginia 23665-5225.

The two principal radicals HO and HO_2 play a pivotal role in tropospheric and stratospheric chemistry. They take part in several catalytic cycles responsible for the removal of odd oxygen. They are involved in many important coupling reactions e.g. $HO_2 + NO \rightarrow OH + NO_2$. They undergo association reactions that form moderately stable reservoir compounds such as HNO_3 and they react in the troposphere with certain hydrocarbon compounds and thereby remove them before they may be transported to the stratosphere.

Results on the complexes of HO with ClO and HO_2 with Cl to form ClOOH will be presented. GVB calculations on ClOOH complex predict stability with respect to ClO and HO fragments. Configuration interaction studies (first order and selected singles and doubles) to describe the binding with respect to various fragments, the equilibrium geometry and the potential role in the chemistry of the atmosphere will be presented. The MCSCF and CI results will be compared and the effect of correlation energy treatments on the properties predicted for the ClOOH complex will be discussed.

B 20

MC SCF Calculation of Electronic Transitions in some Transition Metal Complexes

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MC SCF calculations have been performed for the $CoCl_4^{2-}$ and $VO(H_2O)_5^{2+}$ ions, as well as for the vanadyl ion imbedded in various model surroundings. $CoCl_4^{2-}$ is ionic and VO^{2+} covalent, and the two systems therefore cover the range of chemical binding. The $CoCl_4^{2-}$ ion has been imbedded in the field from a Cs_3CoCl_5 crystal in order to investigate the significance of the Madelung potential. Only the d-d transitions have been studied, and the correspondence with experiment is excellent.

ELECTRONIC STATES OF NS/NS^+ AND SiF/SiF^+ OBTAINED BY CI METHODS

B21

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ABSTRACT

Using double zeta plus polarization and Rydberg basis functions, potential curves for low lying valence and Rydberg states of NS and SiF have been obtained by large scale multireference single and double excitation configuration interaction (MRD CI) methods. Besides the lowest $^2\Sigma^+$ states of NS and SiF, as discussed earlier [S. P. Karna and F. Grein, Int. J. Quantum Chem. **29**, 755 (1986)], the lowest $^4\Pi$ state of SiF is predicted to be a "semidiffuse" state. Calculated spectroscopic constants, generally better than obtained in other theoretical studies, for both the molecules are in very good agreement with the experiment. Comparison with the isoelectronic PO molecule shows that the electronic spectrum of NS is closer to PO than SiF. Several hitherto unknown doublet and quartet states of SiF are predicted. A theoretical explanation for the predissociation observed in the $C^2\Sigma^+$ ($2^3\Sigma^+$) state of NS will be given.

Several low-lying excited states of NS^+ and SiF^+ have been studied. Despite their being isoelectronic, a marked difference in the electronic spectrum of these ten electron systems is found. Whereas many states studied for NS^+ have been found to be stable, in SiF^+, except for the lowest $^1\Sigma^+$ and $^3\Pi$, all states are either metastable or repulsive. Interestingly, the electronic spectrum of NS^+ shows a striking similarity to those of N_2 and PN molecules and a systematic trend in the T_e of electronic states is found in going from N_2 to NS^+ to PN.

Potential energy curves and calculated spectroscopic constants along with the ionization potentials of the neutral molecules will be given.

B22 THE SELF-INTERACTION CORRECTED GENERALIZED EXCHANGE LOCAL SPIN DENSITY-FUNCTIONAL THEORY. S. Manoli and M.A. Whitehead, Department of Chemistry, McGill University 801 Sherbrooke St. West, Montreal, Quebec, CANADA H3A 2K6

A local spin density-functional scheme with generalized exchange, the LSD GX scheme, has been developed based on correct normalization conditions for an electron gas around a nucleus of charge Z. There are no adjustable parameters; the parameters B_1, B_2 and α^{lim} are constant for all atoms once the shape of the Fermi hole is chosen. These parameters are rigorously calculated without assuming an approximate shape for the Fermi hole correlation factor. The exchange density using this unspecified Fermi correlation factor reduces exactly to the homogeneous free electron gas exchange density at the high electron density limit (1).

The LSD GX exchange density is corrected for self-interaction by splitting the Fermi hole into self-interaction and pure-exchange holes. The theoretical relationship between this new GX-SI scheme and other self-interaction corrected schemes current in the literature is discussed and, calculations using these schemes are compared with each other.

(1) S. Manoli and M.A. Whitehead, submitted for publication.

B 23 COMPOSITE NATURAL ORBITALS FOR ELECTRON CORRELATION IN LARGE SYSTEMS.

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A new device of constructing approximate natural orbitals (NO's) is proposed. These orbitals are expected to be useful in configuration interaction (CI) calculations of a large system which is regarded as consisting of fragments. It is well known that convergence of CI depends on an orbital set from which configuration state functions are created. A way of constructing approximate NO's from NO's of fragments is proposed. The usefulness of the composite NO's is demonstrated on C_4H_6 which is regarded as double C_2H_4. Excitation evergies calculated by single and double CI with the truncated composite NO's of (14σ, 8π correlating orbitals) agree within 0.2 eV with those calculated with a full orbital set (37σ, 12 correlating orbitals), while the truncated SCF MO's of the same size as the composite NO's gave disastrous excitation energies.

B24

Structure and Stability of Small and Medium Size Beryllium and Aluminum Clusters. A Theoretical Study.

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Abstract

The structure and stability of small Al_n clusters (n=2,3,4,5,13) has been investigated using ab initio quantum chemical techniques. Inclusion of polarization functions (one or two sets of d functions on each center) is found to be more important than correlation for the geometry of the clusters. In addition, the d functions improve the dissociation energies substantially, both at the self-consistent field (SCF) and configuration interaction (CI) levels of approximation. Low-lying, two-dimensional structures are found even for Al_{13}, where a diamond-shaped planar structure is only 1.3 eV higher in energy than the icosahedral lowest-energy geometry. The structures studied were suggested from dynamics simulations using a semi-empirical potential incorporating both two- and three-body forces. Accurate ab initio calculations on diatomic and triatomic systems will in turn be used to obtain reliable potentials, in particular for interactions between different types of atoms.

Neither for Al_{13} nor for Be_{13} is the lowest-energy structure that of the bulk (Al fcc and Be hcp). For Be_{13}, with one central atom and its twelve nearest-neighbors, the fcc structure is 1 eV lower than hcp. Extending the Be_{13} cluster by the nearest neighbors of the outer shell yields Be_{55}, for which we have compared the stabilities of the fcc and hcp structures. The fcc structure is still lower than the bulk hcp, but the difference per atom is substantially reduced. The dissociation energy per atom is substantially larger in Be_{55}, while the energy per bond is the same as for Be_{13}. An accurate expansion of the Be 2p orbital is required to describe the large s-p hybridization in the clusters.

B 25

CONDUCTION BAND STRUCTURE OF SOLID ARGON AND XENON

by P. Plenkiewicz, B. Plenkiewicz and J.-P. Jay-Gerin, Department of Nuclear Medicine and Radiobiology, Faculty of Medicine, University of Sherbrooke, Sherbrooke, Quebec, Canada, J1H 5N4.

The electronic conduction-band structures of solid argon and xenon has been calculated with the Augmented Plane Wave Method using a newly-developed norm-conserving pseudopotentials for Ar and Xe. The histogram of the conduction-band density of states (DOS) has been obtained and compared to that resulting from the analysis of low-energy electron transmission experiments. A reasonable agreement has been found between both DOS spectra which permits to give a physical interpretation of the maxima and minima observed in electron transmission experiments.

B26

AB INITIO SELF-CONSISTENT-FIELD APPROACH TO MOLECULAR SOLIDS UNDER PRESSURE: MOLECULAR ORBITAL EFFECTIVE POTENTIALS.* Susanne Raynor, Department of Chemistry, Rutgers University, Newark, NJ 07102 U.S.A

Traditional theoretical approaches to the study of molecular solids have used models based on simulation with finite clusters of molecules or have involved the use of pair potential approaches. Neither is appropriate for modeling solids under pressure: unless a tremendous number of molecules are included in the cluster, the cluster model lacks the long range molecular interactions necessary to study events occurring in the interior of the crystal; and the pair potential approach breaks down at pressures high enough to make many-body interactions important. Our approach takes maximum advantage of the crystal periodicity and, in so doing, leads to a convenient partitioning of the crystal energy. Molecular reactions and interactions can then be studied directly, with all many-body interactions included. In this paper, we will discuss the development of molecular orbital effective potentials useful in the application of our method.

*Supported by Rutgers University Research Grant #2-02291.

B 27

POTENTIAL ENERGY CURVES USING UNRESTRICTED MØLLER-PLESSET PERTURBATION THEORY WITH SPIN ANNIHILATION. H. Bernhard Schlegel, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

Unrestricted Hartree-Fock and unrestricted Møller-Plesset perturbation theory are convenient methods to compute potential energy curves for bond dissociation, since these methods approach the correct dissociation limit. Unfortunately, a spin unrestricted wavefunction can contain large contributions from unwanted spin states that can distort the potential energy surface significantly. The spin contamination can be removed by projection or annihilation operators. As is well known, the spin project unrestricted Hartree-Fock bond dissociation curves have a large kink at the onset of the UHF/RHF instability and a spurious minimum just beyond. However, the spurious minimum disappears and the kink is very much less pronounced at the unrestricted Møller-Plesset level with spin projection. Bond dissociation potentials for LiH and CH_4 are computed at the fourth order Møller-Plesset level plus spin projection. Good agreement was found with full CI and MR-CISD calculations. Other examples include radical additions, abstraction reactions and formation of diradicals.

B 28 CALCULATED BARRIER HEIGHTS FOR OH + C_2H_X (X = 2,4) USING UNRESTRICTED MØLLER-PLESSET PERTURBATION THEORY WITH SPIN ANNIHILATION. C. Sosa and H. Bernhard Schlegel, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

The reaction of OH radical with C_2H_2 and C_2H_4 has been studied using ab initio molecular orbital techniques. Reactants, loose clusters, transition structures, and intermediate radicals were optimized at HF/3-21G and HF/6-31G* levels. The barrier heights have been computed using unrestricted Hartree-Fock and Møller-Plesset perturbation theory up to fourth order including single, double, and quadrupole excitations. Spin contamination of the UHF wavefunction has been corrected by annihilating the largest and higher spin contaminants. The vibrational frequencies were computed using analytical gradient methods at the HF/3-21G level. The barrier height for these reactions are overestimated at the MP2, MP3, and MP4 levels. Single annihilation of the largest spin contamination lowers the barrier height by 4 - 10 kcal/mol for both systems and increases the C-O bond distance by ca. 0.2 A.

B29 CONVERGING BOUNDS TO THE EIGENVALUES OF THE ATOMIC SCHRODINGER EQUATION.

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A method proposed by S.R. Singh(1981) for computing converging lower bounds to atomic eigenenergies is briefly reviewed, and a parallel method for determining converging upper bounds is explored. Both methods require the Hamiltonian in question to be decomposable into an unperturbed part plus a non-negative pertubation, with the eigenvalues and the eigenfunctions of the unperturbed operator explicitly known. Computationally, the methods involve the evaluation of fixed points of a sequence of functions over a small portion of the negative real line, the functons being the eigenvalues of a small to medium size matrix-valued function defined on an identical domain. Along with the bounds, the methods also produce approximate eigenfunctions. A somewhat surprising result concerning the upper bound method is that it can be shown to be equivalent to the Ritz-Rayleigh method, although the computational procedure involved is quite different. As a preliminary numerical example, we present the results for the ground state of helium.

Abstract (Dr. M.C. van Hemert)
for the 9th Canadian Symposium on Theoretical Chemistry, June 23-27, 1986

B30

Ab initio treatment of the ArH emission spectra.
H. Dohmann, M.C. van Hemert* and S.D. Peyerimhoff, Institute for Theoretical Chemistry, Bonn University, Germany.

We have used recently calculated ab initio potential curves and nonadiabatic couplings, for the computation of the emission spectra of the ArH excimer. From the Fermi-Golden rule expression for the linewidth, we find that the bound excited sigma states are predissociated to such an extend that observable emission spectra can stem only from the non-predissociated pi states. This is in agreement with the discrete linespectrum observed by Johns(2) and assigned by him on the basis of the rotational fine structure as a pi to sigma transition. Our calculated line positions and linewidths for the (2)doublet pi to A doublet sigma transition are very close to the experimental ones, provided we take into account both the first and second order derivative terms for the radial part of the kinetic energy coupling.
Our prediction of the continuum emission for the (1)doublet pi to X doublet sigma transition is identical, within experimental accuracy, to the emission recently observed in the 200 to 400 nm region(3). The calculated radiative lifetime of the lowest vibrational level of the excited state is also within the experimental range.
We also report the results of a more refined treatment, where the Schroedinger equation for nuclear movement in the sigma states is solved with the help of a close coupling procedure. This procedure was earlier found to be very succesful in the treatment of photodissociation caused by radial coupling(4). From the resulting detailed information on the lineshapes- also Fano profiles are predicted- we infer predissociation rates in general agreement with the Fermi-Golden rule results.

(1) H. Dohmann, P.J. Bruna and S.D. Peyerimhoff, to be published.
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(4) E.F. van Dishoeck, M.C. van Hemert, A.C. Allison and A. Dalgarno, J. Chem. Phys., 81, 5709 (1984).

*permanent adress: Gorlaeus Laboratories, Leiden, The Netherlands.

B 31 THEORETICAL STUDY OF COADSORPTION OF CO AND NO ON A Rh(100) SURFACE. Dragan L. Vuckovic and Roald Hoffmann, Department of Chemistry, Cornell University, Ithaca, New York 14853 U.S.A.

Adsorption of CO and NO, and their coadsorption on the Rh(100) surface was investigated using Extended-Hückel tight-binding calculations. The surface was represented by a two dimensional three layer slab, using the experimental fcc structure of Rhodium metal. All the calculations were done using a single-face adsorption model. The coverage dependence for several adsorption sites was investigated for CO and NO, along with the different possible arrangements for their coadsorption. The results are given in terms of overlap populations and orbital population analysis.

B32

COMPUTATIONAL STUDIES OF SMALL TRANSITION METAL CLUSTERS

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The nature of the metal metal bond in small transition metal clusters will be discussed using examples selected from transition metal diatomic and triatomic species.

B33 CALCULATIONS USING THE GENERALIZED EXCHANGE LOCAL SPIN DENSITY-FUNCTIONAL THEORY. S. Manoli and M. A. Whitehead, Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, CANADA H3A 2K6

Results calculated using the Generalized Exchange scheme (LSD GX) of Manoli and Whitehead (1) are presented and compared to the corresponding ones calculated using the $X\alpha$ and free electron (LSD FE) exchange potentials.

A comparison of the total energies and eigenvalues show that the LSD GX scheme gives better results than the LSD FE scheme and better trends than the $X\alpha$ scheme when compared to the corresponding Hartree-Fock results (1).

The inter-configurational total energy differences of the transition metals have been calculated using these schemes and, the LSD GX results are clearly the best when compared to the corresponding experimental ones.

The ionization potentials (IP) have been calculated using the transition state method (removing half an electron from the highest occupied atomic orbital), the $\Delta E(SCF)$ method and by adding correction terms to the fully occupied orbital eigenvalue. These correction terms were derived from the work of Gopinathan (2) which determined the relationship between the $X\alpha$ and HF eigenvalues. A comparison of the results of calculations using these three methods with the LSD GX, $X\alpha$ and LSD FE schemes to the experimental IP's show that, overall, the LSD GX and $X\alpha$ results are close to each other and better than the corresponding LSD FE ones and, that the LSD GX and $X\alpha$ IP's are very close to the experimental ones.

The LSD GX results were obtained without the use of an adjustable parameter such as the α^{HF} of the $X\alpha$ scheme and hence, this scheme is more reliable.

(1) S. Manoli and M.A. Whitehead, submitted for publication.
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B34 RESONANCES IN MOLECULAR PHOTOABSORPTION AND PHOTOIONIZATION SPECTRA: T.J. Gil, J.A. Sheehy, C. Winstead, and P.W. Langhoff, Indiana Univerity, Bloomington, IN 47405 USA

Recent theoretical studies of resonance phenomena in electronic excitation and photoionization spectra are reported. The X-ray absorption spectrum of a series of sulfur-containing molecules near the sulfur K edge is investigated. This series includes H_2S, OCS, SO_2, CS_2, SF_4, and SF_6. Assignments of experimental features are possible in many cases, and the effect of the molecular environment on K-edge spectra is illuminated. Valence shell calculations on the partial photoionization cross sections of N_2O account for the main features observed experimentally and illustrate the effect of σ^* and π^* virtual valence orbitals on the partial cross sections. A study of the $4\sigma_g^{-1}$ ionization channel in CO_2 is also reported, with particular reference to the effect of the $4\sigma_u$ (σ^*) virtual orbital on this channel and to the significant discrepancies between theory and experiment and among various theoretical results.

B 35 AN EXAMINATION OF THE MOLECULAR PROPERTIES OF 5-THIO-α-D-GLUCOPYRANOSE, 6-THIO-β-D=FRUCTOPYRANOSE, AND α-D-GLUCOPYRANOSE BY AB INITIO LCAO-MO CALCULATIONS.

Abbas Farazdel, Vedene H. Smith, Jr., Walter A. Szarek and Robert Woods, Department of Chemistry, Queen's University, Kingston, Ontario Canada K7L 3N6.

Ab initio SCF LCAO-MO calculations have been performed on the title compounds and are discussed in terms of net atomic charges and Mulliken population analysis, with a particular emphasis on the possible consequences of these features as regards the sweet taste of these sugars.

B 36 Prediction of Vibrational Frequencies Including Anharmonic Corrections From Analytic Higher Derivatives

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Our recently developed analytic third derivative method for both closed- and open-shell SCF wavefunctions has been used to calculate cubic force constants analytically and quartic force constants by finite differences of third derivatives. Harmonic frequencies have been calculated analytically for SCF wavefunctions and by finite differences of analytic gradients for CI wavefunctions including single, double, triple, and quadruple excitations. Anharmonic constants, obtained from SCF cubic and quartic force constants, have been used to evaluate anharmonic corrections to the harmonic frequencies. The resulting fundamental frequencies predicted at the SCF level (using a DZ+P or better basis set) are still found to deviate substantially from the experimentally observed frequencies. When the SCF anharmonic corrections are applied to the CI harmonic frequencies, the resulting theoretical fundamental frequencies are found to agree significantly better with experiment. Geometries, dipole moments, IR intensities, rotational constants, and vibration-rotation interaction constants for a series of small molecules will also be discussed.

B37

Excitation Energies of Be in the Range 0-10eV: A Comparison of Perturbation-Type Green's Functions, Multiconfigurational Linear Response, ΔMCSF, and ΔFull CI Calculations

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The excitation energies of Be atom 0-10eV were calculated using second-order perturbational-type particle-hole Green's functions, multiconfigurational linear response, (also known as multiconfigurational time dependent Hartree-fock (MCTDHF)), Δmulticonfigurational self consistent field (MCSCF), and Δ full CI. The basis for each of these calculations was a <9s9p5d> contracted Gaussian set.

The MCSCF initial states used in the MCTDHF calculations were obtained by choosing all possible configurations in several different relatively small active spaces of orbitals. With our largest complete active space (CAS) MCSCF state (2s2p3s3p3d) as an initial state the MCTDHF excitation energies from the ground state are in excellent agreement with both experiment and full CI, typically with differences starting in the third figure beyond the decimal point (in eVs). In additon the S(0) and S(-2) (polarizability) sums were obtained. Furthermore, several MCTDHF calculations were performed where the initial state was an excited state of Be. Agreement between MCTDHF excitation energies and oscillator strengths starting from either the ground state or an excited state is excellent.

All the MCSCF states were fully characterized. It is again demonstrated (e.g. for the second ^1D and first ^3D states) that MCSCF calculations in particular for non-lowest states of a certain symmetry may yield spurious, unphysical, or approximations to higher energy solutions and that extreme care must be taken in using and interpreting MCSCF calculations or (non-full) CI calculations using these orbitals.

B38

Quantum-Chemical Analysis of Vibrational Intensity Distributions in the S_0-S_1 Absorption Spectra and Raman Excitation Profiles of Azulene.

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Abstract

The vibronic, Franck-Condon and Dushinsky activity of the totally-symmetric modes of azulene in S_0-S_1 transitions is investigated by quantum-chemical methods. It is found that the 900 cm^{-1} and 1400 cm^{-1} mode mixing proposed earlier to explain the relative intensities of Raman fundamentals in the region of the S_1 state is not supported by the calculations. The alternative mechanism arising from vibronic activity of the a_1 modes produces signs of the non-Condon parameters in agreement with those found from fitting the Raman excitation profiles; however, the absolute value of this parameter for the 900 cm^{-1} mode is almost an order of magnitude too small. Thus, although quantum-chemical calculations favour non-Condon effects over Dushinsky effects in shaping the relative intensities of Raman fundamentals, they do not give a conclusive answer. It is argued that such an answer can be obtained from measurements of the 900 cm^{-1} + 1400 cm^{-1} combination band Raman excitation profiles.

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