8th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY
8e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE

INTERNATIONAL CONFERENCE INTERNATIONALE

1983 August 7 - 12 août

Halifax, N.S.

SECOND ANNOUNCEMENT

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The 8th Canadian Symposium on Theoretical Chemistry will be held August 7-12, 1983 at Dalhousie University, Halifax, Nova Scotia.

TECHNICAL PROGRAM

The program will include invited papers and contributed posters on the following topics:

ANALYTICITY - DILATION AND COMPLEX COORDINATES
COLLISION THEORY OF ATOMS AND MOLECULES
DENSITY FUNCTIONAL THEORY
MANY-BODY PROBLEM IN QUANTUM CHEMISTRY
MULTIPHOTON PROCESSES AND DYNAMICS IN INTENSE FIELDS
NONLINEAR DYNAMICS OF CONSERVATIVE AND DISSIPATIVE SYSTEMS
QUANTUM BIOLOGY AND THEORETICAL BIOPHYSICAL CHEMISTRY
RELATIVISTIC QUANTUM CHEMISTRY
SOLITONS IN DYNAMICS AND QUANTUM CHEMISTRY
STRUCTURE AND SURFACE CALCULATIONS

INVITED SPEAKERS

L.C. Allen (Princeton, USA)
P. Brumer (Toronto, Canada)
M.S. Child (Oxford, England)
E. Clementi (IBM, USA)
A. Dalgarno (Harvard Obs., USA)
G.H.F. Diercksen (Max Planck, W. Germany)
W. Domcke (Heidelberg, W. Germany)
T.F. George (Rochester, USA)
W.A. Goddard III (Cal Tech, USA)
F. Grein (New Brunswick, Canada)
N.C. Handy (Cambridge, England)
B.R. Henry (Manitoba, Canada)
G. Herzberg (NRC, Canada)
J.O. Hirschfelder (Wisconsin, USA)
R. Hoffmann (Cornell, USA)
S. Huzinaga (Alberta, Canada)
R.E. Kapral (Toronto, Canada)
A. Kuppermann (Cal Tech, USA)
R. Lefebvre (Orsay, France)
R.J. LeRoy (Waterloo, Canada)
G. Malli (Simon Fraser, Canada)
J.P. Malrieu (Toulouse, France)
C. Mavroyannis (NRC, Canada)
C.W. McCurdy (Ohio State, USA)
J.N. Murrell (Sussex, England)
H. Nakamura (Inst. Molec. Sci., Japan)
G. Nicolis (Brussels, Belgium)
R.G. Parr (North Carolina, USA)
M.J. Rice (Xerox, USA)
S.A. Rice (Chicago, USA)
M. Shapiro (Weizmann Inst., Israel)
I. Shavitt (Ohio State, USA)
B. Shizgal (British Columbia, Canada)
R.L. Somorjai (NRC, Canada)
A. Veillard (Strasbourg, France)
I. Wladawsky-Berger (IBM, USA)

CONTRIBUTED PAPERS

Contributed papers will be welcomed in all areas of theoretical chemistry. All contributed papers will be given in poster format. A two-minute summary of each poster will be presented to the entire conference. The title should be given on the registration form, and an abstract supplied on a separate sheet. All abstracts should be typed and include the title, authors (underline the speaker), affiliations and text of abstract. In order to reduce the cost of printing the abstracts it would be appreciated if the abstracts could be limited to about 17 cm in width and 12 cm in height. Abstracts should reach Halifax by June 1, 1983.

REGISTRATION FEES

The registration fee is $160 Cdn (about $130 US) if paid before June 1. 1983. Graduate students and post-doctoral fellows are eligible for a reduced fee of $120. The registration fee includes full participation in the conference, the book of abstracts, complimentary coffee breaks, the reception on Sunday evening, and the lobster dinner on Thursday evening. A registration form is attached to this circular.

SOCIAL PROGRAM

The conference will open with a reception for all delegates and registered spouses at 8:00 p.m. on Sunday, August 7th in the Victorian Lounge of Shirreff Hall.

A cruise (by ticket only) on the Bluenose II, an accurate replica of the famous schooner shown on the Canadian dime, is planned for the evening of Tuesday, August 9th.

A lobster dinner will be held in the Great Hall of the Dalhousie University Faculty Club on Thursday, August 11th. An alternative meal will be available for those who do not wish to sample Atlantic Canada's famous crustacean. The dinner is included in the registration fee. Additional tickets may be purchased for $25 per person.

GENERAL INTEREST PROGRAM FOR REGISTERED SPOUSES

One activity will be offered each day during the conference. These activities will be designed to introduce our visitors to some of the cultural and historical aspects of Halifax which is the capital city of Nova Scotia and the major population centre of the Atlantic Provinces. Each activity will include morning coffee, lunch or afternoon tea. The General Interest Program registration fee includes the Sunday evening reception and the Thursday evening lobster dinner.

In addition to the general interest program for registered spouses, information on harbour tours, walking tours and bus tours will be available at the Registration Desk. The conference organizers will be pleased to provide general information on the city of Halifax and the Atlantic Provinces of Canada. Some visitors may wish to take advantage of the variety of yachts which are available for charter.

ACCOMMODATION

Blocks of rooms have been booked on campus and at two hotels which are close to the centre of Halifax. Please use the attached accommodation reservation form to reserve the type of accommodation which best suits your requirements.

Shirreff Hall South and Oxford Streets

This charming residence, former home to several generations of young Dalhousian ladies, is within a five minute walk of the conference site. All major recreational facilities (50 m indoor swimming pool, indoor and outdoor tennis courts, squash and racketball courts, ice rink, etc.) are adjacent to the residence.

The rates are as follows:

Single room (with sink)	$25 per night
Single room (without sink)	$22 per night
Twin room (with sink)	$36 per night ($18 per person)
Twin room (without sink)	$30 per night ($15 per person)

The above rates include all bedding and towels, daily maid service, breakfast and parking.

Dresden Arms Motor Hotel 5530 Artillery Place

Located on a quiet street below historic Citadel Hill and adjacent to one of Halifax's more fashionable streets, the Dresden Arms is a contemporary 4-storey hotel which has been recently renovated. The hotel is about 1 km from the conference site. There will be no additional charge for one or two children under the age of 12, if the parents pay the twin rate. The rates are as follows:

Single (1 person, 1 bed)	$50 per night
Double (2 persons, 1 bed)	$55 per night
Twin (2 persons, 2 beds)	$60 per night

These rates do not include breakfast.

Lord Nelson Hotel South Park and Spring Garden

The Lord Nelson offers historic decor and traditional hospitality in a central location which overlooks The Public Gardens, the oldest surviving formal Victorian Gardens in North America. The hotel is a pleasant 10-minute walk from the conference site. Children 14 years of age or under are free of charge when staying in the same room as their parents. The rates are as follows:

Single (1 person, 1 bed)	$52 per night
Double (2 persons, 1 bed)	$59 per night
Twin (2 persons, 2 beds)	$59 per night

These rates do not include breakfast.

Please note:

All rates are currently subject to a Health Services Tax of 10%. Hotels will guarantee accommodation only if reservations are received by June 1, 1983, after which date reservations will be honoured only if space is available.

MEALS

Delegates may purchase meals on a cash basis at several sites on the Dalhousie University campus. Lunch and dinner will be available in the dining hall of Shirreff Hall at a flat rate of about $4.00 and $5.50, respectively. Each meal will include a salad bar, selection of hot dishes, beverages and a variety of desserts. Quantities will not be limited. Delegates are also welcome to visit the Dalhousie University Faculty Club where light snacks are available in the Earl of Dalhousie, a pub on the lower level, and full-course meals are available in the dining room. The Faculty Club maintains reciprocal relationships with many of its counterparts at other North American Universities. The cafeteria of the Student Union Building will serve salads, sandwiches, fast foods and complete meals to delegates. Most of Halifax's many fine restaurants are within 1 or 2 km of the University, while several fast food outlets are within 1 km of the conference site.

GENERAL INFORMATION

The technical sessions will be held in the Dalhousie Arts Centre from 8:45 am, Monday, August 8th through to midday, Friday, August 12, 1983. An evening session is planned for Monday, August 8th.

Direct air service to Halifax is available from Amsterdam, London, Boston, New York, Montreal, Toronto and other major Canadian cities.

Delegates may purchase daily or weekly passes to the Dalplex, a large recreational complex adjacent to Shirreff Hall.

REGISTRATION

The registration fee includes full participation in the conference, the book of abstracts, complimentary coffee breaks, the reception on Sunday evening and the lobster dinner on Thursday evening. Registration will take place on Sunday, August 7th from 1:00 p.m. to 8:00 p.m. in the Dalhousie Arts Centre and on Monday August 8th from 8:00 a.m. to 4:00 p.m.

Please complete the attached registration form and mail it, together with a bank draft, money order or cheque, payable in Canadian funds to the Symposium on Theoretical Chemistry. Please return the completed form to:

8th Canadian Symposium on Theoretical Chemistry
Department of Chemistry
Dalhousie University
Halifax, Nova Scotia B3H 4J3
Canada

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Halifax, N.S.

Canada

co-chairmen/co-présidents

R. J. Boyd
Department of Chemistry
Dalhousie University
Halifax, N.S.

A. D. Bandrauk
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General Program for Registered Guests

S. L. Boyd
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We are also pleased to acknowledge the valuable advice, comments and suggestions which we have received from our colleagues within the scientific community. Many thanks are due to the staff of the Dalhousie University Conference Centre and other operational and service groups within the University. And finally a special thank you for the excellent secretarial assistance provided by Deanna Cosman, Beverley Embley and Sandra Simmons.

SCHEDULE OF INVITED LECTURES AND POSTER SESSIONS

	Monday	Tuesday	Wednesday	Thursday	Friday
Chairmen 9:00-9:45 9:45-10:15	M.A. Whitehead G. Herzberg J.N. Murrell	J.P. Laplante S.A. Rice R.E. Kapral	M.Z. Zgierski M.J. Rice A. Ovchinnikov	D.M. Bishop R.G. Parr J.P. Malrieu	W. Forst M.S. Child B.R. Henry
10:15-10:45	COFFEE BREAK				
Chairmen 10:45-11:15 11:15-11:45 11:45-12:15	J.S. Wright A. Veillard W.A. Goddard R.J. LeRoy	R. Wallace J.O. Hirschfelder T.F. George C. Mavroyannis	N.C. Baird Poster Session 3	D. Salahub P. Pyykko S. Huzinaga G. Malli	S.D. Peyerimhoff I. Shavitt N.C. Handy D. Stein
12:15-13:45	LUNCH				
Chairmen 13:45-14:30 14:30-15:00	R.F. Snider P. Pechukas M. Shapiro	J.J. Kaufman E. Clementi L.C. Allen	W.G. Laidlaw P. Brumer B. Shizgal	V.H. Smith A. Kuppermann C.W. McCurdy	
15:00-15:30	COFFEE BREAK				
Chairmen 15:30-16:00 16:00-16:30	F. Cummings H. Nakamura Poster Session 1	P.G. Mezey R.L. Somorjai Poster Session 2	M.C. Zerner F. Grein Poster Session 4	K.E. Banyard R. Lefebvre W. Domcke Poster Session 5	
Chairman 19:30-21:00 21:00-22:00	W. Siebrand R. Hoffmann Poster session 1 (cont'd.)				

All lectures will be held in the Sir James Dunn Theatre of the Dalhousie Arts Centre. The complete scientific program is listed on the following pages.

Table of Contents

	Page
Acknowledgements	2
Schedule of Invited Lectures and Poster Sessions	3
Table of Contents and Explanation of Codes	4
Information on Poster Sessions	5
Complete Scientific Program*	6
List of Participants	20
Abstracts†	35

Explanation of Codes in List of Participants

L-X indicates an invited lecture on day X

C-X indicates a session to be chaired on day X

PI-J indicates contributed paper number J in poster session PI

The days of the week are abbreviated as M, Tu, W, Th and F in this program.

*In the case of papers with more than one author, only the speaker is listed in the program.

†In alphabetical order by speaker.

8th Canadian Symposium on Theoretical Chemistry

Information on Poster Sessions

All contributed papers will be given in two parts. A two-minute summary of each paper will be presented in the Sir James Dunn Theatre of the Dalhousie Arts Centre. The second part will consist of a poster presentation in the designated area adjacent to the Theatre. Authors are requested to take note of the following:

(a) An overhead projector will be supplied for the two-minute summaries.

(b) Authors are advised to use a maximum of four transparencies for their mini-lectures.

(c) The first transparency should contain only the title, author(s), affiliation(s) and number of the paper.

(d) Transparencies (view-graphs) should be designed to be readable under normal conditions. Authors are encouraged to avoid overcrowding, small printing and illegible writing.

(e) A supply of blank transparencies and pens will be available at the registration desk for last-minute changes.

(f) The poster boards are approximately 1.2 m (4 feet) high and 2.4 m (8 feet) wide.

(g) A supply of tacks and tape will be available at the registration desk, but authors with special requirements are requested to bring their own supplies.

(h) Authors should remember that two minutes is not sufficient time to present a complete account of their work. It is recommended, therefore, that the mini-lecture be viewed as an opportunity to attract the attention of the other participants. The subsequent poster presentation provides an opportunity to describe the details.

Papers will be presented according to the following schedule:

Session	Set-up	Summaries	Poster	Take-down
P1	8:00-16:00 Monday	16:00-16:40 Monday	21:00-22:00 Monday	22:00 Mon.- 10:00 Tues.
P2	10:00-16:00 Tuesday	16:00-16:40 Tuesday	16:45-17:45 Tuesday	17:45 Tues.- 8:30 Wed.
P3	8:30-10:45 Wednesday	10:45-11:25 Wednesday	11:30-12:30 Wednesday	12:30-13:30 Wednesday
P4	13:30-16:00 Wednesday	16:00-16:40 Wednesday	16:45-17:45 Wednesday	17:45 Wed.- 10:00 Thurs.
P5	10:00-16:30 Thursday	16:30-17:10 Thursday	17:15-18:15 Thursday	18:15 Thurs.- 13:00 Fri.

8TH CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY

PROGRAM FOR MONDAY, AUGUST 8, 1983

8:45-9:00	Introduction and official opening R. J. Boyd, A. D. Bandrauk, D. D. Betts
SESSION A	M. A. Whitehead, presiding
9:00-9:45	Triatomic Hydrogen and the Ammonium Radical, **G. HERZBERG**, National Research Council of Canada.
9:45-10:15	Many-valued Surfaces and Their Approximate Single Valued Representation, **J. N. MURRELL**, University of Sussex.
10:15-10:45	Coffee Break
SESSION B	J. S. Wright, presiding
10:45-11:15	Potential Energy Surfaces for the Photochemical Reactions of Organometallics, **A. VEILLARD**, Universite L. Pasteur, Strasbourg.
11:15-11:45	Mechanisms of Catalatic Reactions, **W. A. GODDARD, III**, California Institute of Technology.
11:45-12:15	Oribting Resonance Model for Recombination of Physisorbed Atoms, **R. J. LEROY**, University of Waterloo.
12:15-13:45	Lunch
SESSION C	R. F. Snider, presiding
13:45-14:30	Remarks on "Quantum Chaos", **P. PECHUKAS**, Columbia University.
14:30-15:00	Dissociation and Intramolecular Dynamics, **M. SHAPIRO**, The Weizmann Institute.
15:00-15:30	Coffee
SESSION D	F. E. Cummings, presiding
15:30-16:00	Electronic Transitions in Atomic and Molecular Dymanic Processes, **H. NAKAMURA**, Institute for Molecular Science, Japan.
16:00-16:40	Summaries of papers to be presented in poster format following the lecture of Professor R. Hoffmann.

L. C. Allen Princeton University	[1.1.1] propellane
J. Andzelm University of Alberta	Model Potential Calculations on Interaction Energies in Weakly Bonded Systems.
D. Dao-Dehareng Universite de Liege	Dynamical Study of Nonadiabatic Unimolecular Reactions: The conical Intersection between the $\tilde{B}\,^2B_2$ and $\tilde{A}\,^2A_1$ States of H_2O^+.
C. A. Deakyne College of the Holy Cross	Bond Length Changes Resulting from Halogen Substitution of Oxirane.
M. Dupuis Lawrence Berkeley Laboratory	Multiconfiguration Hartree-Fock Studies of Molecular Electronic States and Reaction Pathways.
A. R. Gregory West Virigina University	The Formate Anion: An Ab initio Study of its Structure, General Harmonic Force Field and Fundamental Vibrational Frequencies.
K. D. Jordan University of Pittsburg	Ionization Potentials and Electron Affinities of Small Carbon Clusters.
S. Kanfer Weizmann Institute	TBA
L. L. Lohr University of Michigan	Theoretical Studies of the Gas-Phase Proton Affinities of Molecules Containing Phosphorus-Carbon Multiple Bonds.
B. Maessen University of California	Calculation of the Lower Vibrational Energy Levels of Formaldehyde by a Variational Method.
P. G. Mezey University of Saskatchewan	Towards Computer-aided Quantum Chemical Synthesis Design.
A. M. de P. Nicholas Dalhousie University	The Stability of Open-Shell Species - The Relative Net Stabilization Energy, $\Delta SE^{\cdot}[R^{\cdot},RX]$, of Alkyl Radicals ($R^{\cdot}$) in the Gas Phase

H. Nohira Saitama University	The Minimum Deformation of Orbital Patterns. The Principle for the Unification of Fukui-Woodward-Hoffmann Theory.
J. M. Sichel Universite de Moncton	X α-SW Study of Molecular Chemisorption of Oxygen on Silver.
R. W. Wetmore University of Guelph	TBA
J. S. Wright Carleton University	MRD-CI Calculations of Potential Surfaces Using Bond Functions.
D. Zeroka Lehigh University	Ligand Field Model of the Optical Spectrum of Anhydrous CO(II)-Exchanged Zeolite A.
T. Ziegler University of Calgary	A Theoretical Study of the Triple Bond in Binuclear Compounds of Cr, Mo, and W, by the Hartree-Fock-Slater Transition State Method.
R. T. Pack Los Alamos	First Quantum Corrections to Second Virial Coefficients for Anisotropic Interactions. Simple, Corrected Formula.

SESSION E W. Siebrand, presiding

19:30-21:00 Some Advice on how Theoreticians can Interact with Chemists, **R. HOFFMANN**, Cornell University.

21:00-22:00 Poster Session P1 (Complimentary refreshments available in Room 401).

PROGRAM FOR TUESDAY, AUGUST 9, 1983

SESSION F J. P. Laplante, presiding

9:00-9:45 Structure and Properties of the Liquid-Vapor Interface of a Metal, **S. A. RICE**, University of Chicago.

9:45-10:15 General Structure of Bistability in Far-From-Equilibrium Dynamical Systems, **R. KAPRAL**, University of Toronto.

10:15-10:45 Coffee

SESSION G R. Wallace, presiding

10:45-11:15 Comparison of Two-State Systems in Classical and Quantized Electromagnetic Fields, **J. O. HIRSCHFELDER**, University of Wisconsin and University of California.

11:15-11:45 Laser-Modified Molecular Dynamics, **T. F. GEORGE**, University of Rochester.

11:45-12:15 Stimulated Raman and Third-Order Nonlinear Spectra at High Photon Densities, **C. MAVROYANNIS**, National Research Council of Canada.

12:15-13:45 Lunch

SESSION H J. J. Kaufmann, presiding

13:45-14:30 Theoretical and Computional Chemistry in Large Chemical Systems: Biosystems in Particular, **E. CLEMENTI**, IBM Corporation, Poughkeepsie, N.Y.

14:30-15:00 Electronic Mechanisms in Enzyme Catalysis, **L. C. ALLEN**, Princeton University.

15:00-15:30 Coffee Break

SESSION I P. G. Mezey, presiding

15:30-16:00 Proteins and Differential Geometry, **R. L. SOMORJAI**, National Research Council of Canada.

16:00-16:40 Summaries of papers to be presented in poster Session P2.

B. G. Adams University of New Brunswick	Quasi-Degeneracy Effects and Coupled-Pair Analysis of the Ground State Energy of the Be Isoelectronic Sequence.
D. Belford New York University	Effect of the Non-Additive Energy Contribution to Preferred Orientations in Water Clusters.
S.-I. Chu University of Kansas	New Development in Floquet Theory and Quasi-Energy Methods for Intense Field Multiphoton Processes.
P. Csavinszky University of Maine	Gradient Expansion Correction to the Dirac Exchange Term in Statistical Models of an Atom.
P. F. Endres Bowling Green State University	Molecular Dynamics Studies of van der Waal's Clusters.
W. Forst Laval University	Relaxation of Internal Energy Following Laser Excitation.
G. Fritzsch Max-Planck-Institut Frankfurt	An Analysis of Enzyme Inactivation Exhibiting Biphasic Time Courses.
H. Fujimoto Kyoto University	Elucidation of Reactive Regions in Molecules.
F. H. Horne Michigan State University	Analytical Solutions of the Linearized Poission-Boltzmann Equation for Various Axial Ionic Strength Distributions in Cylindrical Membrane Pores.
C. Jaffe University of Toronto	The Classical Limit of the Wigner Formulation of Quantum Mechanics.
U. Kaldor Tel-Aviv University	Degenerate Many-body Perturbation Theory: Excited and Ionized States of N_2.
J. J. Kaufmann Johns Hopkins University	Three-Dimensional Electrostatic Molecular Potential Contour Maps. A. Stereoelectronic Requisites for Biomedical Molecules. B. Cationic Polymerization.
K. Kitaura Osaka City University	Effective Fragment Potential for Large Molecules.

J. P. Laplante Royal Military College, Kingston	Oscillating Photochemical Reactions: Study of the 9,10 Dimethyl Anthracene/-Chloroform System.
T. T. Nguyen-Dang Universite de Sherbrooke	The 'Dressed' Molecule Picture of Strong Field Dynamics.
S. H. M. Nilar University of Alberta	A Theoretical Simulation of Interactions in Transmembrane Ionic Channels.
P. Pyykko University of Helsinki	Quantum Chemistry Without Basis Sets: Hartree-Fock-Slater and Hartree-Fock Calculations on Diatomic Molecules.
H. B. Schlegel Wayne State University	Ab Initio Molecular Orbital Studies on Carbene and Silylene Insertions into Single Bonds.
D. Schuch Frankfurt (Main)	Nonlinear Schrodinger-Type Field Equation for the Description of Frictionally Damped Free Motion and Free Fall.
J. M. Ugalde Dalhousie University	Angular Aspects of the Fermi Hole in Atoms.

16:45-17:45 Poster Session P2

PROGRAM FOR WEDNESDAY, AUGUST 10, 1983

SESSION J M. Z. Zgierski, presiding

9:00-9:45 Theoretical Concepts in the Physics of Conducting Polymers, **M. J. RICE**, Xerox Webster Research Center.

9:45-10:15 Electron Correlation Effects in Large Molecules with Conjugated Bonds, **A. A. OVCHINNIKOV**, Institute of Chemical Physics, Moscow.

10:15-10:45 Coffee Break

SESSION K N. C. Baird, presiding

10:45-11:25 Summaries of papers to be presented in Poster Session P3.

W. H. Adams Rutgers University	Convergent or Divergent? Perturbation Calculations on the Interaction of He^+ with H*.
J. Ali McGill University	Bifurcation and Nonlinear Mobilities of Carriers in Semiconductors.
K. E. Banyard Leicester University	Electron Correlation Effects in (a) the 2^1S, 2^3S, 2^1P and 2^3P States of Helium and (b) the ^2S and ^2P States of Some Lithium-like Ions.
A. D. Becke Dalhousie University	Local Exchange-Correlation Approximations and First-Row Molecular Dissociation Energies.
B. L. Clarke University of Alberta	Qualitative Dynamics of Chemical Reaction Networks Using Computer Programmed Theory.
X.-Y. Fu Beijing Normal University	Investigation of Hydrogen Bonds Between CH_3OH and CH_3CN, CH_3NC, CH_3F, H_2O By Ab Initio SCF MO Method.
M. F. Herman Tulane University	Recent Studies Concerning the Semi-classical Theory of Non-Adiabatic Transitions.
K. Hirao Nagoya University	Direct Cluster Expansion Method.
S. Larsson University of Lund	Electron Transfer in Solids, Liquids and Biological Systems.

G. Natanson University of Chicago	The Quantum States of a Moderately Rarefied Fluid of Spinless Bosons.
S. Raynor Rutgers University	Deviations from the Linear Mixture Rule in Nonequilibrium Chemical Kinetics.
P. Saxe Aberdeen Proving Grounds	Unimolecular Reactions of Methylene Amidogen (CH_2N).
V. H. Smith, Jr. Queen's University	Momentum Space Properties of Atoms and Molecules.
A. J. Thakkar University of Waterloo	High Energy Electron Scattering from Molecules.
D. R. Truax University of Calgary	Discrete and Continuum States for the Quantum Mechanical Forced Oscillator.
D. M. Wardlaw California Institute of Technology	Vibrational Spectra from Semi-Classical Mechanics.
M. A. Whitehead McGill University	Electronegativity.
D. L. Yeager Texas A&M University	Multiconfigurational Electron Propagator (MCEP) Ionization Potentials for General Open Shell Systems.
A. Yee Wesleyan University	The Complete Basis Set Correlation Energy of Neon.

11:30-12:30 Poster Session P3

12:30-13:45 Lunch

SESSION L W. G. Laidlaw, presiding

13:45-14:30 Classical Liouville Mechanics and Relaxation Dynamics, **P. BRUMER**, University of Toronto.

14:30-15:00 Electron Thermalization in Inert Gases, B. **SHIZGAL**, University of British Columbia.

15:00-15:30 Coffee Break

SESSION M M. C. Zerner, presiding

15:30-16:00 CI and MCSCF Methods Applied to Ground and Excited States of Molecules. Spin-orbit Studies on Cl_2, **F. GREIN**, University of New Brunswick

16:00-16:40 Summaries of papers to be presented in poster Session P4.

J. S. Binkley Sandia National Laboratories	Heats of Formation of Radical Species Using the BAC-MP4 Method.
E. S. Campbell New York University	Multibody Energy-components for Clusters of Water Molecules and Ice Ih.
C. A. Chatzidimitriou-Dreismann Berlin	Microscopic Theory of Relaxation and D-Fluctuations in Condensed Matter - Experimental Applications.
C. L. Davis University of Florida	Elimination of Nonlinear Optimization in Quantum Chemistry with Singularity-Matching Basis Functions.
G. S. Ezra Cornell University	Adiabatic Approximation for Coupled Oscillators - A Numerical Study.
W. M. Huo NASA-Ames Research Center	Theoretical Study of the Two-Photon Absorption Cross-Section of $X^2\Pi \rightarrow A^2\Sigma^+$ in NO.
K. Ishida Florida State University	Molecular Integrals Arising in the Linear Response Theory of van der Waals Forces.
B. R. Johnson University of Colorado	Large-Order Perturbation Theory in the Stark-Zeeman Effect for Parallel Fields.
O. Nomura Saitama, Japan	Proton Affinity of Germane(GeH_4).
P. D. Pacey Dalhousie University	Two-Dimensional Hindered Rotations in Activated Complexes.
M. Page Aberdeen Proving Ground	Toward Accurate Characterization of Potential Energy Surfaces Analytical Gradient for a Selected Reference MCSCF/CI Wave Function.

G. A. Petersson Wesleyan University	The Complete Basis Set Correlation Energy of H_2O.
E. Radzio-Andzelm University of Alberta	Reliable Gaussian Basis Sets for Calculations of Interaction Energies in Systems of Closed-Shell Atoms.
M. L. Sage Syracuse University	Large Amplitude Vibrations: Coupling Between a Stretch and a Bend.
E. B. Stechel Sandia National Laboratories	Quantum Chaos and a Quantum Measure Space.
M. Takahashi University of Waterloo	Local Finite Order Perturbation Theory Approach to Bond Length Alternation in Cyclic Polyenes.
B. Waite United States Naval Academy	Mode-Specificity in HNC → HCN Unimolecular Isomerization: A Classical + Tunneling Model.
R. Wallace University of Manitoba	Large Amplitude Vibration in Polyatomic Molecules. A Polar Representation of Orthogonal Relative Coordinates.
H. Chojnacki Institute of Organic and Physical Chemistry Poland	Molecular Orbital Formalism for Atom-Antiatom Systems.

16:45-17:45 Poster Session P4

PROGRAM FOR THURSDAY, AUGUST 11, 1983

SESSION N D. M. Bishop, presiding

9:00-9:45 Aspects of Density Functional Theory, R. G. **PARR**, University of North Carolina.

9:45-10:15 TBA

10:15-10:45 Coffee Break

SESSION O D. Salahub, presiding

10:45-11:15 Relativistic Quantum Chemistry: Some Recent Results, **P. PYYKKO**, University of Helsinki and Abo Akademi.

11:15-11:45 Model Potential Method in Molecular Calculations, **S. HUZINAGA**, University of Alberta.

11:45-12:15 Dirac-Fock-Roothaan SCF Wavefunctions for Atoms and Molecules, **G. MALLI**, Simon Fraser University.

12:15-13:45 Lunch

SESSION P V. H. Smith, Jr., presiding

13:45-14:30 The Quantum Mechanical Theory of Collision Induced Dissociation and Three Body Recombination Processes Using Local Hyperspherical Surface Functions, **A. KUPPERMANN**, California Institute of Technology.

14:30-15:00 Calculations on Resonances Using Complex Basis Function Methods: What Happened to the Complex Coordinates Idea? **C. W. MCCURDY**, Ohio State University.

15:00-15:30 Coffee Break

SESSION Q K. E. Banyard, presiding

15:30-16:00 Siegert Quantization, Complex Rotation and Molecular Resonances, **R. LEFEBVRE**, Orsay.

16:00-16:30 Aspects of Nuclear Dynamics in Negative Ion States, **W. DOMCKE**, University of Heidelberg.

16:30-17:10 Summaries of papers to be presented in poster Session P5.

F. G. Amar Columbia University	Reaction Dynamics and the Cage Effect in Microclusters of Br_2Ar_N.
D. Belford New York University	Lower Order Non-Additive Dispersion Multipoles.
S.-I. Chu University of Kansas	Complex-Coordinate Coupled-Channel Methods for Rotational Predissociation of van der Waals Molecules and Autoionization of Quasi-Landau States.
F. E. Cummings Atlanta University	Properties of Hydrogenic Momentum Wavefunctions.
R. L. Flurry University of New Orleans	Apparent R(4) Symmetry in the Singly-Excited States of Helium.
A. D. Isaacson Miami University	Practical Methods for the Calculation of Resonance Lifetimes.
J. J. Kaufman Johns Hopkins University	Prediction of Crystal Densities Using Ab-Initio Potential Functions From Energy-Partitioned Ab-Initio MODPOT/-VRDDO Intermolecular SCF Calculations Plus Dispersion.
M. Klobukowski University of Alberta	Multiconfiguration Model Potential Calculations on Diatomic Halides and Halogen Hydrides.
Z. C. Kornblum Cooper Union	Structure and Lennard-Jones Potential Functions of the Carbon Monoxide Dimer From Semiempirical MNDO Computations.
W. G. Laidlaw University of Calgary	Instability in Porous Media Floods.
W. L. Luken Mississippi State University	Localized Orbitals Based on the Fermi Hole.
G. A. Natanson University of Chicago	On Dynamical Symmetry of Molecular Systems in the High-Barrier Limit.
R. B. Shirts University of Utah	A Classical Model of Absorption and Emission of Radiation in an Intense IR Laser Field.
N. Snider Queen's University	Deductions from the Master Equation for Chemical Activation.

D. I. Sverdlik City University of New York	Thermal Rate Constants - Relating to Some Curiosities of Their Temperature Dependence.
S. Takata Toyama Technical College	Non-Empirical Approximate SCF Calculation of Butadiene.
G. Turcotte Universite de Sherbrooke	Photodissociation Angular Distributions of Diatomics in Intense Fields.
J. T. Waber Northwestern University	Correlation in Exotic Molecules Using Second-Order Many-Body Perturbation Theory for Assessment.
M. Z. Zgierski National Research Council of Canada	Temperature Dependence of Hydrogen Transfer Rate Constants.

17:15-18:15 Poster Session P5

PROGRAM FOR FRIDAY, AUGUST 12, 1983

SESSION R W. Forst, presiding

9:00-9:45 Local and Normal Vibrational Modes, **M. S. CHILD**, Oxford

9:45-10:15 The Local Mode Model: A Sensitive Experimental Test for Molecular Orbital Theory, B. R. **HENRY**, University of Manitoba.

10:15-10:45 Coffee Break

SESSION S S. D. Peyerimhoff, presiding

10:45-11:15 Multiconfiguration SCF and Multireference CI Calculations of Bond Breaking in Molecules, I. **SHAVITT**, Ohio State University.

11:15-11:45 Large Scale Calculations on Small Molecules, **N. C. HANDY**, Cambridge.

11:45-12:15 Supercomputers and Their Performance, D. **M. STEIN**, IBM, Yorktown Heights.

12:15-12:30 Summary of Session S.

12:30-12:40 Concluding comments, V. H. Smith, Jr.

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Quasi-degeneracy Effects and Coupled-Pair Analysis of the Ground State Energy of the Be-isoelectronic Series

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ABSTRACT

The CI method with doubly-excited configurations (D-CI) and the analytic form of the LS-adapted coupled-pair many-electron theory (CPMET) are applied to the ground state of the members Li^-, Be, B^+, C^{2+}, Ne^{6+}. Ar^{14+}, Zn^{26+} of the Be-isoelectronic series. Special attention is given to the reliability of coupled-pair methods for both positive and negative ionic systems. The impact of disconnected quadruply-excited configurations is significant for Li^- and decreases considerably for the positive ions in the series. The present single reference state results indicate that coupled-pair methods are considerably more accurate in the presence of quasi-degeneracy than perturbation theory. It is also emphasized that the description of quasi-degeneracy effects should take into account both the energies of the configurations involved and the relative magnitudes of these configurations in the wavefunction.

Convergent or Divergent? Perturbation Calculations on the Interaction of He^+ with H *

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We shall consider the results we have obtained in applying two symmetry adapted perturbation theories to the problem of ground state He^+ interacting with ground state H. One theory belonged to the Eisenschitz-London class of perturbation theories, the other to the Hirschfelder-Silbey class. The calculations were carried through third order in the wave functions within the configuration interaction approximation using 424 two-electron basis functions. We made an unconventional choice for the zero-order Hamiltonian H°. The conventional H° is the sum of the atomic Hamiltonians. We have found that when the conventional H° is used, the interaction energies calculated for the singlet state are grossly inaccurate at a nuclear separation R of 5.0 bohrs. In addition, we have proved that using the conventional H° causes the Hirschfelder-Silbey type theory to diverge at all finite R for both the singlet and triplet states, and causes the Eisenschitz-London type theory to diverge at all R for the singlet state. The divergent nature of the expansions is manifest in the wave functions at 10.0 bohrs even though the interaction energies are reasonably accurate. The unconventional H°, used in the present calculations, was chosen so that its lowest several eigenstates were in one-to-one correspondence to those of the full Hamiltonians. We are analyzing these new results using the same mathematical and numerical methods that we applied to the results we obtained with the conventional H°.

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BIFURCATION AND NONLINEAR MOBILITIES OF CARRIERS IN SEMICONDUCTORS

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Space charge oscillations in the Gunn oscillators, e.g., GaAs, are believed to be due to the negative differential mobility of carriers. Kroemer (1) proposed an empirical formula for drift velocity, and attempts have been made in the past to derive non-Ohmic drift velocities and negative differential mobilities by using a linearized Boltzmann equation which was solved approximately by a displaced Maxwell distribution function (2). In view of the fact that non-Ohmic behavior is due to nonlinear effects in the transport process, the displaced Maxwellian method is not satisfactory. An alternative theory will be presented. A pair of nonlinear evolution equations (3) for conduction currents of carriers are deduced from nonlinear Boltzmann equations for transport processes. Their solution provides drift velocities. The equations have cubic nonlinearities and can have three steady states, depending on parameters in the equations and the electric field strength E. One steady state is stable below the critical field E_c and shows an Ohmic behavior only at sufficiently low fields, becoming non-Ohmic as E increases; it becomes unstable and non-Ohmic for $E > E_c$. As E crosses E_c, there appear two additional steady states. One of them, which corresponds to a negative differential mobility characteristic, is stable for $E > E_c$, whereas the other is unstable in the region $E_m < E < E_c$, but eventually becomes stable in a manner reminiscent of a pitchfork bifurcation that contains an unstable portion in the upper bifurcated branch. This branch therefore has a switching as well as a hysteresis effect. The nonlinear drift velocity calculated compares well with the experimental data by Kabashima et al. (4). When parameters in the equations are changed, there also appear oscillatory solutions, and the corresponding entropy production becomes oscillatory. The bifurcation phenomena and oscillatory solutions will be discussed and the numerical results thereof will be presented.

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ELECTRONIC MECHANISMS IN ENZYME CATALYSIS

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Abstract

Although the type of reaction catalyzed by most simple enzymes, as well as their kinetics and general properties, have been known for some time, only limited knowledge has been obtained concerning the catalytic role of active site residues and the nature of their intermediates and transition states.

We are employing *ab initio* electronic structure computations to address this latter problem and we have obtained results for several enzymes including chymotrypsin, RNase A, and carbonic anhydrase. In this talk we will focus attention on the electronic mechanism in the zinc metalloenzyme, carbonic anhydrase.

From the studies to date, it is possible to suggest a few general principles. Similarities and contrasts between biological catalysts and those typically employed in research and industrial chemistry will be brought out also.

[1.1.1]PROPELLANE

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ABSTRACT

Wiberg and Walker have recently synthesized [1.1.1]propellane, 
the most strained organic molecule known to be stable at room temperature. Although each of the two bridgehead carbons, C_1 and C_3, possess inverted configurations, they are separated by a normal carbon-carbon single bond distance (1.54 Å) and are stable against formation of the diradical by 65 kcal/mol. We have applied *ab initio* electronic structure methods to investigate the C_1-C_3 bond and find a novel, non-axial orbital arrangment which we term σ bridge π. This bonding pattern appears characteristic of inverted configurations held together by short bridges and we show that 1,3-diborabicyclo[1.1.1]pentane, 
contains a BB bond almost identical to that in [1.1.1]propellane. An unusually short BB separation of 1.61 Å is predicted. Although bicyclo[1.1.1]pentane and 1,3 diazabicyclo[1.1.1]pentane do not formally possess 1-3 bonds, their 1,3 separations are considerably shorter than expected for non-bonded interactions (computed to be 1.87 and 1.96 Å, respectively). Both molecules retain some σ bridge π character.

REACTION DYNAMICS AND THE CAGE EFFECT IN MICROCLUSTERS OF Br_2Ar_N

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ABSTRACT: We present the results of a molecular dynamics trajectory study of the photodissociation/recombination reaction of Br_2 in argon clusters with between 8 and 54 argon atoms (less than one to two solvent shells). Initial conditions of the clusters correspond to the cold, collision-free regime obtainable in a supersonic molecular beam. Following excitation of the Br_2 to the dissociative continuum several outcomes are possible, including dissociation of the Br_2, caging and recombination of the diatomic, and caging followed by solvation of the Br radicals by the argon atoms. The influence of cluster size on the cage effect is discussed as is the effect of varying the temperature and the initial excitation conditions. We compare our results to liquid phase and matrix studies of this type of reaction. Stagnation of vibrational relaxation of recombined Br_2 is observed in clusters as it is in the liquid phase. The mechanism of the relaxation is discussed and the stagnation phenomenon interpreted in terms of a sliding nonlinear resonance effect. Finally, lifetimes of the clusters are calculated in order to assess the feasibility of detailed experiments on these species.

Model Potential Calculations on Interaction Energies in Weakly Bonded Systems

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Sigeru Huzinaga, Mariusz Klobukowski and Elżbieta Radzio-Andzelm
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Model potential (MP) method developed by Huzinaga et al. has been applied to studies on interactions in weakly bonded systems. The MP parameter optimization procedure has been modified so as to put greater emphasis on accurate representation of the outer part of valence orbitals and consequently to ensure reliable description of valence atomic region which is proved to be very important for good reproduction of interaction energies in weakly bonded systems.

The present results for homonuclear pairs of inert-gas atoms up to xenon compare very well with those of accurate all-electron calculations.

The intermolecular correlation effects have been also included by calculating dispersion term using pseudo-valence orbitals with both the Epstein-Nesbet and the Møller-Plesset definitions of the unperturbed hamiltonian.

The MP SCF results augmented with dispersion energy (Epstein-Nesbet scheme) agree well with the experimental ones.

The method described above has been also applied to investigations of the non-additive effects in clusters of inert-gas atoms and interactions in systems composed of inert-gas atoms, halogen hydrides or halogen diatomics.

Electron Correlation Effects in (a) the 2^1S, 2^3S, 2^1P and 2^3P States of Helium and (b) the ^2S and ^2P States of Some Lithium-like Ions.

by

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Abstract

Correlation effects are examined in the low-lying excited states of He and comparisons are made with ground-state studies. Coulomb holes and various partial 'holes' are determined in order to assess the influence of correlation in different regions of space. Comparison between, firstly, singlet and triplet states and, secondly, S- and P- states gives rise to several intriguing and mind-bending results.

For the Li-like ions, the correlated wavefunctions are partitioned so as to examine correlation effects within the individual two-electron intra- and inter-shells. The ^2S-state yields results for the KαKβ-, KαLα- and KβLα- shells which can be contrasted with findings for the corresponding shells within the ground-state of the Be-like ions.

Finally, the Coulomb holes obtained for the inter-shells within the ^2S and ^2P states of Li may be viewed against the results deduced for the above mentioned excited-states of He.

Local Exchange-Correlation Approximations and First-Row Molecular Dissociation Energies

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Recently, we have reported the results of accurate Hartree-Fock-Slater calculations on selected first-row diatomic molecules which show very encouraging agreement with experiment[1]. In the worst cases, however, the HFS dissociation energies were found to overestimate the experimental values. Therefore, we have examined several refinements of the Hartree-Fock-Slater theory and their effects on molecular bond lengths, dissociation energies, and vibrational frequencies. Among them, gradient corrections to the HFS exchange energy and also some local correlation approximations based on recent parametrizations of electron gas data are considered. We find that a local exchange-correlation approximation with gradient corrections gives dissociation energies in significantly better agreement with experiment than the Hartree-Fock-Slater approximation.

1) A.D. Becke, J. Chem. Phys. 76, 6037 (1982).

Effect of the Non-Additive Energy Contribution to Preferred Orientations in Water Clusters

David Belford and Edwin S. Campbell
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Energetically preferred configurations of $(H_2O)_3$, $(H_2O)_4$ and $(H_2O)_6$ have been determined for 3 different models derived by fitting the 229 HF dimer energies of Kistenmacher et al.: (i) the additive analytical fit of Clementi et al.; (ii) the non-additive model of Campbell and Mezei; (iii) the additive component of the non-additive model. Since differences in the weighting of data points in models (i) and (ii) lead to differences in structures preferred by the additive models (i) and (iii), the significance of the non-additive contribution can be determined only by a comparison of models (ii) and (iii). This shows that the non-additive component introduces significant quantitative differences and, for $(H_2O)_6$, a structure of a different symmetry type. The non-additive model gives optimal distances for $(H_2O)_6$ similar to the experimental values for condensed phases. Evidence supports the inference that the orientational effect of non-additivity is larger when the configuration differs from the unconstrained minimum for a group of H_2O molecules.

Lower Order Non-Additive Dispersion Multipoles

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The positive and negative regions for the three-body, third-perturbation order interactions have been determined for several lower order multipoles to permit the recognition of configurations with attractive or repulsive contributions without calculation. The leading triple-dipole contribution has been evaluated for $(H_2O)_3$, $(H_2O)_4$, planar and staggered $(H_2O)_6$ and ice Ih. In the latter four cases, the energy is smaller than the four-body induction contribution given by the model of Campbell and Mezei. Lattice sums for the geometric factors for dispersion multipoles have been calculated for the ice Ih lattice.

Heats of Formation of Radical Species Using the BAC-MP4 Method

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Heats of formation (ΔH_f^o) of various H, C, N and O containing radical species have been computed using the newly formulated BAC-MP4/6-31G** approach. This method consists of MP4/6-31G** total energies combined with HF/6-31G* zero-point vibrational energies and Bond Additivity Corrections derived from known ΔH_f^os of stable species. Comparing our theoretical results with experimental ΔH_f^os for a variety of molecules containing hydrogen and up to four heavy atoms (C,N and O), we find that energy differences between theory and experiment are typically less than three kcal/mole. For hydrocarbon radicals, the calculated ΔH_f^os are consistent with the experimental findings of Tsang and are several kcal/mole higher than the presently accepted heats of formation based on halogenation studies of Golden and Benson. Our method can be used to establish reliable heats of formation of other radical species for which experimental data are not well known.

Classical Liouville Mechanics and Relaxation Dynamics

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Considerable insight into classical relaxation phenomena and into the classical/quantum correspondence is afforded by the formal Hilbert Space approach to classical distribution dynamics. The theory will be reviewed and simple examples described, with particular emphasis on the eigenfunctions of the classical Liouville operator.

Multibody Energy-components for Clusters of Water Molecules and Ice Ih

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Department of Chemistry, New York University

The multibody and total non-additive energy components have been calculated for $(H_2O)_4$ to $(H_2O)_{48}$ clusters chosen to determine the effects of different factors upon the interaction. Approximate values have also been calculated for ice Ih. The magnitudes of the four-body components for many clusters and for ice Ih have been shown to be in the energy range required for possible effects upon preferred orientations. When the cooperative reinforcement of the induced dipole fields, hyperpolarizabilities and field gradients are neglected, the induced dipole energy has been shown to be strictly two- and three-body. The relative efficiencies of three-body and fully cooperative calculations have been determined.

Microscopic Theory of Relaxation and D-Fluctuations in Condensed Matter - Experimental Applications

C. A. CHATZIDIMITRIOU-DREISMANN

I.N.Stranski-Institut for Physical & Theoretical Chemistry, TU Berlin, Strasse des 17. Juni 112, D-1000 Berlin 12, F.R. Germany

Some basic concepts of the Prigogine star-unitary transformations are discussed in connection with microdynamical processes in condensed molecular matter. The existence of an operator quantity representing the "intrinsic time" of systems being in strong interaction with their environment becomes apparent.

The theory predicts a kind of fluctuations around steady states, which have their origin in the fundamental level of quantum mechanics. The experimental detection of these dynamical (or D-) fluctuations is presented.

The physical relevance of the star-unitary transformation theory within the quantum theory of condensed matter is demonstrated with the aid of current spectroscopic measurements.

Local and Normal Vibrational Modes

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Developments in the theory of local and normal stretching vibrations of symmetrical molecules will be reviewed from both classical and quantum mechanical points of view. The main feature of the classical mechanics is a co-existence at a given energy between two types of motion: local vibrations in which one bond is permanently excited more than the other (or others) and normal vibrations in which energy flows symmetrically from one bond to another. The local type implies a pattern of strict local mode classical degeneracies, which is removed by exponentially small quantum mechanical corrections. This behaviour is elegantly explained by the Chirikov theory of classical resonances, and experimentally confirmed by the term values derived from the overtone spectra of water.

The quantum mechanical developments include the use of few parameter Morse-oscillator based models to fit the spectra of C_2H_2, XH_4 (X = C, Si, Ge) and their isotopic substituents, and YF_6 (Y = S, W, U). Secondly it proves possible to correlate the behaviour of a given molecule between local and normal limits by means of the ratio of the fundamental splitting to the bond anharmonicity, this ratio being very large for normal oscillators and very small for local ones.

MOLECULAR ORBITAL FORMALISM FOR ATOM-ANTIATOM SYSTEMS

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Based on the Hartree-Fock method, the general LCAO MO SCF formalism designed for atom-antiatom systems has been proposed. The total wave function was assumed as the product of the relevant determinantal components describing electron and positron subsets.

In order to consider the effects of intralepton correlation, the configuration interaction formalism has been adapted. The test calculations have been performed for a number of closed-shell diatomic molecular systems.

New Development in Floquet Theory and Quasi-Energy Methods for Intense Field Multiphoton Processes*

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In this conference, several new developments in semiclassical Floquet theory and quasi-energy methods for intense field multiphoton excitation (MPE) and dissociation (MPD) processes will be presented:

(A) Generalized Many-Mode Floquet Theory [1] for the nonperturbative treatment of the interaction of a quantum system with several monochromatic coherent laser fields.

(B) Adiabatic and Non-adiabatic Approximation Methods [2] for Resonant Multiphoton Excitation of Vibrational-Rotational States in Strong Laser Fields.

(C) Non-Hermitian Floquet Theory and Complex Quasi-Energy Methods [3] for MPD of Small Polyatomic Molecules.

*Work supported by DOE and ACS-PRF.

#Alfred P. Sloan Foundation Fellow.

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[3] S.I. Chu, C. Laughlin and K.K. Datta, Chem. Phys. Lett. (in press); S.I. Chu, J. Chem. Phys. 75, 2215(1981).

Complex-Coordinate Coupled-Channel Methods for Rotational Predissociation of van der Waals Molecules and Autoionization of Quasi-Landau States*

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There is currently much interest in the study of spectroscopy, structure and predissociation dynamics of weakly bound van der Waals (vdW) molecules. Recently we have developed two practical approaches for the accurate determination of vibrational and rotational predissociation lifetimes of vdW complexes. These are the complex-coordinate coupled channel (CCCC) methods, one formulated in the space-fixed (SF), the other in the body-fixed (BF) frames of coordinates. The SFCCC theory [1] is more appropriate for the treatment of weak-coupling vdW complexes (such as Ar-H_2), whereas the BFCCCC theory [2] more natural for strong-coupling complexes (such as Ar-HCl). These methods have been applied successfully to a number of vdW molecuels [1-3]. In particular, the calculated widths for Ar-HD [3] are in good harmony with the recent experimental data of McKellar [4]. More recently the CCCC method has been applied successfully for the first determination of autoionization widths of quasi-Landau states of H atom in intense magnetic fields [5].

*Work supported by DOE and ACS-PRF

#Alfred P. Sloan Foundation Fellow

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QUALATIVE DYNAMICS OF CHEMICAL REACTION NETWORKS USING COMPUTER PROGRAMMED THEORY.

Bruce L. Clarke, Dept of Chemistry, Edmonton Alberta, T6G 2G2.

A chemical reaction network is a set of chemical reactions with unspecified rate constants and amounts of the components. For each of the possible values these parameters may take, the concentrations have a dynamics that can be described qualitatively. The most typical kind of dynamics is a single globally attracting steady state. This is the dynamics of closed thermodynamic sytems where the steady state is chemical equilibrium. For systems that have inputs of energy or molecules, or systems that are being studied on a faster time scale than the approach to equilibrium, other kinds of dynamics may occur, such as oscillations, chaos, explosions, evolution, multiple steady states, hysterisis,... .

A considerable body of theory has recently emerged on this subject. This theory permits chemical reaction networks to be classified according to the types of dynamics that are possible if the effective rate constants take suitable values. Such theory is helpful to kineticists who are trying to devise mechanisms that have various kinds of observed exotic dynamics.

The poster will present some of the recent advances in the area and illustrate how these theorems have been programmed for computer in APL so that a nonmathematical kineticist can test reactions mechanisms against the latest theoretical results.

Gradient expansion correction to the Dirac exchange term in statistical models of an atom. P. Csavinszky and F. Vosman. Univ. of Maine, Orono, Maine 04469, U.S.A. In previous work[1,2], aimed to introduce the shell structure of atoms via a variational procedure using the energy density functional formalism, electron densities have been obtained for the Na atom within the Thomas-Fermi-Dirac model. In these calculations the effect of the (modified) Weizsäcker and Hodges gradient expansion corrections to the kinetic energy term has also been ascertained. In the present work[3] we make use of the respective electron densities and calculate the first gradient expansion corrections to the Dirac exchange term. The results show that, for the Na atom, the magnitude of this correction is about 1% of the magnitude of the total binding energy.

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[2]P. Csavinszky, Int. J. Quantum Chem. Symp. No. 15, 387 (1981).

[3]P. Csavinskzy and F. Vosman, Int. J. Quantum Chem. (to be published).

Properties of Hydrogenic Momentum Wavefunctions

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The non-relativistic hydrogenic momentum wavefunctions are used to obtain explicit expressions for $\langle p^s \rangle$ with s an even integer, $-6 \leq s \leq 8$, and a general expression for all s. It is shown that $\langle p^{2-s} \rangle = \left(\frac{Zp_o}{n}\right)^{2-2s} \langle p^s \rangle$, for n the principal quantum number and $p_o = h/a_o$, and that $\langle p^s \rangle$ diverges for $s \geq 2\ell+5$, for ℓ the angular momentum quantum number. Recursion relations for a related ${}_4F_3$ generalized hypergeometric function and similarities to $\langle r^s \rangle$ are discussed.

Dynamical study of nonadiabatic unimolecular reactions : the conical intersection between the $\tilde{B}\,^2B_2$ and $\tilde{A}\,^2A_1$ states of H_2O^+.

D. DAO-DEHARENG : Université de Liège, Belgique

X. Chapuisat : Laboratoire de Chimie Théorique d'Orsay, France

J.C. Lorquet, C. Galloy and G. Raseev : Université de Liège, Belgiqu

Abstract

The conical intersection connecting the $\tilde{B}\,^2A'$ and $\tilde{A}\,^2A'$ states of the H_2O^+ ion is studied. The two potential energy surfaces are calculated ab initio by the SCF/CI method within the C_s point group.
The nonadiabatic coupling matrix elements $\langle \tilde{A}|\partial/\partial q|\tilde{B}\rangle$ are computed for several cross sections throughout the potential energy surfaces. A transformation to the diabatic representation is performed. The linear model is found to be a good approximation in the region close to the apex of the cone. The global functions t(s) and T(S) governing the nonadiabatic transition probability are calculated ; their shapes are those predicted by the Landau-Zener model (in the Nikitin bidimensional version). A dynamical study is undertaken by means of classical trajectory calculations on the upper adiabatic potential energy surface. An averaged transition probability $\overline{P_{tr}}$ is derived.

Excitation of rotation or of the bending mode of H_2O before photon impact has no influence on $\overline{P_{tr}}$. Excitation of the symmetrical or antisymmetrical valence modes of H_2O lowers $\overline{P_{tr}}$. The shape of $\ln(1-\overline{P_{tr}})$ as a function of time indicates the existence of two distinct regimes at short and intermediate time ranges, characterized by two different rate constants k_1 and k_2, respectively. The rate constants are of the order of 10^{14} s^{-1}. k_1 exhibits a maximum as a function of the absorbed energy E_{abs}, whereas k_2 decreases as a function of E_{abs}.

Elimination of Nonlinear Optimization in Quantum Chemistry with Singularity-Matching Basis Functions.

by

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ABSTRACT

The rates of convergence of basis set expansions depend strongly on the suitability of the basis functions for describing the singularities in the wavefunction. Basis functions with singularities matching those of the wavefunction should provide the most rapid convergence. The practical importance of this idea has been demonstrated by some accurate Hartree-Fock calculations.

Singular points of the Fock equations for atoms or molecules occur at the nuclear positions and at $r=\infty$. Asymptotic solution of the equations for large r reveals singularities having both exponential and logarithmic character. The asymptotic exponents of the exponential terms are simply related to the orbital energies. Calculations using these asymptotic exponents demonstrate their optimal character. Energies and properties comparable to the most accurate existing basis set calculations were obtained without significantly increasing the number of basis functions. No exponent optimizations were required.

The nuclear cusp singularities in molecules have a logarithmic angular character that is responsible for the slow convergence of LCAO expansions. Some ideas for overcoming this problem will be discussed.

BOND LENGTH CHANGES RESULTING FROM HALOGEN SUBSTITUTION OF OXIRANE.

Carol A. Deakyne, Joseph P. Cravero, and William S. Hobson, Department of Chemistry, College of the Holy Cross, Worcester, MA. 01610.

Fluorine substituents have been shown to alter the ring bond lengths in oxirane. Orbital compositions, overlap populations, charge distributions, orbital energy splitting diagrams and charge density difference plots obtained from ab initio wavefunctions are investigated to determine the origin of the observed substituent effects. This approach enables us to rationalize the experimentally determined geometry of cis-1,2-difluorooxirane and to predict bond length changes for trans-1,2-difluorooxirane and tetrafluorooxirane and the relative stabilities of cis- and trans-1,2-difluorooxirane. The differences in fluorine substituent effects on oxirane and cyclopropane and the applicability of this approach to chlorinated oxiranes are discussed.

Aspects of nuclear dynamics in negative ion states

by W. Domcke, University of Heidelberg

Abstract:

The Born-Oppenheimer (BO) approximation constitutes one of the fundamentals of molecular physics and chemistry. The BO approximation is an excellent approximation for the majority of low-lying electronic states of neutral molecules and positively charged ions since the spacing of electronic states is large compared to the typical spacings of the nuclear motion (rotation and vibration). Negative ions, on the other hand, are usually weakly bound with respect to the detachment of an electron. Quite often bound states even cross into the electronic continuum as one or more internuclear distances are varied and thus become resonances. Owing to the proximity of the electronic continuum, the BO approximation is generally of limited validity in negative ions and the theoretical treatment of non-BO effects is important. Considering an isolated electronic state of a negative ion, the theoretical description of molecular dynamics beyond the BO approximation based on Feshbach's projection operator formalism is reviewed. In this formalism the nuclear dynamics in the negative ion state is governed by a partly complex, energy-dependent and non-local potential. The ab initio calculation of the complex non-local potential is discussed and methods to solve the equations of motion for such complicated potentials are described. Vibrational excitation in N_2 via the 2.3 eV shape resonance and dissociative attachment in HCl are considered as specific examples.

MULTICONFIGURATION HARTREE-FOCK STUDIES OF MOLECULAR ELECTRONIC STATES AND REACTION PATHWAYS

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The multiconfigurtion Hartree-Fock (MCHF) wavefunction provides a compact representation of many radicals in their ground and excited electronic states in the description of which configuration mixing plays an important role. Furthermore, energy gradients for these wavefunctions are easily calculated. We report MCHF calculations of the structure and properties for ground and in some cases excited electronic states of several molecules including C_2N_2, O_3, and NO_2. MCHF wavefunctions give also a conceptually simple description of bond breaking and bond formation in reactive systems. We report MCHF calculations of reaction pathways for the $O(^3P) + H_2CO$ and $H + O_3$ systems.

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+Also, Department of Chemistry, University of California, Berkeley. This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

ADIABATIC APPROXIMATION FOR COUPLED OSCILLATORS - A NUMERICAL STUDY

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The adiabatic approximation is applied to determine the quantum states of 2 coupled oscillators described by a generalized Hénon-Heiles hamiltonian. Comparison with exact quantum results shows that numerically calculated adiabatic energies are accurate even for excited states. A sequential adiabatic approximation is also applied to calculate the energy levels of a model 3-dimensional hamiltonian.

APPARENT R(4) SYMMETRY IN THE SINGLY-EXCITED STATES OF HELIUM. R. L. Flurry, Jr., Department of Chemistry, University of New Orleans, New Orleans, LA 70148. It is well known that the energy levels of the H atom can be found from the Casimir invariants of the [k,0] irreducible representations (irreps) of the R(4) [or SO(4)] group. The n^2 degeneracies are reflected in the dimensions of the irreps. Various workers have attempted to describe many-electron atoms in terms of R(4) or broken R(4) symmetry. Recently, it has been found that the doubly-excited states of He have apparent R(4) symmetry. [See D. R. Herrick, Adv. Chem. Phys., LII, 1-115, (1983).] We report here that the degeneracies of the singly-excited singlet states of He are reflected in the dimensions of the [k,k] irreps of R(4). If spin-orbit interaction is neglected, the degeneracies of the singly-excited triplet states are the dimensions of the [k,k-2] irreps. Empirical equations that accurately express the energy as a function of the n quantum number and the Casimir invariant of the appropriate irrep will be presented.

RELAXATION OF INTERNAL ENERGY FOLLOWING LASER EXCITATION.

W. Forst, Department of Chemistry, Laval University, Quebec Canada G1K7P4.

Using the exponential model for collisional transition probability, time profiles of average internal energy are computed for initial Poisson distribution following laser excitation. It is assumed that the system relaxes via V - T transfer, i.e. that the relaxing molecules are highly dispersed in rare gas buffer. It is shown that the time dependence of average vibrational energy is directly related to bulk-average energy transfer $\langle\langle \Delta E \rangle\rangle$, a macroscopic property which is a function of time, initial excitation level and (for a given heat bath gas) of heat bath temperature, and is only distantly related to average energy transfer per collision $\langle \Delta E \rangle$, a microscopic property. These effects will be demostrated on the relaxation of SF_6 in argon following absorption of several CO_2 laser photons.

An analysis of enzyme inactivation exhibiting biphasic time courses

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The inactivation of enzymes due to the substitution of ligands by covalently binding analogs is studied. For a variety of possible reaction schemes describing the inactivation, the kinetic equations are linearized. The time courses of the solutions exhibit biphasic shapes as these are frequently observed in such reactions. A particular type of inactivation is analyzed where the time of transition from one branch to the other of the biphasic curve is practically independent of the concentration of the analog. An analysis of the eigenvalues from different reaction models shows that for these time evolutions the enzyme exists necessarily in two states, only one of which is active.

Families of curves obtained for different concentrations of the analog reveal geometric properties which are characteristic of the enzyme mechanism involved. A graphical method is proposed which enables one to
1) easily discriminate between the two enzyme mechanisms, and to
2) determine the essential kinetic parameters.

As a preliminary attempt, the models have been fitted to the experimental data of three different sets of families of curves. It is demonstrated that a two-sites model of inactivation of (Na^+-K^+)-ATPase postulated in the literature cannot be valid.

INVESTIGATION OF HYTROGEN BONDS BETWEEN CH_3OH AND CH_3CN,CH_3NC,CH_3F,H_2O BY AB INITIC SCF MO METHOD

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(Beijing,Normal University,Beijing,China)
Tang Tin-Hua(T.H.Tang)
(Tianjin Normal University,Tianjin,China)

abstract

The hydrogen bond complexes:CH_3OH-CH_3CN,CH_3OH-CH_3NC, CH_3OH-CH_3F,CH_3OH-H_2O are studied by SCF MO method. Using STO-2G basis sets,the geometries of the above complexes are optimized.It is found that they all have a nearly colinear moiety.The hydrogen bond stabilization energies are calculated by means of 4-31G basis sets. The energy components at eqilibrium geometries of these complexes are calculated according to the"Morokuma's energy decomposing scheme".The results obtained show that the more strong the hydrogen bond,the more electrostatic its nature.

ELUCIDATION OF REACTIVE REGIONS IN MOLECULES

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By applying pairwise unitary transformations to the molecular orbitals of the reagent and reactant in a composite interacting system, it is shown that the electron delocalization in interactions is represented succinctly in terms of a few sets of paired hybrid molecular orbitals of fragment species. They are found to be localized beautifully in particular regions around the reaction sites both in the reagent part and in the reactant part, specifying the structural units that characterize the given type of chemical reaction. These orbitals in pairs are called the "interaction frontier orbitals (IFO)", providing a generalized extension of the basic frontier orbital concept. The derivation of these orbitals in connection with the configuration analysis of the self-consistent-field wave function of the composite system is discussed. Several examples are presented to show that the multifarious reactivities of organic molecules can be illustrated by the use of this method.

LASER-MODIFIED MOLECULAR DYNAMICS

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Both theory[1] and experiment[2] during the past decade have demonstrated that under the proper conditions laser radiation can interact directly with the dynamics of molecular processes, such as bimolecular collisions and unimolecular reactions. The mechanisms by which radiative coupling can influence and modify various dynamical processes are discussed. Particular attention is paid to bimolecular collisions, and the following gas-phase processes are considered: energy transfer,[1] ionization,[1,3] resonance formation,[4,5] chemical reactions[6] and line broadening.[7-9] There is increasing interest in laser-modified surface processes, and theoretical approaches are reviewed for the following: (1) resonance fluorescence of an atom near a metal surface, where the surface-dressed optical Bloch equations are solved for the population inversion and power spectrum of scattered light;[10] (2) charge transfer at a semiconductor, where ion neutralization is enhanced by the excitation of surface states.[11]

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Abstract of Talk to be Presented at the 8th Canadian Symposium on Theoretical Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, 7-12 August 1983.

MECHANISMS OF CATALYTIC REACTIONS

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We will examine the mechanisms of homogeneous and heterogeneous reactions. Major points are how the nature of a metal-ligand bond controls whether a reaction will be concerted and how the nature of this bond is determined by the specific metal involved and the character of the other ligands on that metal. We will also discuss the nature of chemisorbed intermediates on metal surfaces and how the surface-adsorbate bonding affects reactions on the metal surface. The theoretical principles will be illustrated by a detailed discussion of some of the following reactions:

1) 2s + 2s: $L_nM{-}R + H{-}H \longrightarrow L_nM\quad H + H\quad R$

2) Metathesis: $L_nM{=}CH_2 + R_2C{=}CR_2 \longrightarrow L_nM{=}CR_2 + R_2C{=}CH_2$

3) Ethylene Epoxidation: $H_2C{=}CH_2 + \frac{1}{2}O_2 \xrightarrow[Ag]{} H_2C\overset{O}{\diagup\diagdown}CH_2$

4) Fischer-Tropsch Synthesis: $CO + H_2 \xrightarrow[M]{}$ Alkanes, alkenes, ..., etc.

THE FORMATE ANION: AN AB INITIO STUDY OF ITS STRUCTURE, GENERAL HARMONIC FORCE FIELD AND FUNDAMENTAL VIBRATIONAL FREQUENCIES. A. R. Gregory (Department of Chemistry, West Virginia University, Morgantown, WV 26506, USA), K. G. Kidd (Department of Energy, Mines and Resources, Ottawa, K1A 0E4, Canada) and G. W. Burton (Division of Chemistry, National Research Council Canada, Ottawa, K1A 0R6, Canada).

The general harmonic force field of the formate anion has been calculated by ab initio restricted Hartree-Fock theory using the minimal STO-3G and split valence 4-31G basis sets. This work was carried out in conjunction with an experimental study in which the ion's force field was determined from its vibrational frequencies in polycrystalline sodium formate by an improved refinement procedure. The ab initio results proved valuable in that study as a guide to the true physical values of the harmonic force constants.

As expected, the 4-31G basis gives better results than the STO-3G basis. The agreement between the 4-31G and the experimental results suggests that interactions in the crystal are of secondary importance in determining the experimental force field. However, there are discrepancies between the 4-31G values and the experimental values for the force constants which exceed the empirical guidelines for such calculations on neutral molecules. These deviations may be real and due to the different environments of the ion in the two studies or they may be due to experimental and theoretical errors.

Conjugative delocalization of an oxygen lone pair in the molecular plane into an antibonding CH bond orbital provides a simple and consistent explanation for the weakness of CH bonds in $HCOO^-$ and related species. The inductive effect cannot account for this overall weakness, but it can account for the increase in CH bond strength from H_2CO and $HCOO^-$ to HCOOH and $HCOOCH_3$ and its decrease from H_2CO to CH_3CHO.

CI and MCSCF Methods Applied to Ground and Excited States of Molecules. Spin-orbit Studies on Cl_2

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For Cl_2, various properties based on spin-orbit coupling were calculated, using ab initio spin-orbit methods presently being developed by Buenker, Peyerimhoff and coworkers.

First, the transition probability for the spin-forbidden transition from $X^1\Sigma_g^+$ to $2^3\Pi_u$, which has been observed to be quite large, has been investigated. It's oscillator strength is calculated to be about 1/8 of the oscillator strength of the allowed $2^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition. Spin-orbit coupling occurs almost entirely via $2^1\Pi_u$.

Second, the spin-orbit splitting of $2^3\Pi_u$, of which the 0 and 1 components are known experimentally, has been studied by first- and second-order perturbation theory.

Finally, predissociation of $1^1\Sigma_u^+$, which is dipole allowed from the $X^1\Sigma_g^+$ ground state, into $2^3\Pi_u$, has been investigated. This problem relates to observed but unexplained fluorescence in the 40,000 cm^{-1} region.

8th Canadian Symoposium on Theoretical Chemistry

Abstract for paper entitled

Large scale calculations on small molecules,

by

N.C. Handy

The methodology for large scale configuration interaction calculations is reviewed. In particular the 'external-space' unitary group algorithms used with the Davidson iterative procedure, and the integer representation of the CI coefficients using determinants and the Cooper-Nesbet iterative procedure, are discussed. Applications to multireference single plus double replacement CI and full CI calculations are given.

Some full CI calculations on small molecules with double-zeta size basis sets are reported, ready as benchmarks for comparison with perturbation related calculations. In addition some full CI calculations on Be_2 and $(H_2)_2$ are also reported.

A very large basis set calculation on LiH will be reported. In particular discussion will concentrate on the effects of high angular momentum basis functions (f,g) in the attempt to produce a near exact variational energy at equilibrium geometry.

The effects of modern computing technology on the future of CI calculations will be mentioned.

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The Local Mode Model: A Sensitive Experimental Test for Molecular Orbital Theory.

Bryan R. Henry, Kathleen M. Gough and Allan W. Tarr, Department of Chemistry, University of Manitoba, Winnipeg, Canada R3T 2N2.

The theoretical basis for the local mode description of highly excited XH-stretching vibrations is reviewed. The model is applied to gas phase overtone spectra where it is used to explain subtle variations in CH bond lengths in substituted aromatic molecules. The predicted bond length variations are correlated with geometry optimized M.O. results and with M.O. charge distributions. The factors affecting local mode overtone intensities are discussed.

Recent Studies Concerning the Semiclassical Theory of Non-Adiabatic Transitions

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Semiclassical approximations for the theory of non-adiabatic collisions are considered. The multidimensional formalism developed is a generalization of the one-dimensional theory previously reported [J. Chem. Phys. 76, 2949 (1982)]. The formal analysis of the theory indicates that the resulting series of multiple non-adiabatic transitions can always be chosen so as to satisfy the Schrodinger equation in a term by term fashion. The more problematical questions concerning the accuracy and convergence properties of the multiple transition series is studied numerically for some simple model problems.

Triatomic Hydrogen and the Ammonium Radical

G. Herzberg
National Research Council of Canada

Until recently Rydberg spectra of molecules whose ground state is unstable (repulsive) have been known only for two diatomic systems: He_2 and ArH. The discovery of a Rydberg spectrum of triatomic hydrogen represents the first example of a polyatomic system of this kind. The analysis of the spectra of H_3 and D_3 has supplied a good deal of information about triatomic hydrogen, its electronic states, its geometrical structure and about Jahn-Teller interaction in its degenerate electronic states. The characteristic which makes possible the existence of stable Rydberg states of H_3 is the high proton affinity of the parent molecule H_2. It is to be expected that other molecules with a high proton affinity will also have neutral hydrogen adducts which are stable in their Rydberg states. One case (in addition to H_3) where such a spectrum has been identified is the ammonium radical NH_4 or ND_4. The first spectral feature to be assigned to NH_4 is the Schuster band of ammonia which is easily observed in any discharge through NH_3 at high pressure. Experiments with deuterium and ^{15}N substituted ammonia show that the Schuster band is due to NH_4. A second spectrum with somewhat different excitation conditions was first observed by Schüler, Michel and Grün in 1955. At high resolution the principal bands show a fairly well resolved fine structure (not yet fully understood) with a doublet head. Isotope experiments confirm that the molecule responsible for this spectrum also has four H atoms and only one N atom, i.e., is NH_4 or ND_4.

DIRECT CLUSTER EXPANSION METHOD

K.HIRAO, Department of Chemistry, College of General Education,
Nagoya University, Nagoya, Japan

The *direct* cluster expansion formalism for large-scale wave function calculations, based on an integral-list driven procedure, is presented in a new form. The new approach allows us to calculate the correlated ground state wavefunction and to make the direct determination of excitation energies and various detachment and attachment energies, such as ionization potentials and electron affinities, in the Symmetry-Adapted-Cluster (SAC) and SAC-CI framework. Application is made to the ground state and low-lying singlet and triplet excited states of glyoxal, $(CHO)_2$ and its positive and negative ions.

Some Advice on how Theoreticians can Interact with Chemists

Roald Hoffmann

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An attempt will be made to communicate to the audience the speakers' experience in chosing chemically interesting problems, constructing explanations, and communicating them to experimentalists. A case study approach will be taken, focusing on a recent problem in transition metal carbene complex chemistry.

ANALYTICAL SOLUTIONS OF THE LINEARIZED POISSION-BOLTZMANN EQUATION FOR VARIOUS AXIAL IONIC STRENGTH DISTRIBUTIONS IN CYLINDRICAL MEMBRANE PORES. Richard E. Rice and Frederick H. Horne, Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A.

For a charged cylindrical capillary in a membrane separating two aqueous electrolyte solutions, we obtain analytical solutions to the linearized Poisson-Boltzmann equation for various axial ionic strength $\{I(z)\}$ distributions ranging from I uniform in z to the general case of I^m linear in z, with m any positive or negative real number. The general solution is a linear combination of modified Bessel functions of the first and second kind, of fractional order. The boundary conditions required for obtaining complete solutions are developed from a charge balance at each end of the cylinder. A preliminary report of some of this work appeared in J. Chem. Phys. 75, 5582 (1981).

Model Potential Method in Molecular Calculations

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A number of approximate methods have been proposed in order to widen the scope of reliable molecular electronic calculations. The methods, known as pseudopotential, effective core potential, or model potential methods, aim at simplifying the treatment of chemically inert core electrons. Such a method has been developed during the past decade in our laboratory [1,2]. Recently our model potential (MP) method has been modified so as to allow for approximate treatment of relativistic effects [3].

The aim of the present paper is to construct new MP parameters and basis sets for nine atoms (F, I, Kr, Xe, Sc, Cr, Ni, Ca, Ag) and test their performance in molecular calculations (NiCO, $Ni(CO)_4$, CrO, ScO, CaO, F_2, I_2, IF, KrF_2, XeF_2, XeF_4, AgH). Consistently satisfactory results of these test calculations render a strong support to the view that our model potential method is a reliable and economical tool for molecular structure calculations.

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PRACTICAL METHODS FOR THE CALCULATION OF RESONANCE LIFETIMES. Alan D. Isaacson, Department of Chemistry, Miami University, Oxford, Ohio 45056.

A knowledge of the energies and lifetimes of electronic resonance states is necessary for understanding several physical processes, including electron-molecule scattering and chemiionization reactions. While the energy of a resonant state can be approximated from standard electronic structure calculations, the lifetime (or width) of a resonance has proved much more difficult to model accurately. Recent approaches to calculating resonance widths in molecular systems include those which employ a basis set of real-valued Slater functions augmented with a few complex-valued Slaters which are important in representing the continuum component of the scattering wavefunction, as well as those which employ a basis set of real-valued Gaussian functions augmented with a relatively large number of complex Gaussians. However, in order to obtain the greatest degree of both accuracy and practicality, it is desirable to employ real-valued Gaussian basis sets augmented with a minimum number of complex-valued functions, if any. To this end, known resonances exhibited by a one-dimensional model barrier were studied with several techniques involving basis sets containing at most a single complex-valued function. The results demonstrate that when proper conditions on the problem are imposed, a basis set containing a single complex-valued Gaussian function provides useful accuracy.

Molecular integrals arising in the linear response theory of van der Waals forces†

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General formulas are derived for molecular integrals which arise in the linear response theory when it is applied to the van der Waals interactions between molecules. These integrals are essentially the matrix elements of the Fourier transformed double Coulomb operator between any cartesian Gaussians. The computational aspects of these formulas are also discussed.

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†Submitted to Chemical Physics, May 13, 1983.

The Classical Limit of the Wigner Formulation of Quantum Mechanics

by

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and
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Abstract: We show that in the classical limit the Wigner representation of quantum mechanics reduces to the Liouville formulation of classical mechanics. This has a number of important consequences. In particular we discuss the implications for semiclassical quantization and relaxation phenomena. This involves examining the correspondence between the eigendistributions of the respective propagators, and results in a new semiclassical formulation.

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Large-Order Perturbation Theory in the Stark-Zeeman Effect for Parallel Fields.*

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The perturbation expansion for the energy of the ground state of the hydrogen atom in parallel electric and magnetic fields has been calculated to tenth order in the square of each field strength. The perturbation coefficients have been found empirically to obey certain recurrence relations when the order in one field or the other is large. Although the expansion itself is divergent, the coefficients are used to form two-variable rational approximants which are much better behaved. The state actually has a finite lifetime since Stark tunnelling occurs along the common field axis, and it is shown that the perturbation expansion, when combined with numerical analytic continuation techniques, yields the associated complex energy eigenvalue.

*Supported by NSF grants CHE80-11442 and PHY82-00805 through the University of Colorado.

Ionization Potentials and Electron Affinities of Small Carbon Clusters[1]

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Recent determinations of the mass spectra of the positive and negative ions produced in laser microprobe studies of graphite and organic polymers have revealed an even-odd alternation in the intensities of the $C_n^{\pm}$ peaks as a function of cluster size. This has led us to initiate a theoretical study of the structures and energies of the neutral clusters and their anions and cations.

We report here the results of unitary-group MCSCF and CI as well as many-body perturbation theory calculations of the IP's and EA's of C_2 and C_3. The calculations on C_3 reveal that Koopmans' Theorem gives an incorrect ordering on the first two ionization potentials. The largest calculations, including in excess of 200,000 configurations generated from a multireference space and employing MCSCF orbitals, give an EA for C_3 0.2 eV less than the experimental value of 2.0 eV.[2] Calculations are underway for C_4 and its ions, and it is hoped that we can report on these at the conference.

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1. This research was supported by the National Science Foundation.

2. Personal communication, G. B. Ellison.

Degenerate many-body perturbation theory

Excited and ionized states of N_2

G. Hose and U. Kaldor, Chemistry Department, Tel-Aviv University, Tel -Aviv, Israel.

Degenerate MBPT (J. Phys. B 12, 3827 (1979)) is applied to a dozen excited and ionized states of N_2. The perturbation series is calculated to third order and summed via the [2/1] Pade approximant. The average deviation of the vertical excitation and ionization energies from experiment is $\sim$ 0.2 eV.

General Structure of Bistability in Far-From-Equilibrium Dynamical Systems

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A variety of dynamical systems displaced far from equilibrium exhibit bistability and hysteresis involving oscillating states. Examples of such processes from Chemistry, Laser Physics and other areas will be discussed. For strongly dissipative systems such phenomena admit a reduced description in terms of discrete-time, one-dimensional maps, which provide a convenient way to analyze the complex bifurcations in these systems. This class of systems also displays a rich substructure of bistabilities that satisfies simple, universal, scaling laws. Some of the implications of this scaling structure for experimental studies on these dynamical systems will be described.

Three-Dimensional Electrostatic Molecular Potential Contour Maps

A. Stereoelectronic Requisites for Biomedical Molecules

B. Cationic Polymerization

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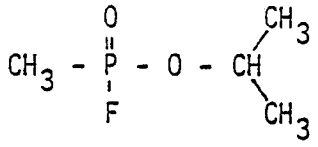
Three-dimensional (3-D) electrostatic molecular potential contour (EMPC) maps serve to delineate the stereoelectronic requisites for biomedical molecules (endogenous and exogenous) interacting with receptor sites, with enzyme active sites and with binding sites on antibodies (natural or synthetic). Quantum chemical calculations, since they depend only on internal body-fixed molecular coordinates, are incapable of distinguishing between optical isomers. However, we derived the concept of generating the EMPC maps relative to a set of external space-fixed coordinates. These 3-D EMPC maps can then be used to generate reverse image holographs which can then be used as templates to prescreen other molecules theoretically. Results will be presented for several examples: The two different optical isomers of GB



[a potent inhibitor of acetylcholinesterase(AChE)] have different toxicities. These 3-D EMPC maps for GB [S(-) (the more toxic isomer) and R(+) (the less toxic isomer] indicate vividly the differences in how these two isomers would fit into the enzyme active site. 3-D EMPC maps will also be presented for some drug molecules.

In the area of cationic polymerization of exotic energetic monomers, EMPC maps predicted correctly the rank order of polymerization prior even to the synthesis of any of the monomers. 3-D EMPC maps allow prediction of optimal co-polymer candidates again prior to experiment.

This research was supported by ONR Biophysics under Contract N00014-81-K-0007 and by ONR Power Programs under Contract N00014-80-C-0003.

Prediction of Crystal Densities Using Ab-Initio Potential Functions From Energy-Partitioned Ab-Initio MODPOT/VRDDO Intermolecular SCF Calculations Plus Dispersion

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To be able to predict crystal densities even for completely hypothetical compounds is of interest.

Our approach aimed at evaluating the intermolecular interactions in molecular crystals and at analyzing the optimal crystal packing is based on nonempirical ab-initio calculations for smaller molecular aggregates (monomers, dimers, trimers, etc.), partitioning the total SCF interaction energies into the different components and then fitting these components individually to functional forms or when necessary recalculating or estimating explicitly for certain interaction components for each different unit cell dimension change.

$$\Delta E_A = \frac{1}{2} \sum_{B}^{\text{lattice}} \Delta E_{AB} + \frac{1}{3} \sum_{B}^{\text{lattice}} \sum_{C \neq B}^{\text{lattice}} \Delta E_{ABC} + \cdots$$

Non-empirical two-body interaction

$$\Delta E_{AB}^{SCF} = E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND,LE}^{(2)} + E_{IND,CT}^{(2)}$$

obtained from ab-initio intermolecular LCAO-MO-SCF calculations using our own rapid efficient programs for ab-initio calculations on large molecular and intermolecular systems, which incorporate a number of desirable optional computational strategies for calculations on such molecules

$E_{EL}^{(1)}$ partitioned into $E_{EL,MTP}^{(1)} + E_{EL,PEN}^{(1)}$

$E_{EL,MTP}^{(1)}$ - multipole (calculated each time for each variation of unit cell parameters of crystal)

$E_{EL,PEN}^{(1)}$ - penetration

$E_{EX}^{(1)}$ - exchange

$E_{IND,LE}^{(2)}$ - long range induction

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Since long range induction terms are not additive (but only the electric field due to surrounding molecules is additive) the long range two-body induction term $E^{(2)AB}_{IND,LE}$ has now been calculated by

$$E^{(2)}_{IND,LE} = -\frac{1}{2}\left[\sum_{a\varepsilon A} \alpha_a (\vec{E}^{B\to A}_a)^2 + \sum_{b\varepsilon B} \alpha_b (\vec{E}^{A\to B}_b)^2\right]$$

where α_a and α_b denote the atomic polarizabilities (fitted to reproduce nonempirical ab-initio values of $E^{(2)}_{IND,LE}$) where $\vec{E}^{B\to A}_a$ or $\vec{E}^{A\to B}$ correspond to the electric field calculated within the atomic multipole expansion.

$E_{IND,CT}$ - short range induction

The short range terms

$E^{(1)}_{EL,PEN}$, $E^{(1)}_{EX}$ and $E^{(2)}_{IND,CT}$ are each fitted to their own potential function

$$\Delta E_{AB} = \Delta E^{SCF}_{AB} + \Delta E^{(2)}_{DISP}$$

$$\Delta E^{(2)}_{DISP} = -\sum_{a\varepsilon A}\sum_{b\varepsilon B} C_{aa}C_{bb}R^{-6}_{ab}$$

Since this is a pioneering study using such atom class-atom class potential functional forms fitted to partitioned ab-initio SCF or ab-initio MODPOT/VRDDO/MERGE wave functions, we investigated carefully such aspects as the comparison of the various intermolecular interaction terms calculated from the potential functions compared to those calculated by ab-initio wave functions. We also investigated for the CRYSTAL program, how many surrounding unit cells had to be included for energy convergence.

We tested the program for heteronuclear polyatomic molecules on CO_2 and the agreement of our theoretically optimized unit cell dimensions with experiment was excellent.

For our first test on predicting unit cell dimensions for an energetic nitrocompound, we investigated the crystal CH_3NO_2. An experimental crystal structure had previously been determined. We calculated the intermolecular interactions for CH_3NO_2 at more than 50 geometries, partitioned the interaction energies, and fit these to functional forms. The agreement of our theoretically optimized unit cell dimensions was very good.

We next used the atom class-atom class potential functions from CH_3NO_2 to optimize the unit cell dimensions for a larger six-member saturated

cyclic trinitramine. The agreement with experiment was excellent - to within better than 0.1%.

Since our method fits the partitioned ΔE_{SCF} results to atom class-atom class potential functions this enables a general library of such potential functions to be built up for the molecular classes of interest.

This research was supported by ONR under Contract N00014-80-C-0003.

Multiconfiguration Model Potential Calculations on Diatomic Halides and Halogen Hydrides

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Calculations using the model potential (MP) method [1] were performed on diatomic halides and halogen hydride molecules. For the iodine atom the quasi-relativistic MP [2] was used. The valence-electron correlation effects were taken into account via the MCSCF scheme [3]. The configurations were chosen according to ODC and OVC rules [4]. The MP-OVC results compare well with the experimental data and with results of all-electron calculations.

Comparison of the MP results in the series SCF--ODC--OVC shows that the MP method exhibits the desired monotonic improvement upon the gradual introduction of electron correlation into the wave function.

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[3] K. Ruedenberg, L.M. Cheung, S.T. Elbert, Int. J. Quantum Chem., XVI (1979) 1069.

[4] A.C. Wahl, G. Das, in: H.F. Schaefer, III (ed.), Modern Theoretical Chemistry, Plenum, 1977, vol. 3, p. 51.

STRUCTURE AND LENNARD-JONES POTENTIAL FUNCTIONS OF THE CARBON MONOXIDE DIMER FROM SEMIEMPIRICAL MNDO COMPUTATIONS. Zvi C. Kornblum. The Cooper Union for the Advancement of Science and Art, School of Engineering, Cooper Square, New York, N.Y. 10003.

A quantum mechanical intermolecular potential is derived by computing dimerization energies for many dimer configurations. The theoretical data is then fit to a functional form, e.g., the Lennard-Jones, Stockmayer, or a generalized empirical potential function. An obvious advantage of the quantum mechanical approach exists when there is little or no experimental data. Quantum mechanical potentials have been mainly determined for strongly hydrogen-bonded systems, such as H_2O and HF, and have been applied in Monte Carlo simulations of their liquids.

This paper will discuss the results of semiempirical MNDO computations on the structure of and Lennard-Jones potential functions for the carbon monoxide dimer, a system that heretofore has never been quantum mechanically investigated. Various uncertainties in the experimentally deduced properties of CO, such as the dimer structure, residual entropy, rotational barriers, potential parameters, and quadrupole forces, will be examined and compared with theoretical results.

THE QUANTUM MECHANICAL THEORY OF COLLISION INDUCED DISSOCIATION AND THREE BODY RECOMBINATION PROCESSES USING LOCAL HYPERSPHERICAL SURFACE FUNCTIONS

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The quantum theory of collision processes in which the number of bodies entering a collision or emerging from it is greater than two presents special conceptual difficulties. All of these difficulties can be overcome using hyperspherical coordinates and wave function expansions in terms of distance-dependent hyperspherical surface functions. This includes, in particular, atom-diatom collisions in which dissociation competes with exchange, and collisions among three atoms in which formation of a diatomic product competes with the energy redistribution process among the three emerging isolated atoms. The formal aspects of this theory will be presented, together with the results of applications to simple systems and their comparison with quasi-classical trajectory calculations.

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OSCILLATING PHOTOCHEMICAL REACTIONS: STUDY OF THE 9,10 DIMETHYL ANTHRACENE/CHLOROFORM SYSTEM

In the past five years, a few photochemical reactions have been reported to display unusual temporal oscillatory behavior. The results of our investigation of the fluorescence oscillations in irradiated 9,10 Dimethyl Anthracene/Chloroform ($DMA/CHCl_3$) solutions will be presented. These results illustrate a large variety of unusual kinetic behavior such as single and miltipeak oscillations, transition from one type of oscillation to another and transitions between "states" of high and low fluorescence intensity. The conditions for which these oscillations are observed will be discussed and a qualitative model of the irradiated $DMA/CHCl_3$ system will be suggested. This model assumes that the instability giving rise to the oscillations is localized within a thin stationary layer of solution. The representation will be discussed in connection with our results. Some relevant recent work in which a Diode Array Rapid Scan Spectrofluorimeter was used to monitor the fluorescence spectrum as a function of time will also be presented.

ELECTRON TRANSFER IN SOLIDS, LIQUIDS AND BIOLOGICAL SYSTEMS

by Sven Larsson, Department of Chemistry, University of Lund, POB 740, S-22007 LUND, Sweden

Electron or hole transport is discussed on the molecular level. The basic electron transfer step is described by a model similar to the Marcus model for redox reactions or the polaron model of Holstein for semiconductors. Four limit cases emerge: adiabatic-barrierless, nonadiabatic-barrierless, adiabatic with barrier and nonadiabatic with barrier. The electron tunneling process is described by many-particle theory. It is found that tunneling is considerably facilitated if a molecule connects the electron exchanging subsystems, as compared to an empty gap. Equations are derived which show that in the long range biological tunneling, it is necessary to have a good molecular contact between the metal ions. Von der Waals gaps lead to increased nonadiabaticity, and this may in fact be a controlling factor in biological transfer. Electron mobility in molecular crystals is discussed as an example of nonadiabatic, barrierless motion.

SIEGERT QUANTIZATION, COMPLEX ROTATION AND MOLECULAR RESONANCES

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A coupled-channel approach has been developed for the determination of complex eigenenergies with Siegert type boundary conditions in the heavy motion of a molecular system [1]. A matching condition has to be satisfied and this can only be done for particular energies, just as for a bound state problem. However the condition of outgoing waves in the open channels is only compatible with a complex energy. It is also possible to proceed to a complex rotation of the coordinate for relative motion. With this procedure bound state energies and resonance energies are treated exactly on the same footing. This variant of the complex rotation method does not make use of a basis of integrable functions. For numerical or piecewise potentials it is possible to use Simon's exterior scaling method [2] to circumvent the problem of analytical continuation. This direct determination of the complex resonances energies offers an alternative to the procedures analyzing the elements of the S matrix. An example implying overlapping resonances is worked out. This involves the excitation of a van der Waals complex, with competition between direct photo-dissociation and photo-predissociation. The interference effect present in such a situation is reflected into the imaginary part of the appropriate complex resonance energy.

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Orbiting Resonance Model for Recombination of Physisorbed Atoms

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The orbiting resonance model for atomic recombination, originally developed for applications to gas phase kinetics[1] is now adapted for describing the recombination of atoms physisorbed on a surface. The model assumes that a population of atoms is initially physisorbed on a surface on which the atoms are free to move about in two dimensions. Atom-atom collisions at appropriate relative energies and impact parameters can then give rise to long-lived orbiting pairs, which may in turn lose internal energy and become truly bound. The surface lowers the dimensionality of the problem (relative to the gas phase process), and plays the role of the third body whose participation preserves energy and momentum conservation. The perturbation driving the second (inelastic) step of the mechanism is provided by the corrugation (roughness) of the surface.

Prediction of rates using this mechanism presumes a knowledge of both the atom-atom and atom-surface interaction potentials. The present work involves the application of this model to the recombination of H or D atoms on the (1,1,1) surface of a Xe crystal. The interaction potential between the isolated atoms is clearly well known in this case[2] and its modification by the presence of the surface may be readily calculated. Similarly, the atom-surface potential which both binds the physisorbed atoms and provides the corrugation which drives the inelastic step, may be obtained by assuming pairwise additivity and summing the known H-Xe pair potential[3] over the semi-infinite crystal using well known techniques[4]. Overall second-order rate constants have been calculated for H and D recombination at T = 4 and 10K. For physisorbed atom concentrations of approximately one atom per five unit cells (i.e. 0.013 $Å^{-2}$), the predicted reaction half lives are:

	$t_{\frac{1}{2}}$(H)/nsec	$t_{\frac{1}{2}}$(D)/nsec
T = 4 K	3.7	0.20
10 K	0.032	0.010

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Theoretical Studies of the Gas-Phase Proton Affinities of Molecules Containing Phosphorus-Carbon Multiple Bonds

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Abstract

Theoretical values for the gas-phase proton affinities (PA's) of phosphaethene, phosphaethyne, and phosphabenzene have been obtained from ab initio SCF calculations employing analytic gradient techniques for geometry optimization. The sensitivity of the results to the choice of basis set and to the inclusion of correlation is discussed. It is concluded that while the PA's for P-site and C-site protonation are found to be nearly equal in both phosphaethene and phosphabenzene at the split-valence SCF level, the inclusion of polarization functions for phosphorus and the consideration of electron correlation both act to favor P-site protonation over C-site protonation, with the isomerization energy being approximately 50 kJ mol^{-1} for the sites.

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Localized Orbitals Based on the Fermi Hole

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The properties of the Fermi hole may be used to transform a set of canonical SCF molecular orbitals into a localized representation of the electronic wavefunction. Except for small changes required to maintain orthogonality, each localized orbital is determined by an explicit linear combination of canonical SCF orbitals. The coefficients in these expressions only depend on orbital amplitudes, and do not require the evaluation of any integrals. Numerical results demonstrate that this method may be applied to large molecules, and convergence problems associated with conventional methods are completely eliminated.

Calculation of the Lower Vibrational Energy Levels of Formaldehyde by a Variational Method

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A six-dimensional variational calculation for the vibrational energy levels of CH_2O and CD_2O is carried out with the complete rotational-vibrational Hamiltonian. Results are reported for different potential functions which have appeared in the literature. The contribution of various terms in the Hamiltonian to the calculated vibrational spectrum is investigated.

DIRAC-FOCK-ROOTHAAN SCF WAVEFUNCTIONS FOR ATOMS AND MOLECULES†

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Abstract

The Dirac-Fock SCF theory[1] has been very successful in the study of relativistic effects in atomic systems using numerical integration methods which will be very complicated for molecular systems.

Alternatively, a matrix form of the Dirac-Fock (relativistic) SCF formalism for use in the basis set expansion method of Roothaan[2] for atoms[3] and molecules[1,4] will be delineated, pointing out the difficulties associated with the relativistic treatment of N-electron systems (N $\gtrsim$ 2). Results of calculations on various atoms and molecules using Slater[3-5] and Gaussian[6]-type basis functions will be presented and discussed.

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STIMULATED RAMAN AND THIRD-ORDER NONLINEAR SPECTRA AT HIGH PHOTON DENSITIES

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We have studied the stimulated Raman spectra arising from the interaction of a three-level atom in the "V" configuration with two strong electromagnetic fields whose initially populated modes ω_a and ω_b are in resonance with the two atomic transition frequencies. The Green's function formalism has been used in the limit of high photon densities to calculate the excitation spectra near the frequencies $\omega=\omega_{ab}=\pm(\omega_a-\omega_b)$. Expressions are derived for the relative intensities, which describe, apart from the usual Raman peak at the frequency $\omega=\omega_{ab}$, four pairs of Lorentzian lines peaked at the frequencies $\omega=\omega_{ab}=\pm\Omega_a/\sqrt{2}$, $\pm\Omega_b/\sqrt{2}$, $\pm\Omega$ and $\pm 2\Omega$, respectively, and having spectra widths of the order of $3\gamma_0/4$. The parameter Ω is defined as $\Omega^2=(\Omega_a^2+\Omega_b^2)/2$, where Ω_a and Ω_b are the Rabi frequencies of the two laser fields and γ_0 is the spontaneous emission propability. Since the Raman process competes with those arising from the third-order nonlinear mixing of frequencies near $\omega=\omega_a-2\omega_b$ and $\omega_b-2\omega_a$, respectively, the excitation spectra for the

latter processes are calculated as well. The excitation spectra near the reduced frequency $X=(\omega-\omega_a+2\omega_b)/\gamma_0=0$ are considered as a function of the reduced Rabi frequencies $\eta_a=\Omega_a/\gamma_0$ and $\eta_b=\Omega_b/\gamma_0$ of the two laser fields, respectively. For $\eta_a<\eta_b$, the spectra consist of a doublet peaked at $X=\pm\eta_b/\sqrt{2}$ and its intensity is constant. When $\eta_a=\eta_b$, the spectra are composed of five pairs of bands peaked at $X=\pm\eta_a\sqrt{0.15}$, $\pm\eta_a/\sqrt{2}$, $\pm\eta_a$, $\pm\eta_a\sqrt{2}$ and $\pm\eta_a\sqrt{3}$. When $\eta_a>\eta_b$, the computed spectra consist of five pairs of bands, where the intensities of the peaks at $X=\pm\eta_b/\sqrt{2}$ and $\pm\eta_a/\sqrt{2}$ are positive indicating absorption, those at $X=\pm\eta_b/2\sqrt{2}$ are negative implying amplification and the two pairs of peaks at $X=\pm\eta_b\sqrt{2}$ have positive and negative components describing the mixed process of absorption-amplification. The intensities of these bands are found to vary as $(\eta_a/\eta_b)^2$ for $(\eta_a/\eta_b)>1$ and, therefore, the intensities of the bands are immensely enhanced as the value of the ratio (η_a/η_b) increases. Results of numerical calculations for selected values of Rabi frequenices are graphically presented and discussed. Comparison between the spectra arising from the processes in question is considered.

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Calculations on Resonances Using Complex Basis Function Methods: What Happened to the Complex Coordinates Idea?

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Resonances are a common feature of electron-atom and electron-molecule scattering as well as of other types of molecular collisions. Low energy (0-5 eV) shape resonances occur in the scattering of electrons from many diatomics and from almost every organic molecule containing a double bond.[1] A more common phenomenon still is the occurrence of higher energy Feshbach resonances in electron-molecule scattering. Vibrational excitation by electron impact and dissociative attachment generally proceed with greatly enhanced cross sections at resonance energies, while autoionization and Penning ionization occur exclusively as resonance processes. For the simplest theoretical treatment of these processes[2] we require the complex resonance energy, $E_{res}(R)$,

$$E_{res}(R) = E_R(R) - i\,\Gamma(R)/2 \ ,$$

where $E_R(R)$ is the position and $\Gamma(R)$ the width, as a function of the nuclear coordinates, R. An obvious, and by now time-worn, problem in theoretical chemistry is to devise a reliable and general way of calculating this complex potential surface which uses only techniques similar to the ordinary bound-state methods of quantum chemistry.

The original complex coordinates idea, which was based on theorems of Balslev, Combes and Aguilar[3] promised to provide just such an approach. By scaling the coordinates of all the electrons in a system by a complex scale factor, $e^{i\alpha}$, according to $\{\vec{r}_i\} \rightarrow \{e^{i\alpha}\vec{r}_i\}$, the wave function associated with the complex resonance energy can be rendered <u>square integrable</u> and that is sufficient to make its calculation possible using the basis function methods of quantum chemistry. But although this formally correct and conceptually simple approach provided numerical results for two-electron systems,[4] it is generally unreliable for many-electron systems and is beset with numerical instabilities for most molecular systems.

The subject of this talk is the second generation of "direct methods" for computing complex resonance energies which are not subject to the computational

pathologies which limit the complex coordinates approach. Most of the second generation methods (and all of the ones to be discussed here) can be viewed as variants of a complex variational principle which alleges that the following expression for the complex resonance energy

$$E_{res} = \frac{\int (\Psi)^{GDT(*)} H \Psi \, d\tau}{\int (\Psi)^{GDT(*)} \Psi \, d\tau}$$

is stationary with respect to (real and complex) variations in Ψ.[5] Among the methods and calculations which will be reviewed and placed in the context of a complex variational principle are:

1) The Method of Complex Basis Functions[6]
2) The Complex Self-Consistent-Field Approximation[7] (and molecular applications)
3) The Complex Stabilization Method[8]
4) The Saddle-Point Complex-Rotation Method[9]
5) The Analytic Continuation of Stabilization Graphs[10]

I will attempt to outline the state of the art in resonance calculations by "direct methods" and to give an indication of the possibility of using these techniques for calculations on nonresonant scattering problems.

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Towards Computer-aided Quantum Chemical Synthesis Design

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Abstract:

In the last decade computational quantum chemistry has become an important complement of experimental chemistry, as it can provide detailed information on molecular processes that is not available using current experimental methods. One area of experimental chemistry that has not yet been the target of a systematic effort by quantum chemists, is computer aided quantum chemical synthesis design, and only isolated attempts and results have been reported so far. Whereas some of the computational difficulties still appear formidable, there are good reasons to be optimistic: on the one hand there is a continuous and still accelerating improvement in the available computer technology, and on the other hand, some of the more advanced mathematical techniques lead to substantial simplifications.

The topological model of potential energy hypersurfaces and the differentiable manifold theory of the nuclear configuration space offer some computational simplifications. Reaction topology forms a rigorous quantum chemical basis for a topological definition of molecular structure and reaction mechanisms, and it leads to a global quantum chemical reaction network model, within which all possible reactions involving a given set of nuclei and electrons can be analysed.

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Many-valued surfaces and their approximate single-valued representation

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The potential energy surfaces of many simple polyatomic molecules are many-valued. The ground state of H_2O, for example, must, by the Wigner-Witmer rules, satisfy the following dissociation scheme

$$H_2O(\tilde{X},{}^1A_1) \rightarrow \begin{cases} H_2(X,{}^1\Sigma_g^+) + O({}^1D) & (a) \\ H_2(a,{}^3\Sigma_u^+) + O({}^3P) & (b) \\ OH(X,{}^2\Pi) + H({}^2S) & (a) \\ OH(A,{}^2\Sigma^+) + H({}^2S) & (b) \end{cases}$$

There are two sheets to this surface which we can associate with diabatic states (a) and (b) whose dissociation fragments are indicated in the above scheme. The 2-valued surface can be represented by the eigenvalues of a 2x2 matrix and analytical functions for the elements of this matrix have been published [1].

For dynamical calculations (e.g. classical trajectories) the use of many-valued surfaces is expensive and approximate single-valued representations have usually been used. In this paper a new approach is described for the construction of such surfaces which appears to have general applicability and which balances the necessary approximations with accuracy for dynamical calculations. The method will be described in detail for H_2O and in general terms for the more complicated ground state surface of H_2O_2.

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Electronic transitions in atomic and molecular dynamic processes

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There are four basic interactions which govern electronic transitions in the low energy atomic and molecular processes. Theoretical treatments of these interactions are reviewed briefly. A particular attention is paid to the nonadiabatic transitions induced by radial and rotational coupling in atomic collisions. A unified treatment of these transitions is shown to be possible by using the recently proposed dynamical-state representation.[1] A general many-state spectroscopy as well as collision problem can be dealt with uniformly by the semiclassical formalism in this representation. Some practical applications are presented.[2,3] Discussions will also be made about a possible generalization of the basic idea to a wider class of dynamic problems.[4]

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The Quantum States of a Moderately Rarefied Fluid of Spinless Bosons

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A well-understood model for a fluid is the Gartenhaus-Schwartz nuclear model, a collection of N identical particles held together by pairwise harmonic attractions with no other forces. While this model is useful as an extreme soluble limit, it is desirable to have a more realistic limiting case to treat molecular fluids, especially to take into account the short-range repulsions between atomic particles. The quantum states of a cluster of spinless identical bosons are derived for the Gartenhaus-Schwartz model perturbed first by an arbitrary pairwise interaction and then by the specific example of a pair-wise δ-function interaction. The explicit relation is established between the quantum states of such a 5-atom cluster and a nearly-rigid van der Waals molecule formed by the same atoms.

ON DYNAMICAL SYMMETRY OF MOLECULAR SYSTEMS IN THE HIGH-BARRIER LIMIT

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The effective potential energy surfaces for nuclear motion in the configurational spaces of molecules can usually be treated as decomposable into "feasible" domains separated by infinite barriers. An approximate global Hamiltonian is represented as a sum of localized Hamiltonians. Its energy levels generally form a highly degenerate set, the basis of some additional symmetry of the Hamiltonian. The ith localized Hamiltonian is defined in the ith feasible domain and must be invariant under those symmetry operations of the accurate Hamiltonian which convert this domain into itself. Feasible permutations and permutation-inversions give the best known example. For an impurity molecule rotating in a crystal field one has to introduce feasible operations of a new kind: the so-called "perrotations" which are products of pure permutations and proper or improper rotations. In the space of dynamical variables feasible operations generate dynamical symmetry groups: "the dynamical permutation-inversion group" for an isolated molecule and " the dynamical perrotation group" for a molecule rotating in a crystal. Different examples are discussed.

THE 'DRESSED' MOLECULE PICTURE OF STRONG FIELD DYNAMICS

by

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ABSTRACT

The general molecular Hamiltonian is reexamined by the methods of quantum electrodynamics (QED) in the case of strong fields. General couplings are derived which go beyond the space-translation method. These couplings account for multiphoton infrared, absorption, electronic absorption and photon scattering in molecular systems for intense fields where perturbative methods are no longer valid. The reduction of the QED method to the classical methods used in present dynamics is obtained and criteria for the validity of the classical methods are established. Examples will be illustrated of strong field effects (i.e. dressing of electrons and nuclei) on reaction dynamics.

THE STABILITY OF OPEN-SHELL SPECIES - THE RELATIVE NET STABILIZATION ENERGY, $\Delta SE°[R^{\cdot},RX]$, OF ALKYL RADICALS ($R^{\cdot}$) IN THE GAS PHASE. *A. Martin de P. Nicholas and Donald R. Arnold, Department of Chemistry, Dalhousie University, Halifax, N.S., B3H 4J3.*

The net stabilization energy of an open-shell species ($R^{\cdot}$) is defined with respect to R(RX), the R component of the closed shell species RX. These components (R(RX)) are chosen such that they contain the same (or approximately the same) number of electrons as $R^{\cdot}$ and differ from it only in the spatial arrangement of atoms and distribution of charge.

This work shows that relative BDH(R-H) values cannot be equated to relative radical stabilization energies. The $\Delta SE°[R^{\cdot}, RX]$ values measured relative to the ethyl radical show that the methyl radical is more destabilized and the n-propyl, iso-propyl and t-butyl radicals are more stabilized than predicted from the corresponding relative BDH(R-X) values.

A Theoretical Simulation of Interactions in Transmembrane Ionic Channels

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Interaction energies calculated from a $\frac{1}{R}$ expansion are used to determine the central energy barrier in the transport of Li^+, Na^+, K^+ and Ca^{2+} through the transmembrane ionophore Gramicidin A. The $\frac{1}{R}$ expansion used has been parameterized to reproduce ab-initio energies.

On the basis of the results obtained for their interaction with the ionophore, it is shown that the toxicity of tetrodotoxin and saxitoxin may be due to the blocking of the channel pore, thus interferring with the ionic transport.

Similar studies on the anesthetic activity of diethyl ether showed a preferred attachment of the ether to the pore (by comparison with water) and a more favourable interaction with acetylcholine than with Na^+ in the synaptic cleft.

THE MINIMUM DEFORMATION OF ORBITAL PATTERNS. THE PRINCIPLE FOR THE UNIFICATION OF FUKUI-WOODWARD-HOFFMANN THEORY

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The frontier orbital theory developed by K.Fukui and the orbital symmetry conservation theory by R.B.woodward and R.Hoffmann stand out in sharp contrast to each other on the theoretical frameworks, particularly in which the former takes account of the frontier molecular orbitals of only reactants, whereas the latter does the symmetry of molecular orbitals of both reactants and products.

We now wish to show more clear-cut definitions of concerted reactions and correlation diagrams, and then elucidate that the two types of chemical reaction theory described above can be consistently unified to form a new basic principle of a minimum deformation of orbital patterns in a concerted reaction as a more complete and inclusive chemical reaction theory.

PROTON AFFINITY OF GERMANE(GeH_4)

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By ion-beam scattering experiment, Lampe suggested that the proton affinity of GeH_4 is 7.01~7.11eV and the GeH_4 should be more basic than methane and silane. Theoretically, on the other hand, Hartmann calculated the proton affinity of GeH_4 by the one-center expansion method, assuming the protonated Germane (GeH_5^+) to be C_{3v}, C_{4v}, and D_{3h} symmetry. In his calculations, the D_{3h} structure gave the lowest energy and the proton affinity was obtained to be 6.04eV. However, Hartmann did not consider the C_s structure for GeH_5^+, so we studid the proton affinity of GeH_4 by ab initio LCAO-MO method by taking into consideration both structure D_{3h} and C_s. The basis set used in our calculation is an extended basis set including f orbitals for the germanium. The very interesting result is obtained that the GeH_5^+ is lowest in energy when it has the C_s symmetry. The calculated proton affinity is to be 6.87eV and is good agreement with the experiment. Moreover, the calculated structure of GeH_5^+ seems to be σ-complex between GeH_3^+ and H_2.

Two-Dimensional Hindered Internal Rotations in Activated Complexes. *Philip D. Pacey and Brian D. Wagner, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3*

Bending motions in an activated complex, of the form AB_2, are treated as a two-dimensional internal rotation hindered by a sinusoidal potential function. Energy levels and thermodynamic quantities are calculated for such motions and the results are incorporated into activated complex theory and are applied to several reactions of current interest. Replacement of the usual harmonic bending potential by a sinusoidal one has the following effects: (i) the concept of reaction path degeneracy is replaced by nondegenerate states, (ii) the zero point energy of the complex is decreased, (iii) at low temperatures, Arrhenius plot curvature is greater, (iv) at high temperatures, the expression for the rate constant has the same form as that from simple collision theory.

FIRST QUANTUM CORRECTIONS TO SECOND VIRIAL COEFFICIENTS FOR ANISOTROPIC INTERACTIONS. SIMPLE, CORRECTED FORMULA.[a)]

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ABSTRACT

A simple formula for the first quantum correction to the second virial coefficient, valid for the interaction of any like or unlike combination of atoms, diatomics, spherical top, or symmetric top molecules is given. It is found that the commonly used formulas of Wang Chang contain an error that omits an anisotropic contribution. The sizes of the different contributions to the quantum correction are discussed. As examples, calculations for He-SF_6 and He-CO_2 are reported.

[a)]Work performed under the auspices of the US Department of Energy.

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Toward Accurate Characterization of Potential Energy Surfaces Analytical Gradient for a Selected Reference MCSCF/CI Wave Function

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The Configuration Interaction Technique, coupled with a smoothly varying, qualitatively correct multiconfigurational reference function promises to provide a tractable, accurate means of investigating potential energy surfaces. A great deal of this promise comes from recent developments in analytical potential energy gradient techniques for CI wavefunctions using as references all of the configurations in an MCSCF.

The gradient formalism is extended here to include CI wavefunctions which consist of excitations from only selected MCSCF configurations. The difficulty is that, contrary to the MCSCF energy, both the CI energy and its derivative may not be invariant to some of the rotations among the partially occupied (active) orbitals of the MCSCF. This ambiguity in the CI energy is commonly removed by requiring that the active orbitals be natural orbitals, as well as satisfy the MCSCF stationary conditions. We similarly remove this ambiguity in the gradient by requiring that the following two conditions be satisfied to first order upon a perturbation of the molecular geometry: 1. The MCSCF variational conditions and 2. The Natural Orbital condition on the active orbitals. The first requirement leads to the so called coupled perturbed MCSCF equations and the second requirement leads to new equations which serve to define the direction of mixing of the active orbitals with nuclear perturbation.

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Abstract

Aspects of Density Functional Theory

Robert G. Parr

Recent developments in the density functional theory of few-electron systems will be reviewed, including the formal theory for fractional particle number,[1] the consequences of the fact that real systems always have integral particle number,[1,2] the question of how to determine the chemical potential from an electron density,[2] a discovery concerning the covalent radius of an atom,[3] and the definition of the hardness of a chemical species.[4]

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Remarks on "Quantum Chaos"

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Ancient,[1] medieval,[2] and modern[3] calculations in quantum ergodic theory will be briefly reviewed. Then the controversial question, By what sign shall we recognize "quantum chaos"? will be addressed. Some think that "quantum chaos" reveals itself in the spatial pattern of eigenfunctions; others, in the spectral pattern of eigenvalues. All are right. In the semiclassical limit $h \to 0$ the spatial pattern of eigenfunctions determines the spectral pattern of eigenvalues, by the "statistical mechanics" of the "equations of motion" that govern the eigenvalues as h varies.[4] The distribution of energy eigenvalues to be expected in a chaotic system will be derived and discussed.

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The Complete Basis Set Correlation Energy of H_2O

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The major source of error in most molecular ab-initio calculations is the effect of truncation of the one-electron basis set on the correlation energy. The use of atomic pair natural orbitals to construct a DZ+P basis set reduces this error for H_2O by 0.030 hartree (E_{corr} = -0.2687) relative to conventional DZ+P basis sets of contracted Gaussian functions. Extrapolation of the correlation energy to a complete basis set using the asymptotic convergence of pair natural orbital expansions reduces this error by an additional 0.092 hartree (calculated: -0.3611, experimental: -0.370±.003 hartree). Without extrapolation the DZ+P basis sets give 0.0063 hartree extra correlation energy in H_2O relative to Neon, the united atom limit. However, the asymptotic extrapolation reverses the sign of this difference and favors correlation in Neon by 0.0158 hartree in agreement with experiment (0.019±.003), suggesting that complete basis set extrapolations will be useful for calculating changes in the correlation energy.

QUANTUM CHEMISTRY WITHOUT BASIS SETS:
HARTREE-FOCK-SLATER AND HARTREE-FOCK CALCULATIONS ON DIATOMIC MOLECULES

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Fully numerical, two-dimensional (2D) approaches to quantum chemical calculations on linear molecules are developed. The angular variable, ϕ, is treated analytically and the other two numerically. Relaxation methods with 7-point finite-difference approximations are used to solve the Schrödinger equation, the Poisson equation for V_c and a Poisson-like equation

$$\nabla^2 V_x^{ab} = 4\pi\psi_a\psi_b \qquad (1)$$

for the exact exchange potential V_x. Results are presented for the one-electron molecules H_2^+ and HeH^{++} [1], the two-electron molecules H_2 and HeH^+ [2], the HF limits of LiH and BH[3] or the HFS limits of 2nd-row diatomic molecules, up to F_2. A HFS bond-length for Cr_2 is also reported.
Our numerical accuracy is believed to exceed that of McCullough's seminumerical or Becke's analogous 2D-HFS results by about two orders of magnitude.

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RELATIVISTIC QUANTUM CHEMISTRY: SOME RECENT RESULTS

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Work by others includes 1) Improved high-precision studies of few-electron atoms, notably by Hata and Grant, 2) Inclusion of core-valence correlation by polarisation potentials, by explicit CI in pseudopotential molecular calculations, or by a local-density correlation method.

Work in the author's group includes a) An interpretation of the photoelectron spectra of bismuth trihalides, with evidence for a novel, relativistic hybridization, dominated by the spin-orbit splitting of Bi[1], b) A cluster-model study of nuclear spin-spin coupling and densities of states in solid CdTe, HgTe and PbTe[2], c) A suggestion that Pitzer's relativistic hybridization rules would already influence the ionic dissociation potentials of the halogen molecules[3], d) Explicit tables of relativistic representation and rotation matrices for 38 point groups[4] and e) A discussion on the relativistic theory of NMR chemical shifts[5].

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Reliable Gaussian Basis Sets for Calculations of Interaction Energies in Systems of Closed-Shell Atoms

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Energy-optimization method of constructing Gaussian atomic basis sets which allows for reliable description of electron distribution in valence atomic region has been developed and applied to prepare medium-size minimal basis sets for inert-gas atoms from neon to xenon. Molecular minimal and split-valence calculations for homo- and hetero-nuclear pairs of inert-gas atoms have been performed.

The present values for interaction energies compare well with those obtained using more extended basis sets, particularly for systems consisting of heavier atoms.

The present results indicate that medium-size Gaussian basis sets prepared according to the proposed method can be useful for calculations on weakly bonded systems of closed-shell atoms, particularly those composed of heavier elements, where at fairly low cost reasonable values of interaction energies can be obtained.

Deviations from the Linear Mixture Rule in Nonequilibrium Chemical Kinetics, J. E. Dove and J. S. Halperin, University of Toronto; S. Raynor, Rutgers University.

In experimental studies of vibrational relaxation, dissociation, or isomerization of molecular gases, it is common to use mixtures of the reacting gas with inert diluents. Rate constants for the reaction in pure reactant gas or pure diluent gas are then evaluated by extrapolation using the linear mixture rule (LMR):

$$k_{LMR} = \sum_i x_i \, k_i \, ,$$

where x_i is the mole fraction of gas i and k_i is the rate constant for the reaction in pure component i. However, this rule is only obeyed rigorously for first order or pseudo-first order processes having a single rate-determining step or which proceed at thermal equilibrium. We will demonstrate theoretically that deviations from the linear mixture rule are always positive or zero ($k_{true} \geq k_{LMR}$) and will show with model calculations that these deviations may lead to large overestimates of the true pure component rate constants when the linear mixture rule is used.

Abstract of invited talk to be presented at the 8th Canadian Symposium on Theoretical Chemistry, Dalhousie University, Halifax, Nova Scotia, August 7-12, 1983.

Theoretical Concepts in the Physics of Conducting Polymers. M.J. Rice, Xerox Webster Research Center, Webster, N.Y. 14580, USA

Over the course of the past few years the soliton model[1,2] of lightly doped polyacetylene has rekindled theoretical interest in the physics and, in particular, the elementary excitations of linearly conjugated polymers.[3] Here, the central concepts and achievements of this research activity will be reviewed. A short description of the origin of the soliton model will introduce the talk. This will be followed by pictorial accounts of the pivitol concepts of the half-filled Peierls insulator, the soliton, the polaron and their connection with model relativistic field theories.[4-7] The intriguing phenomenon[8] of fractional charge will be focused upon and illustrated particularly for the case of the diatomic conjugated polymer[9] $+A = B+_x$. The fascinating connection with relativistic field theory will be illustrated for the linear carbon polymer polyyne, $+C \equiv C+_x$, which will be suggested[10] to be a potential experimental realization of a four flavored fermion field coupled to a spontaneously symmetry-broken Bose field.

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Structure and Properties of the Liquid-Vapor Interface of a Metal

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ABSTRACT

Recent theoretical studies of the structure and properties of the liquid-vapor interface of a metal will be described. It is found that the change in electron density in the transition zone between liquid and vapor induces a change in the ion-ion interaction which in turn leads to density oscillations, with a spacing of about an atomic diameter, for several layers into the bulk liquid. This layering induces anisotropy in the electrical conductivity at the surface, and also influences the dynamics of collective surface excitations. Experimental tests of the theoretical predictions will be discussed.

LARGE AMPLITUDE VIBRATIONS: COUPLING BETWEEN A STRETCH AND A BEND.

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The energy levels and spectroscopic intensities for two coupled vibrations is determined where one of the vibrations is a strongly anharmonic stretch which is undergoing large amplitude motion while the other is a bend. In particular a comparison will be made between spectra predicted with a model in which G-matrix elements are taken as constants and a model in which the actual dependence of G-matrix elements is considered. These results will be applied to gas phase spectra of methanol in the region of high overtones of the O-H stretch.[1,2]

Calculations will be made using an anharmonic oscillator basis where the potential is assumed to include one Gaussian factor times a constant plus an inverse square term. Like the Morse potential, this model has three parameters, the force constant at equilibrium, the equilibrium bond length, and the dissociation energy. It has the advantage of a vanishing wavefunction for zero bond length. This basis set yields finite matrix elements for the kinetic energy which has inverse first and second power dependence on bond length.[3]

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[3] M. L. Sage, to be published.

Unimolecular Reactions of Methylene Amidogen (CH_2N)

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Methylene amidogen has been observed or invoked as a decomposition product of nitramines such as RDX and HMX and as an intermediate in flames using NO_2 as the oxidizer. However, under experimental conditions, it has a rather short lifetime. We have undertaken an ab initio study of several of the unimolecular reactions of methylene amidogen in part to understand the short lifetime, but also to provide data for modeling the decompostion of the nitramines. The reactions studied include the hydrogen migration to form HCNH; elimination of a hydrogen atom from both CH_2N and HCNH; the cis-trans isomerization of HCNH; and, less thoroughly, the elimination of H_2. Structures of the various stationary points were found at both CASSCF and single reference CISD levels of theory using a basis of at least double-zeta plus polarization quality. Further calculations with larger basis sets and multi-reference CISD have been performed, especially for the elimination of H from CH_2N. The barrier for this last reaction is substantially lower than that in all of the other reactions with the exception of the cis-trans isomerization.

* NRC-BRL Postdoctoral Fellow.

Ab initio molecular orbital studies on Carbene and Silylene Insertions into Single Bonds

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The reactivity toward insertion into single bonds has been examined for a series of substituted carbenes (CH_2, CHF and CF_2) and silylenes (SiH_2, SiHF and SiF_2). For insertion into H_2, dramatic increases in the barrier height have been found in both the carbon and the silicon series as the number of fluorines is increased. Insertions into CH_4, SiH_4, CH_3F and SiH_3F show similar trends. Full geometry optimization of the reactants, transition structures and products was carried out at HF/3-21G and HF/6-31G*. Vibrational frequencies and zero point energies were computed at the HF/3-21G level. Heats of reaction and barrier heights were calculated with fourth order Møller-Plesset perturbation theory (MP4SDQ) at the Hartree-Fock geometries.

Nonlinear Schrödinger-Type Field Equation for the Description of Frictionally Damped Free Motion and Free Fall

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With the aid of a recently developed new theory for the description of dissipative systems (see e.g. J. Math. Phys., April 1983) frictionally damped free motion and free fall can be described by nonlinear Schrödinger-type field equations with logarithmic nonlinearity. A wavepacketlike solution as well as time-dependent wave solutions are derived and discussed. In the limit of disappearing friction ($\gamma \to 0$) the solutions turn into the well-known solutions of the respective linear Schrödinger field equation. The same also applies to the mean values of position, momentum and energy, as well as to the uncertainty product of position and momentum. For $\gamma \neq 0$, however, interesting new effects appear. So, e.g. for time $t \to \infty$ in contrast to the linear theory the uncertainty product does not diverge any more, but asymptotically approaches a definite constant value which depends on characteristic parameters of the system like its mass, initial width and friction constant γ.

Multiconfiguration SCF and Multireference CI Calculations of Bond Breaking in Molecules

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The calculation of potential energy surfaces which provide a balanced treatment of different regions of the surface, including asymptotes and spin-recoupling regions, is best carried out in a multireference context, with orbitals specifically optimized for this type of treatment. A comparison will be presented of multireference and single-reference based treatments of the symmetric stretching mode and bond breaking in the water molecule in a DZ basis, for which full CI results are now available for reference. Also described will be a series of attempts to calculate an accurate potential energy curve for the oxygen molecule in the ground state, extending to the dissociation limit, by MCSCF and multireference CI methods. The requirements for a satisfactory description of this potential curve appear to be rather extensive, both in terms of the basis set and the reference space. Selection techniques designed to make such treatments feasible will also be discussed.

This work has been carried out in collaboration with Drs. Franklin B. Brown of Ohio State University and Ron Shepard of Argonne National Laboratory, and with the support of the National Science Foundation.

A Classical Model of Absorption and Emission of Radiation in an Intense IR Laser Field

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Classical and Quantum results are compared for absorption, stimulated emission, and spontaneous emission of a diatomic molecule in an IR laser field. One, two and three dimensional models of the molecule are used. The model is that of Miller[1] in which the laser is taken to be an extra vibrational degree of freedom of the system. The relevance of chaotic classical trajectories is discussed. It is found that phenomena (such as spontaneous emission) considered by some to be quantum mechanical effects can be accurately modelled by the classical mechanics.

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Abstract of Invited Paper:

Eighth Canadian Symposium on Theoretical Chemistry - Halifax, August 1983:

ELECTRON THERMALIZATION IN INERT GASES:

The thermalization of electrons in inert gases (He, Ar, Kr, and Xe) is examined with a discrete ordinate method of solution of the Boltzmann equation. The Boltzmann (integral) equation reduces to the Lorentz Fokker Planck (differential) equation for this system owing to the small electron-moderator mass ratio. In a recent paper, Shizgal [1] introduced a new efficient method of solution of the hard sphere Lorentz Fokker Planck equation for the study of electron thermalization in inert gases. The purpose of the present paper is to demonstrate that this method of solution is applicable to realistic electron-moderator cross sections.

The relaxation of electrons in inert gases has been considered previously by Mozumber [2,3]. In this work, the electron velocity distribution function (VDF) was assumed to be a local maxwellian characterized with the time dependent electron temperature and bulk velocity. The relaxation is then followed with a numerical integration of the moment equations for the temperature and bulk velocity.

Knierim et.al. [4] employed the expansion of the electron VDF in Burnett functions about a local maxwellian characterized by the time dependent temperature. The VDF is determined with a numerical integration of moment equations of the LFP equation.

The method employed by Shizgal [1] involves the expansion of the electron VDF in speed polynomials [5,6] about a maxwellian characterized by the (constant) temperature of the moderator. The LFP equation is then solved as a linear initial value problem with efficient matrix methods and the numerical integration of moment equations is not required. The time evolution of the VDF and the energy can be expressed as a sum of a small number of exponential terms, each characterized by an eigenvalue of the LFP operator. The relaxation times for the system are given by the reciprocal of the eigenvalues.

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"Xα-SW study of molecular chemisorption of oxygen on silver"

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Abstract

Oxygen chemisorbs molecularly on a few metal surfaces, notably Ag(110) and Pt(111). We are studying the structure and bonding of the O_2/Ag(110) system by means of Xα-SW calculations on model clusters with as many as 18 Ag atoms.

For the adsorption geometry suggested in the literature (long-bridge site, O_2 parellel to surface grooves), our results do not yield satisfactory agreement with photoelectron spectra. However, calculations for alternate geometries show that best agreement is obtained for a model with a 4-fold site and O_2 perpendicular to surface grooves.

* On sabbatical leave 1981-82 from Université de Moncton.

Deductions from the Master Equation for Chemical Activation

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The master equation for unimolecular decomposition and collisional deactivation of an energetic species A formed by chemical reaction was investigated. The object of this investigation was to test the much used approximation of neglecting upward transitions, i.e. collisional transitions in which energy is added to A. Calculations of κ_a, the collisional frequency ω times the ratio of the rate of decomposition of A to that of deactivation, were performed for the stepladder model for very large and very small ω and for the separable model for small ω. Neglect of upward transitions reduces κ_a. For the stepladder model the amount by which κ_a is reduced is larger for large ω than for small ω. It was also found that κ_a is more sensitive to changes in $\langle\Delta\varepsilon\rangle$, the average internal energy loss from A in deactivating collisions, when ω is small than it is when ω is large. Thus, when comparing computational results with experimental data, one calculates a $\langle\Delta\varepsilon\rangle$ which is too small if one neglects upward transitions, and the amount by which $\langle\Delta\varepsilon\rangle$ is too small is larger for large ω. This conclusion explains both qualitatively and semiquantitatively the discrepancies in $\langle\Delta\varepsilon\rangle$ derived from stepladder model calculations of low pressure and high pressure κ_a's for sec-butyl radicals in the presence of rare gas diluents[1].

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PROTEINS AND DIFFERENTIAL GEOMETRY

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Abstract

We reviewed our analysis of various facets of protein structure via the differential geometry of curves and surfaces. At the lowest level of approximation we represent a protein molecule by a regular space curve passing through its α-carbons. This space curve is naturally approximated in terms of a helical basis set. The helical approximation can then be used to construct an automatic algorithm[1] that identifies local regular features (α-helices, β-strands, turns) as well as the correct β-sheet topologies. The helical approximation also provides the means for the comparison of pairs of arbitrary 3-dimensional protein structures. The morphological metric (MM) algorithm we developed[2] for this purpose exploits the fact that the differential geometric representation of space curves in terms of their curvature $\kappa(s)$ and torsion $\tau(s)$ as functions of the arclength s is Euclidean invariant (i.e. $\kappa(s)$, $\tau(s)$ do not change if the curves are subjected to arbitrary translations and/or rotations in space). This endows our MM algorithm with distinct advantages over current chain fold comparison methods which require local rotations and translations of segments before alignment. The MM algorithm is more global in character, accounts naturally for insertions/deletions and its extremely fast. In fact, we compared over 200 diverse protein pairs. In particular, it enabled us to verify that there is indeed strong correlation between primary sequence similarities and morphological (spatial) ones.

We also considered protein representations at a higher hierarchical level, i.e. as curves lying on surfaces embedded in 3-dimensional space. In fact, the regular secondary features in proteins can be well represented as geodesics on minimal surfaces[3]. In particular, there is a geometrical transformation that carries α-helices (lying on helicoids) into β-barrels (catenoidal surfaces).

Our differential geometric studies were confined to local aspects. Possible generalizations to more global considerations as well as extensions to include additional structural features (e.g. C_β carbons, side chains etc.) are outlined. Implications for protein dynamics/folding are sketched in conclusion.

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QUANTUM CHAOS AND A QUANTUM MEASURE SPACE

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A quantum ergodic theory for finite systems (such as isolated molecules) is developed by introducing the concept of a quantum measure algebra with statistical fluctuations. The basic concept in classical ergodic theory is that of a measure space. A measure space is a set M, together with a specified sigma-algebra of subsets in M and a measure defined on that algebra. A sigma-algebra is closed under the formation of complements and countable unions. A measure is a non-negative and countably additive set function. For this to be further classified as a dynamical system, a measurable transformation is introduced. A measure transformation is a mapping from a measure space into a measure space, such that the inverse image of every measurable set is measurable. In conservative dynamical systems, a measurable transformation is measure preserving, which is to say that the inverse image of every measurable set has the same measure as the original set. Once the measure space and the measurable transformation are defined, ergodic theory can be investigated on three levels, describable as analytic, geometric and algebraic. The analytic level studies linear operators induced by a transformation. The geometric level is concerned directly with transformations on a measure space and the algebraic treatment substitutes a measure algebra for the measure space and basically equates sets that differ only by sets of measure zero. It is this latter approach that is most directly paralleled here. A measure algebra for a quantum dynamical system is defined. This concept then provides a measure of the "size" of the space "covered" in the dynamical evolution of a quantum state. This, together with a á priori estimate of the size of the "available" space determines whether a specified quantum state evolves ergodically. Some further interesting features arise when statistical fluctuations are introduced into the determination of the "available" space.

Local Finite Order Perturbation Theory Approach to Bond Length Alternation in Cyclic Polyenes.

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The finite order many body perturbations, Møller-Plesset and Epstein-Nesbet type partitionings, using the localized Wannier orbitals are applied to the problem of bond length alternation of cyclic polyenes C_NH_N, $N=4\nu+2$, described by the PPP-type Hamiltonian. The localized orbital basis affords an efficient truncation of diagram summations and an elimination of unimportant diagrams. The obtained values of bond length distortions (~0.05Å) and stabilization energies per site (~0.04eV) are similar to those obtained with the RHF, one-parameter AMO and delocalized orbital perturbation theories.

Abstract Submmited for The 8th
Canadian Symposium on Theoretical Chemistry

Non-empirical Approximate SCF Calculation of Butadiene

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π-electron energy levels of the planar butadiene at trans, cis and conformations in which one carbon atom is located in their intermediate and in their outside region, are calculated by the approximate SCF method. We adopted not the Hartree-Fock approximation but the Hartree approximation. No extra-gometrical empirical data are used except the energy of 2pπ electron in a carbon in its valence state. The calculation results give that electronic energies of all the conformations in the internal and outside regions of trans and cis-state, are more higher than the ones of trans and cis-butadiene. The calculated values of electronic energies of trans and cis-butadiene are

-91.49 eV (-94.05 eV) for trans,

and -92.41 eV (-94.90 eV) for cis .

In the brackets the values by the more accurate method are given.

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High energy electron scattering from molecules

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Abstract

An efficient method for the simultaneous calculation of the first Born approximation intensities for elastic and inelastic scattering of fast electrons from molecules has been developed. Illustrative applications to water and diborane will be presented.

Discrete and Continuum States for the Quantum Mechanical Forced Oscillator.

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Abstract: The Lie algebra of space-time symmetries of the Schrödinger equation

$$\{f(t)\partial_{xx} + 2i\partial_t - 2g_2(t)x^2 - 2g_1(t)x - 2g_0(t)\}\Psi(x,t) = 0$$

is the Schrödinger algebra, $s\ell(2,\mathbb{R})\square w_1$. The generators of space-time symmetries, realized as first order differential operators in the coordinates, can be classified into orbits. From each orbit, a representative operator is chosen and diagonalized. This process is equivalent to separating variables and yields a second order, ordinary differential equation similar to a one-dimensional time-independent Schrödinger equation for the harmonic or repulsive oscillators, linear potential or free particle. Depending on the orbit, an operator may have a discrete or continious spectrum and the wave functions are the harmonic oscillator wave functions, parabolic cyclinder functions, Airy functions or plane waves. The results of this analysis could have wide application to problems in scattering theory, or in perturbation theory.

PHOTODISSOCIATION ANGULAR DISTRIBUTIONS OF

DIATOMICS IN INTENSE FIELDS.

by

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A theoretical study of the angular distribution of fragments in the photodissociation of diatomics is presented for low and strong fields. It will be shown that the lifetime of the initial state determines the angular distributions. Coupled equation calculations using the dressed molecule approach and scattering theory will be presented. The results indicate that various degrees of anisotropy are to be expected depending on the saturation of the Stark split individual M_J sublevels of the rotating molecule.

Angular Aspects of the Fermi Hole in Atoms

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Electron correlation in an atom or a molecule is of two different kinds, due to Coulomb and exchange interactions, which are respectively the source of the Coulomb and Fermi holes. A definition of the former was given by Coulson and Neilson (1961), and later extended by Boyd and Coulson (1973) and Boyd and Yee (1982). By use of pair distribution functions it is possible to obtain a very simple and illustrative physical picture of the Coulomb hole. The Fermi hole has been discussed in a similar way by Boyd and Coulson (1974). In the present work angular features of the Fermi hole are analyzed.

The distribution function of the interelectronic distance of any two electrons of like spin (say α), for fixed values of the position of r_1 of a chosen electron, and the angle α between the nucleus, electron 1 and electron 2 is evaluated from both a simple Hartree product type wavefunction and a Hartree-Fock wavefunction. This particular choice of coordinates is most appropriate for the study of the angular aspects of Fermi correlation effects, since explicit mention of the position of the reference electron is made; and the distribution function yields the probability of finding another electron of the same spin around the reference electron, rather than around the nucleus.

Graphs of the Fermi hole for α spin, $\Delta^{\alpha}(r_{12};r_1,\alpha) = f_{HF}^{\alpha\alpha}(r_{12};r_1,\alpha) - f_{H}^{\alpha\alpha}(r_{12};r_1,\alpha)$ versus the interelectronic distance r_{12}, are presented for both the first excited state of helium (2^3S) and the ground state of beryllium. The graphs show some very interesting aspects of the polarization of the Fermi hole.

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Potential energy surfaces for the photochemical reactions of organometallics.

C. Daniel, A. Dedieu, I. Hyla-Kryspin and A. Veillard
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Information about the mechanism of photochemical reactions in organometallic chemistry may be gained

i) either from state correlation diagrams based on the symmetry and spin properties (assuming that some symmetry element is retained during the course of the reaction).

ii) or from potential energy curves calculated at the CI level.

Both approaches will be illustrated. For the following reactions

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO$$

$$HCo(CO)_4 \xrightarrow{h\nu} Co(CO)_4 + H$$

potential energy curves for the ground and excited states have been calculated at the CI level and allow to identify the photoactive excited state.

Qualitative state correlation diagrams based on extended Hückel Calculations are used for the reactions of metal-metal bond cleavage such as

$$M_2(CO)_{2n} \xrightarrow{h\nu} 2M(CO)_n$$

and for the reactions of declusterification such as

$$Ru_3(CO)_{12} + 3CO \xrightarrow{h\nu} 3Ru(CO)_5$$

These diagrams show that the photoactive excited state of the reactant is connected by a single potential energy surface to the ground state of the primary product.

CORRELATION IN EXOTIC MOLECULES

USING SECOND-ORDER MANY-BODY PERTURBATION THEORY FOR ASSESSMENT

by

James T. Waber
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The attachment of fermions which are distinguishable from the electrons to form exotic molecules has permitted us to eliminate the exchange potential and to concentrate on the correlation energy as a source of binding where there would be little if any tendency for electrostatic potential such as for a neutral atom to attract a particle. In contrast, a particles such as a positron or a muon would be strongly bound to an isoelectronic negative ion.

The results obtained with positrons and muons, which differ essentially by their mass, permits us to look how this particle's wave function overlaps with those of the electrons and how it is affected by the particle mass.

MODE-SPECIFICITY IN HNC → HCN UNIMOLECULAR ISOMERIZATION: A CLASSICAL + TUNNELING MODEL

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Microscopic unimolecular isomerization rate constants are calculated for bond-specific preparation of the HNC → HCN system. The dynamical model is that of Waite and Miller [JCP, 73, 3713 (1980)], which incorporates exactly computed classical trajectories coupled with vibrationally adiabatic WKB tunneling probabilities calculated at classical turning points in the reaction barrier region. Rate constants are obtained via a probability branching analysis, utilizing Monte Carlo sampling of initial conditions. Results indicate that at lower energies, mode-specificity is significant, especially for excitation in the weakly coupled CN stretching mode. Mode-specificity is reflected by a somewhat restricted distribution of turning point locations at the reaction barrier. At higher energies, the exact dynamical results correspond more closely with the statistical RRKM model, there being a more random sampling of turning point locations at the reaction barrier. By projecting the classical trajectories (which reveal the effects of intramolecular mode-mode coupling) onto the reaction barrier region and allowing semi-classical tunneling to occur (which includes the reactive aspect of the overall unimolecular process), one can infer the relative importance of the two effects as well as obtain (at least semi-quantitatively) vibrational relaxation rates as a function of energy and mode.

Large amplitude vibration in polyatomic molecules. A polar representation of orthogonal relative coordinates

R. Wallace, Dept. of Chemistry, University of Manitoba.

A general expression for the rovib kinetic energy operator in a system of orthogonal internal coordinates is presented for arbitrary amplitudes of motion. Methods of determining the degree of separability of the potential in such coordinates are illustrated. Solution of the vibrational Schrodinger in the optimal system determines vibrational eigenvalues and eigenfunctions.

VIBRATIONAL SPECTRA FROM SEMI-CLASSICAL MECHANICS

D. M. WARDLAW, D. W. NOID, AND R. A. MARCUS

A spectral analysis method for classical trajectories, presented in Ref. 1, has been used fairly extensively to examine the dynamical properties of molecular and model systems. Results with this technique were shown to be in excellent agreement with quantum mechanical results for the vibrational transition frequencies and dipole matrix elements of a Morse oscillator.[2] In the present lecture, transition intensities for non-resonant and resonant Hamiltonian systems are discussed. Current work is aimed at applying the technique to the vibrational degrees of freedom of triatomic molecules. Advantages and limitations of this spectral analysis are considered.

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[2]M. L. Koszykowski, D. W. Noid and R. A. Marcus, J. Chem. Phys. 86, 2113 (1982).

Address of Wardlaw and Marcus: Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California, 91125.
Address of Noid: Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830.

Electronegativity

S. Manoli and M.A. Whitehead*

As suggested by Bartolotti, Gadre and Parr[1], the electronegativities of the atoms are derived using the spin-polarized $\chi\alpha$ theory. Similar calculations are done using the self-interaction corrected Ξa theory. The relationship between Mullikens electronegativity equation and the eigenvalues in the $\chi\alpha$ and Ξa theories are examined.

[1]L.J. Bartolotti, S.R. Gadre and R.G. Parr, JACS, 102, 2945 (1980).
*Department of Chemistry, McGill University, Montreal, Quebec.

MRD-CI CALCULATIONS OF POTENTIAL SURFACES USING BOND FUNCTIONS

James S. Wright and Richard J. Williams, Dept. of Chemistry, Carleton University, Ottawa, Canada K1S 5B6

Potential curves for diatomic hydrides (H_2, BH, CH, NH, OH, FH) have been calculated with good accuracy using multi-reference CI calculations and a double-zeta polarization basis set which includes bond functions. The curves are fitted over the whole range by generalized Morse functions. Binding energies for these hydrides are accurate to 0.1 eV and vibrational levels are well reproduced. Two triatomic surfaces have been generated by these methods including F + H_2 and O + H_2. Cuts through these surfaces are fitted and connected, up to dissociation, by a generalized Morse function-cubic spline approach. The bond functions play an important role in providing balanced basis sets which describe atomic and molecular regions with the same accuracy. Other extensions will be given.

Multiconfigurational Electron Propagator (MCEP) Ionization Potentials for General Open Shell Systems

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Abstract

We have theoretically developed a multiconfigurational electron propagator (MCEP) technique for the determination of ionization potentials for general open shell atomic and molecular systems. In order to do this, we have used and extended the generalized spin-symmetry adapted operators of Pickup and Mukhopadhyay. To properly account for correlation effects we have additionally included ionization and electron affinity operators analogous to the $|\Gamma><0|$ state transfer operators necessary in multiconfigurational linear response.

MCEP ionization potentials have been evaluated for both O_2 and N_2 and used to carry out detailed examination and interpretation of their respective PES and ESCA spectra. The MCEP results are extremely encouraging for both principal and shake-up IP's. For example, if only single electron removal operators are included in a calculation where the reference state is a multiconfiguration reference state (i.e., an open shell generalization of Koopman's theorem) the lowest verticle $^2\Pi_u$ ionization potential in O_2 is calculated to be 24.63 eV. Our final multiconfigurational one-electron propagator result is 17.77 eV. Experiment is 17.7 eV. The substantial drop in energy from 24.63 eV to 17.77 eV stresses the multiconfigurational nature of the $A^2\Pi_u$ ion state of O_2^+ and originates from the near-degeneracy of the three $^2\Pi_u$ states of the single valence electronic configuration $\pi_u^3\pi_g^2$ of O_2^+. This 7 eV drop occurs only with the inclusion of the transfer type IP and EA operators.

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The Complete Basis Set Correlation Energy of Neon

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The spherical symmetry of atoms permits the use of very large basis sets, providing definitive values of the components of the correlation energy. These definitive values then allow a detailed error analysis of simple approximations suitable for molecules. In the case of Neon, a relatively small DZ+P set of atomic pair natural orbitals gives a total third-order correlation energy of -0.2624 hartree with an RMS error of 0.0039 hartree in the individual pair correlation energies. Extrapolation to a complete basis set using the asymptotic convergence of pair natural orbital expansions gives a total correlation energy of -0.3769 hartree (experimental: -0.389±.001) and reduces the RMS error in the individual pair energies to 0.0005 hartree.

LIGAND FIELD MODEL OF THE OPTICAL SPECTRUM OF ANHYDROUS CO(II)-EXCHANGED ZEOLITE A.

D.Zeroka, P.J.Hutta, and K.Klier, Department of Chemistry, Lehigh University, Bethlehem, PA 18015

The objective of this study is to reinvestigate the interpretation of the electronic spectrum of anhydrous Co(II)-exchanged zeolite A in light of some recent observations(1) of extra-framework AlO_4 defects located in the sodalite units of divalent ion exchanged zeolite A. Hutta(2) in earlier work found that the calculated ligand field term diagrams of the electronic spectrum could be brought into agreement with the observed optical transitions only if ligands extraneous to the zeolite framework were postulated. The present study addresses the question of whether the AlO_4 species act as these ligands. Up to 21 oxygen atoms which form 3 rings or 6 rings about the cubic 111-axis which passes through the Co(II) ion are taken into account in a ligand field model in a stepwise manner, wherein the nearest neighbors are considered first,the next nearest neighbors second,etc. It has been determined that the AlO_4 defect,if present, can influence the term splitting to only a small degree. An electric field of negative polarity between 30° and 70° with respect to the 111-axis fits the observed spectrum(3) better than the ligand field of the framework and AlO_4 oxygens. In addition, the possibility of the electronic spectrum arising as a superposition of spectra for the Co(II) ion in two different sites will be considered.

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(2) P.J.Hutta,PhD Thesis, Lehigh University,1974.
(3) R.Kellerman and K.Klier in "Surface and Defect Properties of Solids",volume 4, The Chemical Society, London, 1975, p25.

TEMPERATURE DEPENDENCE OF HYDROGEN TRANSFER RATE CONSTANTS

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The rate constants, k, of hydrogen (deuterium) exchange chemical reactions of the type R_1-X-H+Y-$R_2 \rightleftarrows R_1$-X+H-Y-R_2 show remarkable deviations from the standard Arrhenius equation. Experimentally it was found that lnk often yields a straight line if plotted against T rather than 1/T.

We have developed a model, similar to those used in the theory of radiationless processes, to describe proton (deuterium) transfer between molecules. It takes into account the X-H(Y-H) vibration of a bond that is broken (formed) in the chemical reaction and the X....Y vibration that changes the distance of proton donating and accepting atoms. The probability of proton transfer is then described by the Golden Rule

$$P^{Y\leftarrow X}_{wW,vV} = 2\pi \left| \langle W_Y(Q) w_Y(q) \left| J \right| v_X(q) V_X(Q) \rangle \right|^2 \delta(\varepsilon) \ .$$

where $|V\rangle$, $|W\rangle$ denote vibrational wavefuntions of the X....Y oscilaltor and $|v_X\rangle$, $|w_Y\rangle$ are the wavefunctions of the X-H, Y-H oscillators, respectively. J is the intermolecular coupling operator, the delta function represents energy conservation and q, Q are the corresponding oscilator coordinates.

This model leads to a quasilinear dependence of lnk on T in the temperature range $0.2\Omega \lesssim k_B T \lesssim \Omega$, where Ω is the frequency of the Y....X vibration. It gives temperature independent rate constant at very low temperature consistent with the notion of tunnelling through a barrier. Finally, it allows an easy assessment of the change of k(T) caused by the substitution of hydrogen by deuterium.

We will present a comparison of experimental data of different chemical reactions of hydrogen (deuterium) exchange with our model calculations. It will demonstrate that this model gives a very good description of lnk(T) curves for physically meaningful input parameters.

A Theoretical Study of the Triple Bond in Binuclear Compounds of Cr. Mo and W, by the Hartree-Fock-Slater Transition State Method.

Tom Ziegler, Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4

The fragment ML_3 was studied as an essential building block for the binuclear complex M_2L_6. The calculated equilibrium geometry of the d^3 fragments CrL_3, MoL_3 and WL_3 for various ligands (L: H, Cl, OH, NH_2 and CH_3) was in each case trigonal planar. The preferred calculated geometry of M_2L_6 was a staggered conformation. Both ML_3 and M_2L_6 are stabilized by strong electronegative ligands such as OH. The choice of metal atom (Cr, Mo, W) does not influence the stability of ML_3. The binuclear compounds M_2L_6 on the other hand have the strongest metal to metal bond in the case of W. It will be shown that the strength of the W≡W bond is due to relativistic effects also included in the study.

Addenda

8th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY
8e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE

ADDENDUM NUMBER 1

INVITED LECTURES

The invited lectures of J. P. Malrieu and G. Malli will not be given. At 9:45 AM on Thursday, Professor R. F. W. Bader, McMaster University, will present an invited lecture entitled, "Properties of the Charge Density in Relation to Chemical Concepts".

LATE REGISTRANTS

R. F. W. Bader	McMaster University, CANADA
G. Corey	University of Waterloo, CANADA
K. A. Cox	Philip Morris, U.S.A.
E. Ludena	Caracas, VENEZUELA
R. D. Olmsted	3M Company, U.S.A.
J. S. Perkyns	Dalhousie University, CANADA

CANCELLATIONS

P2-5 by P. F. Endres will not be presented but the author will be present.

H Chojnacki (P4-19 will not be presented)

G. Malli (invited lecture cancelled)

J. P. Malrieu (invited lecture replaced by R. F. W. Bader)

ABSTRACTS

Abstracts which did not arrive in time for inclusion in the program booklet are reproduced on the following pages.

STRUCTURE OF WATER AND COUNTERIONS IN DNA

Enrico Clementi

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Monte Carlo simulation have been performed to study the hydration of two DNA conformers: the right-handed B-DNA and the left-handed Z-DNA, both in the double helix conformation. The models used to represent the polyelectrolytes consist of three full pitches (60 and 72 nucleotides units for B- and Z-DNA, respectively).

The simulations have been carried out at a temperature of 300 K with 500 water molecules per pitch and as many counterions as necessary to neutralize DNA. In the present studies three different mono-charged counterions have been considered: Li^+, Na^+ and K^+. During the Monte Carlo process either the water molecules or the counterions are subject to displacements (1).

The Monte Carlo walks, for these six simulations, have been analyzed in such way to give, for the counterions, informations about their position (not yet determined by experiments), and the number of water molecules in their first hydration shell. Some of the counterions have, in the first hydration shell, the same number of water molecules as determined for the same ion in solution (2), but some other loose one or even two water molecules and complete their coordination by binding DNA atoms. There is a preference for the three kind of ions here analyzed, to bind either the PO^- groups or the N7 atoms in

quanine and adenine (3).

The water structure in the first hydration shell of the DNA is analyzed for specific sites (for example for the nitrogen or the oxygen atoms at the bases) or for groups of sites (for example the bases or the PO^-). For both DNA conformers, the polyelectrolyte looses water from the first hydration shell if K^+ is replaced with Na^+ or Na^+ with Li^+.

As known in B-DNA, there are two grooves, the minor and major. The water was found to be highly structured in both grooves. In the minor groove there is either a long filament of water molecules running along the groove or small filaments connecting two phosphate groups belonging to the same strand. In the major groove the water molecules form filaments connecting phosphate groups belonging to two different strands (4). The first and the last type of filaments are stable for a sufficiently long time as to be detected, by X-ray diffractions, as shown recently (5).

These results have been obtained performing, for each of the six simulations, 10^6 displacements (after equilibration). As known, after each displacement, the interaction energy of the system namely, the interaction energy between water-DNA, water-ions, ion-ion, ion-DNA and water-water is computed. In the present study the interaction energies are calculated with potentials obtained by fitting thousands of ab initio computations (6); for the water-water the MCY potential (7), obtained from Configuration Interaction computations, has been used.

References

1) Clementi, E. and Coronqiu, G., Biomolecular Stereodynamics, Sarma, R., Ed., Adenine Press, New York (1981).
2) Clementi, E. and Barsotti, R., Chem. Phys. Letters, 59, 21 (1978).
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THE DISCRETE VARIABLE APPROACH TO BOUND MOLECULAR STATES

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The 'discrete variable method' has been investigated in the context of both bound state and scattering calculations of triatomic systems. The method gives a prescription for quadrature points and weights based on the representation which diagonalizes the position operator. The eigenvalues thus obtained define the quadrature points for the evaluation of the potential matrix element. The quadrature weights are given by the elements of the transformation from this new representation to the (usual) target state representation. Highly accurate bound state energies of methyl iodide (in the quasi-triatomic approximation) have been computed with this method.

Effective Fragment Potential for Large Molecules

K.Kitaura, K.Ohta*, and K.Morokuma*
Department of Chemistry, Osaka City Univ., Osaka 558, Japan
and *Institute for Molecular Science, Okazaki 444, Japan

A new apporoximate MO method, named the effective fragment potential method, is proposed for calculating electronic structures of large molecules such as solvation clusters, transition metal complexes and model systems of enzymes.

The method replaces the 'inactive' electrons, which do not actively participate the phenomena of interest, by an effective one-electron potential and only the 'active' electrons are explicitly taken into calculations. It can be regarded as an extension of the atomic effective core potential to molecules. If successful, the method has a potential of drastically reducing computer time for very large systems. We present the theoretical formalism, parametrization for NH_3 and test calculations for NH_3 complexes.

DISSOCIATION AND INTRAMOLECULAR DYNAMICS

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ABSTRACT

The manner by which various dissociation experiments can serve as effective probes of intramolecular dynamics of small polyatomic molecules is discussed. Fast and slow dissociation processes are shown to yield complementary information. Examples pertaining to specific molecules such as CH_3I, H_2O, the Ar-N_2, He-I_2 van der Waals complexes and dissociative photoionization of H_2 are given.

8th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY
e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE

ADDENDUM NUMBER 2

INVITED LECTURES

The abstract of Dr. Hirschfelder's lecture was inadvertently omitted from the program but is included in this addendum.

ADDITIONAL CORPORATE DONOR

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LATE REGISTRANTS

S. Fliszar	Universite de Montreal, CANADA
R. R. Gupta	Rajasthan University, INDIA
H. Kobeissi	Lebanese University, LEBANON
A. W. Salotto	Pace University, USA
W. L. Taylor	Monsanto Research Corp., USA

CANCELLATIONS

Ernest M. Loebl
Xiao-Yuan Fu (P3-6 will not be presented)
D. Dao-Dehareng (P1-3 will not be presented)

ADDITIONAL PAPERS

H. Kobeissi will present a paper entitled, "Integral Expressions of the Diatomic Rotational Harmonics" in Poster Session P4 in the vacancy created by the cancellation of H. Chojnacki.

R. N. Diffenderfer will present a paper entitled, "Theoretical description of a CS_2 dissociation surface", as contribution number 20 in Poster Session P1 on Monday.

R. R. Gupta will present a paper entitled, "Theoretical studies on diamagnetic susceptibility of amides and their N-substituted derivatives", in Poster Session P3 in the vacancy created by the cancellation of X.-Y. Fu.

E. Ludena will present a paper entitled, "An approximate universal functional for the energy in density functional theory", as contribution number 20 in Poster Session P5 on Thursday.

COMPARISON OF TWO STATE SYSTEMS IN CLASSICAL AND QUANTIZED ELECTROMAGNETIC FIELDS

by

P. K. ARAVIND AND J. O. HIRSCHFELDER

University of Wisconsin-Madison, Theoretical Chemistry Institute

and

University of California-Santa Barbara, Chemistry and Physics Departments

ABSTRACT

The dynamics of a two level system interacting with periodic (single-mode) classical and quantized fields are treated separately -- algebraic and numerical results are given.

CLASSICAL: The Floquet formalism for the time development operators of molecular systems in periodic fields is derived. Almost degenerate perturbation theory is used to determine single and multi-photon transition probabilities for a two state system with greater accuracy than the Rabi rotating wave approximation. The off-diagonal elements of the density matrix give the dynamical polarizability.

QUANTUM: The two level system in a quantized field is treated in the framework of the Jaynes-Cummings model but without making the rotating wave approximation. The effects of coherent, chaotic, and photon-number fields on the dynamics of the system are determined. Entropy production and irreversibility are discussed. The effect of the anti-rotating component of the field on the collapse and revival of atomic coherence is investigated.

To be presented at the 8th Canadian Symposium on Theoretical Chemistry, Halifax, Nova Scotia, August 7-12, 1983.