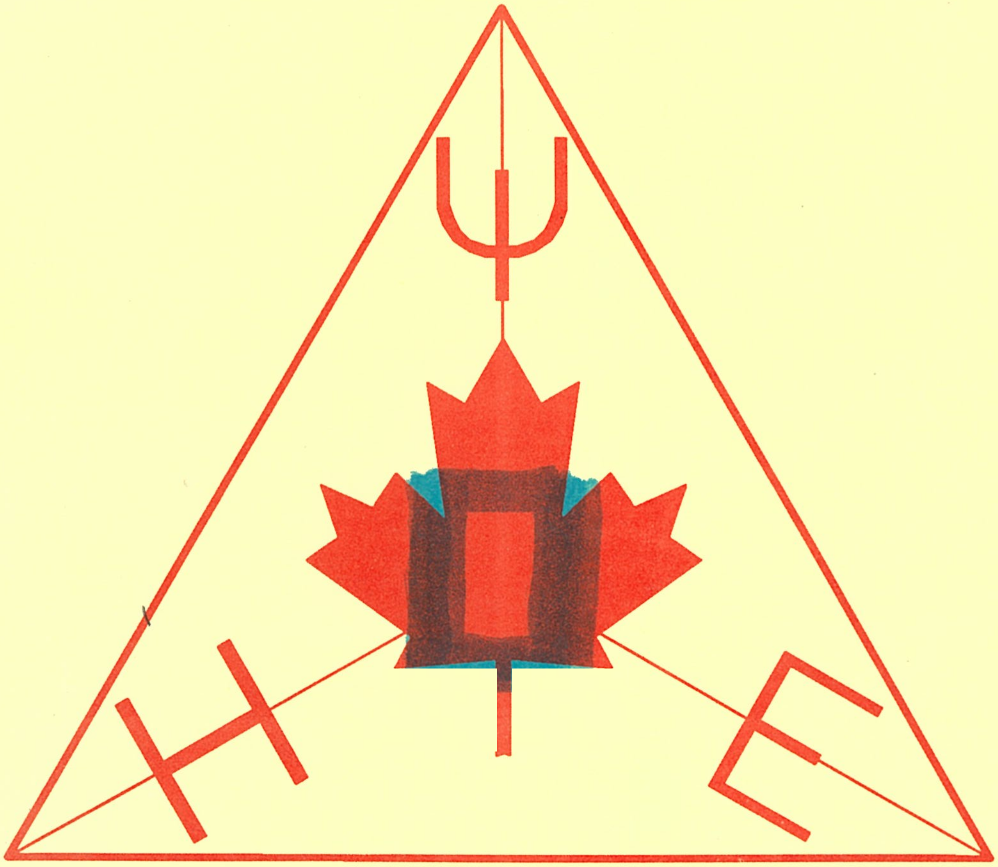
Program and Abstracts

Programme et Résumés



10th CANADIAN SYMPOSIUM ON THEORETICAL CHEMISTRY
10e SYMPOSIUM CANADIEN SUR LA CHIMIE THEORIQUE

AUGUST 24 – 30, 1989 *BANFF, ALBERTA*

10th Canadian Symposium on Theoretical Chemistry
PROGRAM*

DATE	MORNING	AFTERNOON	EVENING
Thursday, August 24		**2:00 p.m.–7:30 p.m.–Registration**	**7:30 p.m.–Plenary Lecture** **8:30 p.m.–Mixer**
Friday, August 25	8:30 a.m.–Electronic Structure Theory (F1) 8:00 a.m. – Registration (until 12:00 noon)	1:30 p.m.–Novel Approaches 1 (F2) *2:00 p.m. – Walking tour of historic Banff*	7:30 p.m.–Novel Approaches 2 (F3) 7:30 p.m.–Posters: Electronic Structure Theory (F4) 7:30 p.m.–Posters: Solid State Chemistry (F5) 7:30 p.m.–Reception (Multiflow Computer)
Saturday, August 26	8:30 a.m.–Theoretical Biology (S1) 9:30 a.m.–Algebraic Methods (S2) MB 251 *10:00 a.m. – visit to Cascade Gardens*	FREE *2:00 p.m. – walk to Cave and Basin*	6:45 p.m.–Theoretical Solid State Chemistry (S3) 7:30 p.m.–Posters: Theoretical Biology (S4) 7:30 p.m.–Posters: Algebraic Methods (S5) 7:30 p.m.–Posters: Novel Approaches (S6) 7:30 p.m.–Posters: Solitons, Evolution and Chaos (S7) 7:30 p.m.–Posters: Density Functional Theory (S8) 7:30 p.m.–Reception (Big Rock Brewery)
Sunday, August 27	FREE 9:00 a.m.–Mountain Lakes and Canyons Bus Tour	FREE *2:00 p.m. – walk to summit of Tunnel Mountain*	**6:00 p.m.–Barbecue**
Monday, August 28	8:30 a.m.–Chemisorption, Surface Phenomena (M1) *9:00 a.m. – Day trip to Sunshine Meadows*	1:30 p.m.–Solitons, Evolution and Chaos (M2)	7:00 p.m.–Electronic Structure Theory 2 (M3) 7:30 p.m.–Reception (Labatt's Alberta Brewery)
Tuesday, August 29	8:30 a.m.–Vibrational Optical Activity (T1) *10:00 a.m. – Bow Valley Trail to Hoodoos*	1:30 p.m.–Evolution of Structure in Fluids and Solids (T2) 5:00 p.m.–Business Meeting	6:45 p.m.–Density Functional Theory (T3) 7:30 p.m.–Posters: Evolution of Structure in Fluids and Solids (T4) 7:30 p.m.–Posters: Electronic Structure Theory (T5) 7:30 p.m.–Posters: Vibrational Optical Activity (T6) 7:30 p.m.–Reception (Nicolet Instruments and IBM)
Wednasday, August 30	8:30 a.m.–Quantum and Nonquantum Aspects of Reaction Dynamics (W1)	12:00 noon–Checkout	

*Accompanying Persons program events in *italics*; events free to all Registered Persons in **bold**.

10th Canadian Symposium on Theoretical Chemistry

INVITED SPEAKERS

M1.4	10:10 am – 10:55 am	**E. J. Baerends** : *Silver–catalyzed Ethylene Epoxidation: on the Role of Pauli Repulsion and the Fermi Level in Chemisorption and Catalysis*
M2.1	1:30 pm – 2:15 pm	**A. D. Bandrauk** : *The Maxwell–Schroedinger Equation and Pulse Propagation in Molecular Media*
T3.1	6:45 pm – 7:20 pm	**A. Becke** : *Basis Set Free Density Functional Quantum Chemistry*
T2.3	3:15 pm – 4:00 pm	**A. Bishop** : *Competing Interactions and Complexity in Condensed Matter*
T2.2	2:15 pm – 3:00 pm	**G. Bluman** : *Symmetry–Based Algorithms to Linearize Partial Differential Equations*
M3.2	7:40 pm – 8:20 pm	**T. D. Bouman** : *Linear Response Calculations of Molecular Properties*
S3.1	6:45 pm – 7:30 pm	**J. K. Burdett** : *Moments and the Energies of Solids*
T2.1	1:30 pm – 2:15 pm	**D. Chandler** : *Electrons on the Move in Liquids*
S1.1	8:30 am – 9:30 am	**E. Clementi** : *Productivity, Global Simulation, and Evolution in Supercomputing and Supercomputers*
F2.4	3:40 pm – 4:10 pm	**C. Fairbridge** : *Application of Fractal Concepts to Problems in Surface Chemistry*
S3.3	8:10 pm – 8:55 pm	**W. A. Goddard III** : *Simulation of Materials: The Theory of High Tc Superconductors*
M2.3	3:00 pm – 3:45 pm	**D. D. Holm** : *Bifurcations and Homoclinic Chaos in Classical Dynamics of Coupled Anharmonic Oscillators*
S2.1	9:30 am – 10:10 am	**F. Iachello** : *Algebraic Approach to Molecular Structure*
M2.5	4:30 pm – 5:15 pm	**R. Kapral** : *A Lattice–Gas Cellular Automaton for a Chemically Reacting System*
F3.1	7:30 pm – 8:00 pm	**D. J. Klein** : *Many–Body Valence–Bond Theory of Conjugated Systems*
S1.4	10:20 am – 11:00 am	**P. A. Kollman** : *The Use of Molecular Dynamics in the Simulation of Free Energies of Association of Molecules*
F2.1	1:30 pm – 2:10 pm	**R. Kopelman** : *Fractal Reaction Kinetics*
S2.2	10:10 am – 10:30 am	**V. A. Kostelecky** : *Atomic Supersymmetry*
M3.1	7:00 pm – 7:40 pm	**W. J. Meath** : *Single– and Multiphoton Absorption for Molecules undergoing Free and Hindered Rotations including Permanent Multipole Moment and Chiral Effects*
F3.4	9:20 pm – 9:50 pm	**P. G. Mezey** : *Shape Analysis of 3–D Molecular Bodies: Molecular Shape Codes from Quantum Chemistry and Topology*
W1.1	8:30 am – 9:15 am	**K. Morokuma** : *Potential Energy Surfaces and Classical Dynamics of Non–adiabatic Processes*
T1.1	8:35 am – 9:20 am	**L. A. Nafie** : *Theoretical Models and Approaches to VCD Calculations*
S2.3	10:50 am – 11:10 am	**J. Paldus** : *Recent Developments in the Unitary Group Approaches to the Many–Electron Correlation Problem*
F1.1	8:35 am – 9:20 am	**J. A. Pople** : *Recent Developments in Electron Correlation Theory*
F3.2	8:00 pm – 8:30 pm	**M. Randic** : *Design of Molecules with Prescribed Properties*
F2.2	2:10 pm – 2:50 pm	**D. H Rothman** : *Immiscible Lattice Gases*
T3.5	8:50 pm – 9:20 pm	**D. Salahub** : *Recent Progress with the LCGTO–MP–LSD Method*
PL	7:30 pm **Thursday**	**H. F. Schaefer III** : *Computers and Theoretical Chemistry: 1965 – 1989, A Personal Perspective*
F1.3	10:20 am – 11:00 am	**P. v. R. Schleyer:** *The Fruitful Interplay between Theoretical and Computional Chemistry: Carbocations*
M1.1	8:30 am – 9:15 am	**E. Shustorovich:** *Calculations of Energy Profiles for Metal Surface Reactions: a Bond–Order Conservation Approach*
F3.3	8:50 pm – 9:20 pm	**V. H. Smith, Jr.** : *Adventures Beyond the Born–Oppenheimer Approximation: Exotic Molecules*
T1.2	9:20 am – 10:05 am	**P. J. Stephens** : *Ab Initio Calculations of VCD Spectra*
M2.4	3:45 pm – 4:30 pm	**J. A. Tuszynski** : *Recent Symmetry Reduction Analyses for Multidimensional PDE's and Pattern Formation*
F2.3	3:10 pm – 3:40 pm	**S. G. Whittington** : *Lattice Animals and Self–avaoiding Surfaces*
F1.2	9:20 am – 10:00 am	**T. Yamabe** : *Electronic Motion Coupled by Molecular Vibrations*

10'th Canadian Symposium on Theoretical Chemistry

Scientific Program*

August 4, 1989

Thursday, August 24, 1989

7:30 pm – Max Bell Auditorium

PLa23 Plenary Lecture : H. F. Schaefer III (University of Georgia):
Computers and Theoretical Chemistry: 1965 – 1989, A Personal Perspective

8:30 pm – Max Bell Foyer
Mixer

Friday, August 25, 1989

8:30 am – Max Bell Auditorium

Electronic Structure Theory 1 (F1)

Organiser – A. Rauk
Chairperson: F. Grein (University of New Brunswick):

	8:30 am – 8:35 am –	Opening Remarks – F. Grein
F1.1	8:35 am – 9:20 am	**J. A. Pople** (Carnegie Mellon University): ***Recent Developments in Electron Correlation Theory***
F1.2	9:20 am – 10:00 am	**T. Yamabe** (Kyoto University): ***Electronic Motion Coupled by Molecular Vibrations***

10:00 am – 10:20 am – **Coffee Break**

Chairperson: J. D. Goddard (University of Guelph):

F1.3	10:20 am – 11:00 am	**P. v. R. Schleyer** (Friedrich–Alexander Universitat Erlangen–Nurnburg): ***The Fruitful Interplay between Theoretical and Computional Chemistry: Carbocations***
F1.5	11:00 am – 11:20 am	T. Noro and M. Yoshimine (IBM Almaden Research Center): ***MRCI Studies of Electron Affinities of Atoms and Molecules.***
F1.6	11:20 am – 11:40 am	R. G. Parr and Z. Zhou (University of North Carolina): ***Absolute Hardness and Relative Hardness – Measures of Aromaticity.***
F1.7	11:40 am – 12:00 am	L. C. Allen (Princeton University): ***A New Look at Electronegativity.***

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*Session codes: F = Friday, S = Saturday, M = Monday, T = Tuesday, W = Wednesday

Friday, August 25, 1989

1:30 pm– Max Bell Auditorium

Novel Approaches 1 (F2)

Organiser – W. G. Laidlaw
Chairperson: W. G. Laidlaw

F2.1	1:30 pm – 2:10 pm	**R. Kopelman** (University of Michigan): ***Fractal Reaction Kinetics***
F2.2	2:10 pm – 2:50 pm	**D. H Rothman** (MIT): ***Immiscible Lattice Gases***

2:50 pm – 3:10 pm – **Coffee Break**

Chairperson: S. M. Rothstein (Brock University)

F2.3	3:10 pm – 3:40 pm	**S. G. Whittington** (University of Toronto): ***Lattice Animals and Self–avaoiding Surfaces***
F2.4	3:40 pm – 4:10 pm	**C. Fairbridge** (Energy, Mines, and Resources, Canada): ***Application of Fractal Concepts to Problems in Surface Chemistry***
F2.5	4:10 pm – 4:40 pm	W. G. Wilson and W. G. Laidlaw (University of Calgary): ***Interacting Ants on Random Structures***

Friday, August 25, 1989

7:30 pm – Max Bell Auditorium

Novel Approaches 2 (F3)

Organiser – P. G. Mezey
Chairperson: D. M. Wardlaw (Queen's University)

F3.1	7:30 pm – 8:00 pm	**D. J. Klein** (Texas A&M University): ***Many–Body Valence–Bond Theory of Conjugated Systems***
F3.2	8:00 pm – 8:30 pm	**M. Randic** (Iowa State University): ***Design of Molecules with Prescribed Properties***

8:30 pm – 8:50 pm – **Coffee Break**

Chairperson: G. L. Malli (Simon Fraser University)

F3.3	8:50 pm – 9:20 pm	**V. H. Smith, Jr.** (Queen's University): ***Adventures Beyond the Born–Oppenheimer Approximation: Exotic Molecules***
F3.4	9:20 pm – 9:50 pm	**P. G. Mezey** (University of Saskatchewan): ***Shape Analysis of 3–D Molecular Bodies: Molecular Shape Codes from Quantum Chemistry and Topology***

Friday, August 25, 1989

7:30 pm – Max Bell 253

Posters – Electronic Structure Theory and Applications (F4)

Wine and Cheese Reception (courtesy of Multiflow Computer)

Methods (F4.1)

F4.1.1 *Coupled–Cluster Approach with Approximate Account of Triple Excitations and its Application to the Cyclic Polyene Model Systems.* P. Piecuch, S. Zarrabian, J. Paldus, and J. Cizek.

F4.1.2 *An Efficient Formulation of the Analytic Gradient of the Singles and Doubles Coupled Cluster Energy.* T. J. Lee and J. E. Rice.

F4.1.3 *A Full Variational Method Based on a Tensor Product Decomposition.* F. A. Senese, C. A. Beattie, J. C. Schug, J. W. Viers, and L. T. Watson.

F4.1.4 *Classical and Non–Classical Forms of the Vinyl Cation: a Coupled Cluster Study.* C. Liang, T. P. Hamilton, and H. F. Schaefer III.

F4.1.5 *Physical Interpretation and Assessment of the GW2 Approximation for Molecules.* M. E. Casida and D. P. Chong.

F4.1.6 *Electron Affinities Revisited.* R. A. Kendall, R. J. Harrison, and T. H. Dunning Jr.

F4.1.7 *A Complete Shape Characterization for Gaussian–type Molecular Charge Density Functions.* P. D. Walker, G. A. Arteca, and P. G. Mezey.

F4.1.8 *Comparison of Potential Energy Maps and Molecular Shape Invarience Maps.* G. A. Heal, G. A. Arteca, and P. G. Mezey.

F4.1.9 *GAMESS: a Portable ab initio Program.* S. T. Elbert and M. W. Schmidt.

F4.1.10 *Study of Orbital Transformation in Configuration Interaction Calculations of Hyperfine Coupling in Nitrogen and the CH Molecule.* B. Engels, S. D. Peyerimhoff, and F. Grein.

F4.1.11 *Core–Valence Correlation and the Binding Energy of Mg_2.* H. Partridge, C. W. Bauschlichter, Jr., L. G. M. Pettersen, A. D. McLean, B. Liu, and A. Komornicki.

F4.1.12 *Application of Multi–Reference Spin–Adapted Coupled–Cluster Formalism to the H_4 Model System.* J. Paldus, L. Pylypow, and B. Jeziorski.

Electronic Structures of Organic and Inorganic Systems (F4.2)

F4.2.1 *Ab Initio Structure Calculations of Hydrogen Ionic Clusters.* M. Farizon, B. Farizon–Mazuy, and H. Chermette.

F4.2.2 *What is the Most Stable Structure of NS_2 Molecules?* Y. Yamaguchi, Y. Xie, R. S. Grev and H. F. Schaefer III.

F4.2.3 *A Molecular Orbital Study of the Conformational and Electronic Properties of Sulfamide, $H_2NSO_2NH_2$* . O. Mo, J. L. G. De Paz, M. Yanez, I. Alkorta, J. Elguero, P. Goya, and I. Rozas.

F4.2.4 *Ab Initio Calculation of the Electronic Structure and Spectra of Cu^+ :NaF.* Victor Luana and R. M. Pitzer.

F4.2.5 *Theoretical d–d Spectrum of Cr^{3+}:MgO.* J. M. Recio, V. Luana, E. Francesco, and L. Pueyo.

F4.2.6 *Theoretical Calculation of the Electronic Structure ana d–d Spectrum of the MnF_6^{2-} Complex Ion.* M. Florez, V. Luana, and L. Pueyo.

F4.2.7 *Ab Initio Characterization of the Gaseous Oxides P_2O_x (x=1–5).* L. L. Lohr, Jr.

F4.2.8 *Ab Initio Computational Studies of C8H6 and S4N2C2: Main Group Inorganic Analogues of Pentalene?* J. D. Goddard.

F4.2.9 *Aryloxide Derivatives of Actinide(IV) Polypyrazolylborates. Structural Trends of Uranium (IV) Bis[hydrotris–(pyrazol–1–yl)borate] Complexes.* I. Santos, J. Marcal, N. Marques, A. M. T. S. Domingos, A. P. de Matos, M. J. Calhorda, A. R. Dias, and A. M. Galvao.

F4.2.10 *Basis Set Influence on Stationary* N_4H_2 *Geometries.* A.–M. Kelterer, M. Ramek, and H. P. Fritzer.

F4.2.11 *The Reaction of Aluminium Atoms with Methane.* H. Yu and J. D. Goddard.

F4.2.12 *Role of Sulfuranyl Radicals in Primary Radical Displacement Reactions at Sulfur.* K. F. Ferris, J. A. Franz, C. P. Sosa, and R. J. Bartlett.

F4.2.13 *The Electronic Structure of Hypervalent Chlorine–Oxygen Compounds.* D. H. Phillips.

F4.2.14 *Intramolecular Hydrogen Bonding in β–Alanine and 3–Aminopropanol.* M. Ramek and A.–M. Kelterer.

F4.2.15 *Counterpoise Corrections on Equilibrium Geometries and Interaction Energies of a Simple H–Bonded Complex: Formamide and* H_2O. D. Dehareng and G. Dive.

F4.2.16 *Explorations on the Potential Surfaces of* AH_n *– Benzene Complexes.* B. V. Cheney and M. W. Schulz.

F4.2.17 *New Criteria for Aromaticity.* P. Friedman and L. C. Allen.

F4.2.18 *A Theoretical Study of the* $-B^{-}C-$ *Triple Bond.* I. L. Alberts and H. F. Schaefer III.

F4.2.19 *Ab Initio Search for the Structure of the 4–Protoadamantyl Cation.* R. Dutler, A. Rauk, S. M. Whitworth, and T. S. Sorensen.

F4.2.20 *Stable Structures of Small Cations Important in the Initial Stages of Soot Formation.* B. Weiner .

F4.2.21 *Wavelength Dependency of 1,3–Cyclohexadiene to 1,3,5–Hexatriene Ring Opening Reaction.* S. Nakamura and M. Irie.

Friday, August 25, 1989

7:30 pm – Max Bell Foyer

Posters – Theoretical Solid State Chemistry (F5)

Wine and Cheese Reception (courtesy of Multiflow Computer)

F5.1 *The Pivot Algorithm and Polygons: Results on the FCC Lattice.* E. J. J. Van Rensburg and S. G. Whittington.

F5.2 *Charge State Stability of Ni and Cu in MgO.* J. M. Vail, J. Meng, and P. Jena.

F5.3 *Ab Initio Studies of the Beryllium Bulk/Cluster Interface.* R. B. Ross, C. W. Kern, R. M. Pitzer, and W. C. Ermler.

F5.4 *Valence and Core Electronic Structure of the 90K Superconductor Y–Ba–Cu–O.* W. Mueller.

F5.5 *Electronic Structure: Many–Particle Spectrum of Superconducting* $YBa_2Cu_3O_7$. G. A. R. Lima, R. Mota, and A. Fazzio.

F5.6 *High–Order Interactions in High–Pressure Molecular Solids.* S. Raynor.

F5.7 *Rovibrational Dynamics of Arbitrary N–Body Systems.* D. H. Li and J. Jellinek

F5.8 *Relationship Between Stability, Geometry, and Bonding in Small Lithium Clusters: A Charge Density Topological Approach.* C. Gatti, P. Fantucci, and G. Pacchioni.

F5.9 *A New Quantum Mechanical Description of Solid Neon.* A. Pendas, E. Francisco, V. Luana, and L. Pueyo

F5.10 *On the Abstraction of Hydrogen from Diamond (111) Surfaces.* S. M. Valone.

F5.11 *Hartree–Fock and Matt–Littleton Calculations on Defects in α–Quartz.* F. Sim.

F5.12 *Calculation of the Electronic Correlation Energu of Silicon using the Local Ansatz.* F. Sim.

Saturday, August 26, 1989

8:30 am – Max Bell Auditorium

Theoretical Biology (S1)

Organiser – A. Rauk
Chairperson: R. Paul (University of Calgary)

S1.1 8:30 am – 9:30 am **E. Clementi (IBM):**
Productivity, Global Simulation, and Evolution in Supercomputing and

		Supercomputers
S1.2	9:30 am – 9:50 am	R. J. Woods, W. A. Szarek, and V. H. Smith, Jr. (Queen's University): ***An Examination of the Conformations responsible for the Sweetness of Hexuloses Using the Semi–Empirical Molecular Orbital Method, AM1.***

9:50 am – 10:20 – **Coffee Break**

Chairperson: R. Paul (university of Calgary)

S1.4	10:20 am – 11:00 am	**P. A. Kollman** (University of California, San Francisco): ***The Use of Molecular Dynamics in the Simulation of Free Energies of Association of Molecules***
S1.5	11:00 am – 11:20 am	A. Goldblum (Hebrew University of Jerusalem): ***Structural Effects on the Acidity of Aspartic Proteinases.***

Saturday, August 26, 1989

9:30 am – Max Bell 251

Algebraic Methods (S2)

Organiser – D. R. Truax
Chairperson: D. C. Moule (Brock University)

S2.1	9:30 am – 10:15 am	**F. Iachello** (Yale University): ***Algebraic Approach to Molecular Structure***
S2.2	10:15 am – 11:00 am	**V. A. Kostelecky** (Indiana University): ***Atomic Supersymmetry***

11:00 am– 11:15 am – **Coffee Break**

Chairperson: K. V. Darvesh (Dalhousie University)

S2.3	11:15 am – 12:00 am	**J. Paldus** (University of Waterloo): ***Recent Developments in the Unitary Group Approaches to the Many–Electron Correlation Problem***
S2.4	12:00 am – 12:20 am	G. L. Malli (Simon Fraser University): ***Ab Initio Relativistic Calculations for the Diatomics of Heavy and Superheavy Elements***

Saturday, August 26, 1989

6:45 pm – Max Bell Auditorium

Theoretical Solid State Chemistry (S3)

Organiser – T. Ziegler
Chairperson: R. J. Boyd (Dalhousie University)

S3.1	6:45 pm – 7:30 pm	**J. K. Burdett** (University of Chicago): ***Moments and the Energies of Solids***

S3.2 7:30 pm – 7:50 pm B. I. Dunlap (Naval Research Laboratory):
LDF Studies of Titanium Hydride Clusters

7:50pm – 8:10 pm – **Coffee Break**

Chairperson: J. M. Vail (University of Manitoba)

S3.3 8:10 pm – 8:55 pm **W. A. Goddard III** (California Institute of Technology):
Simulation of Materials: The Theory of High Tc Superconductors

S3.4 8:55 pm – 9:15 pm B. T. Thole, R. Broer and W. C. Nieuwpoort (University of Groningen):
Electronic Structure of Copper Oxides: Importance of Local Relaxations and Charge–Transfer Excitations

S3.5 9:15 pm – 9:35 pm R. Wu and L. C. Snyder (SUNY – Albany):
The Computation by MINDO/3 of Local–Mode Vibrational Frequencies of Carbon and Oxygen Defects in Crystalline Silicon.

Saturday, August 26, 1989

7:30 pm – Max Bell 253

Posters – Theoretical Biology and Biophysical Chemistry (S4)

Beer Reception (courtesy of Big Rock Brewery, Ltd)

S4.1 ***An Algorithm for Computing Molecular Volume.*** C. Hungenahally and P. G. Mezey.

S4.2 ***Theoretical Study of Sodium Channel Blocking by Amiloride and its Analogs.*** C. Plant, C. A. Venanzi, and T. J. Venanzi.

S4.3 ***The Effect of Molecular Conformation on the Determination of Potential Derived Atomic Charges.*** P. V. Maye and C. A. Venanzi.

S4.4 ***Use of Semi–Empirical (AM1) Ionization Potentials to Examine Single Electron Transfer (SET) reactions of Chemical and Biological Significance.*** E. Pop, M. E. Brewster, D. Doerge, J. J. Kaminski, and N. Bodor.

S4.5 ***A Method for Characterization of Foldings in Protein Ribbon Models.*** G. A. Arteca and P. G. Mezey.

Posters – Algebraic Methods (S5)

Beer Reception (courtesy of Big Rock Brewery, Ltd)

S5.1 ***Application of a Pade–Approximation Formula for the Kinetic Energy Functional of Atoms.*** P. Csavinszky.

S5.2 ***Born and Born–Meyer Potentials as Antiannihilation Barriers in Atom–Antiatom Interactions, with Reference to Cold Fusion.*** G. Van Hooydonk.

S5.3 ***Finitude of the Number of Elements.*** I. O. Oriade.

S5.4 ***An Analysis of Reaction Spheres and Reaction Tori.*** X. Luo and P. G. Mezey.

S5.5 ***An Approximation to*** $E \otimes \varepsilon$***,Vibronic States.*** L. Yin and O. Goscinski.

S5.6 ***An Induced*** S_n ***–Symmetry Schemes for Spin 1/2 Clusters: Liouville Space Contrasts between Diagrammatically Derived Kotani Forms and the Exact IRs Defining the*** $S_n/SO(3)$ ***Carrier Spaces for*** $(k_i = 1)$***–Spin Clusters.*** F. P. Temme.

S5.7 S_n ***–Adapted Liouville Space IX: Role of Scalar Invarients and Lexical Combinatorics over a Field in Deriving Explicit*** $|KQ(k_1 - k_4):[\lambda]S_4 \gg$ ***Tensor Bases.*** F. P. Temme.

S5.8 ***Electrostatic Calculations with the Maxwell Invariant Representation of Spherical Harmonics: General Results*** *for Harmonics Defined by a Cylindrically Symmetric Distribution.* E. S. Campbell and D. Belford.

Posters – Novel Approaches (S6)

Beer Reception (courtesy of Big Rock Brewery, Ltd)

S6.1 *The Probability of Occurrence of Knots in Random Ring Closure in Dilute Polymer Solutions.* C. E. Soteros, S. G. Whittington, and D. W. Sumners.
S6.2 *A Computer Algorithm and Examples for Reaction Globe Generation.* I. Balint and P. G. Mezey.
S6.3 *The Exact One–Electron Model of Molecular Structure.* G. Hunter.
S6.4 *Half–Bound States.* M. S. Krishnan and R. F. Snider.

Posters – Solitons, Evolution and Chaos (S7)

Beer Reception (courtesy of Big Rock Brewery, Ltd)

S7.1 *Generalized Coherent State Analysis of Dovydov Solitons.* B. Mechtly, P. B. Shaw, and B. Weiner.
S7.2 *A Model of Unimolecular Reactions with Slow IVR.* N. Snider

Posters – Density Functional Theory and Applications (S8)

Beer Reception (courtesy of Big Rock Brewery, Ltd)

S8.1 *Spin–Orbit Coupling in the Local Spin Density–Scattered Wave Method.* S. Nour, M. Morin, C. Mehadji, D. R. Salahub, and H. Chermette.
S8.2 *Variational Principle for Obtaining Approximate Solutions of the Thomas–Fermi Equation for Atoms in a Strong Magnetic Field.* M. D. Glossman and E. A. Castro.
S8.3 *Response Coefficients for Atoms and Molecules.* M. Galvan, A. Garritz, J. L. Gazquez, R. Vargas, and A. Vela.
S8.4 *The Application of the Hartree–Fock–Slater Method to the optimization of Transition Structures.* L. Fan and T. Ziegler.

Sunday, August 27, 1989

9:00 am – Mountain Lakes and Canyons Bus Tour
6:00 pm – BBQ

Monday, August 28, 1989

8:30 am – Max Bell Auditorium

Chemisorption and Related Surface Phenomena (M1)

Organiser – T. Ziegler
Chairperson: V. H. Smith (Queen's University)

M1.1 8:30 am – 9:15 am **E. Shustorovich (Kodak):** ***Calculations of Energy Profiles for Metal Surface Reactions: a Bond–Order Conservation Approach***
M1.2 9:15 am – 9:35 am N. Rosch (Technical University of Munich):

		Coadsorption on Transition Metal Surfaces
M1.3	9:35 am – 9:55 am	C. E. Wulfman (University of the Pacific) and L. A. Curtis (Argonne): ***Theoretical Studies of Small Copper Oxide Clusters.***

9:55 am – 10:10 am – **Coffee Break**

Chairperson:

M1.4	10:10 am – 10:55 am	**E. J. Baerends** (Free University of Amsterdam): ***Silver–catalyzed Ethylene Epoxidation: on the Role of Pauli Repulsion and the Fermi Level in Chemisorption and Catalysis***
M1.5	10:55 am – 11:15 am	J. Koutecky and V. Bonacic–Koutecky (Freie Universitat Berlin) and P. Fantucci (Universita di Milano): ***Specific Character of Chemical Bonds in Elemental Clusters***

Monday, August 28, 1989

1:30 pm – Max Bell Auditorium

Solitons, Evolution and Chaos (M2)

Organiser – R. Paul

Chairperson: B. C. Sanctuary (McGill University)

M2.1	1:30 pm – 2:15 pm	**A. D. Bandrauk** (Universite de Sherbrooke): ***The Maxwell–Schroedinger Equation and Pulse Propagation in Molecular Media***
M2.2	2:15 pm – 2:45 pm	L. J. Bernstein (University of Arizona): ***Local Modes in Molecules.***

2:45 pm – 3:00 pm – **Coffee Break**

Chairperson: R. F. Snider (University of British Columbia)

M2.3	3:00 pm – 3:45 pm	**D. D. Holm** (Los Alamos National Laboratory): ***Bifurcations and Homoclinic Chaos in Classical Dynamics of Coupled Anharmonic Oscillators***
M2.4	3:45 pm – 4:30 pm	**J. A. Tuszynski** (University of Alberta): ***Recent Symmetry Reduction Analyses for Multidimensional PDE's and Pattern Formation***
M2.5	4:30 pm – 5:15 pm	**R. Kapral** (University of Toronto): ***A Lattice–Gas Cellular Automaton for a Chemically Reacting System***

5:15 Business Meeting

Monday, August 28, 1989

7:00 pm – Max Bell Auditorium

Electronic Structure Theory 2 (M3)

Beer Reception (courtesy of Labatt's Alberta Brewery)

Organiser – A. Rauk

Chairperson: D. P. Chong (University of British Columbia)

M3.1	7:00 pm – 7:40 pm	**W. J. Meath** (University of Western Ontario): ***Single– and Multiphoton Absorption for Molecules undergoing Free and Hindered Rotations including Permanent Multipole Moment and Chiral Effects***
M3.2	7:40 pm – 8:20 pm	**T. D. Bouman** (Southern Illinois University, Edwardsville) and A. E. Hansen: ***Linear Response Calculations of Molecular Properties***
	8:20 pm – 8:40 pm	**Coffee Break**
	Chairperson: D. M. Bishop (University of Ottawa)	
M3.3	8:40 pm – 9:00 pm	J. E. Rice and B. Liu. (IBM Almaden): ***The Accurate Determination of Non–Linear Polarizabilities.***
M3.4	9:00 pm – 9:20 pm	G. R. Freeman (University of Alberta): ***Aharonov–Bohm Effect: Interacting Magnetic Fields and Quantum Mechanics.***

Tuesday, August 29, 1989

8:30 am – Max Bell Auditorium

Vibrational Optical Activity (T1)

	Organiser – H. Wieser	
	Chairperson: C. Zimba (Los Alamos National Laboratory)	
	8:30 am – 8:35 am	Welcome
T1.1	8:35 am – 9:20 am	**L. A. Nafie** (Syracuse University): ***Theoretical Models and Approaches to VCD Calculations***
T1.2	9:20 am – 10:05 am	**P. J. Stephens** (University of Southern California): ***Ab Initio Calculations of VCD Spectra***
	10:05 am – 10:25 am – **Coffee Break**	
	Chairperson: C. Zimba (Los Alamos National Laboratory)	
T1.3	10:25 am – 10:50 am	S. Abbate (Universita di Palermo) and A. Moscowitz (University of Minnesota): ***Local Modes, Normal Modes, and Vibrational Circular Dichroism.***
T1.4	10:50 am – 11:15 am	R. Dutler, A. Rauk, R. A. Shaw, and H. Wieser (University of Calgary): ***The Vibrational Circular Dichroism of α–Deuterioethanol***
T1.5	11:15 am – 11:40 am	T. B. Freedman (Syracuse University): ***Vibronic Coupling Formulation of VCD Intensities with Floating Basis Sets***
T1.6	11:40 am – 12:05 pm	P. Polavarapu (Vanderbilt University): ***Ab Initio Raman Optical Activity Calculations.***
T1.7	12:05 pm – 12:30 pm	R. A. Shaw and H. Wieser (University of Calgary): ***The VCD Spectrum of 2–Methyloxetane: Effects of Conformational Mobility and Charge Flow.***

Tuesday, August 29, 1989

1:30 pm – Max Bell Auditorium

Evolution of Structure in Fluids and Solids (T2)

Organiser – R. Paul
Chairperson: R. Wallace (University of Manitoba)

T2.1	1:30 pm – 2:15 pm	**D. Chandler** (University of California, Berkeley): ***Electrons on the Move in Liquids***
T2.2	2:15 pm – 3:00 pm	**G. Bluman** (University of British Columbia): ***Symmetry–Based Algorithms to Linearize Partial Differential Equations***

3:00 pm – 3:15 pm – **Coffee Break**

Chairperson: J. P. Valleau (University of Toronto)

T2.3	3:15 pm – 4:00 pm	**A. Bishop** (Los Alamos National Laboratory): ***Competing Interactions and Complexity in Condensed Matter***
T2.4	4:00 pm – 4:20 pm	P. A. Monson (U. of Massachussetts) and S. O'Shea (U. of Lethbridge): ***Vapour–Liquid Equilibrium for Model Molecular Fluids***
T2.5	4:20 pm – 4:50 pm	M. Otwinowski and R. Paul (University of Calgary): ***Multiparameter Bifurcations in Reaction–Diffusion Systems***

Tuesday, August 29, 1989

5:00 pm – Max Bell Auditorium

Business Meeting – Canadian Association of Theoretical Chemists

Tuesday, August 29, 1989

6:45 pm – Max Bell Auditorium

Density Functional Theory (T3)

Organiser – T. Ziegler
Chairperson: Ajit J. Thakkar (University of New Brunswick)

T3.1	6:45 pm – 7:20 pm	**A. Becke** (Queen's University): ***Basis Set Free Density Functional Quantum Chemistry***
T3.2	7:20 pm – 7:55 pm	V. Tschinke and T. Ziegler (University of Calgary): ***Exchange and Correlation in Density Functional and Ab Initio Methods***

7:55 pm – 8:10 pm – **Coffee Break**

Chairperson: Ajit J. Thakkar (University of New Brunswick)

T3.3	8:10 pm – 8:30 pm	M. Cook (Naval Research Laboratory, Washington): ***Electron Correlation and Density Functional Methods***
T3.4	8:30 pm – 8:50 pm	A. Savin (University of Stuttgart): ***Density Functionals for the Correlation Energy***
T3.5	8:50 pm – 9:20 pm	**D. Salahub** (University of Montreal): ***Recent Progress with the LCGTO–MP–LSD Method***

Tuesday, August 29, 1989

7:30 pm – Max Bell 253

Posters – Evolution of Structure in Fluids and Solids (T4)

Wine and Cheese Reception (courtesy of Nicolet Instruments and IBM Canada)

T4.1 *Theoretical Models of Amphiphilic Self–Assembly.* J. R. Gunn and K. A. Dawson.

T4.2 *Spontaneous Isomerizations and Dynamical Propensities of Some SF_6–$(Ar)_n$ Clusters.* M. A. Kmetic, J. C. Shelley, and R. J. Le Roy.

T4.3 *Hydrodynamic Mode Selection Due to the Electrocapillary Effect.* J. F. Olson, C. Ursenbach, V. I. Birss, and W. G. Laidlaw.

T4.4 *Finite Difference Simulation of Foam Generation.* W. G. Laidlaw and F. Wassmuth.

Posters – Electronic Structure Theory and Applications (T5)

Wine and Cheese Reception (courtesy of Nicolet Instruments and IBM Canada)

Excited States (T5.1)

T5.1.1 *Laser Excitation and Quantum Chemical Studies of the First Excited States of Formic Acid.* F. Ioannoni, and D. C. Moule.

T5.1.2 *Rydberg States of the Ethynyl Radical.* A. G. Koures and L. B. Harding.

T5.1.3 *Molecular Orbital Theory for Excited States.* J. B. Foresman, M. Head–Gordon, J. A. Pople, and M. J. Frisch.

T5.1.4 *Hund's Rule and Singlet–Triplet Energy Differences for Molecules.* K. V. Darvesh, P. D. Fricker, and R. J. Boyd.

T5.1.5 *Diatomic Anions with Nine Valence Electrons.* F. Grein.

T5.1.6 *Extraction of Excitation Energies from Oscillator Strength Moments.* Z.–M. Hu and A. J. Thakkar.

T5.1.7 *Low–Lying Singlet States in the Two–Photon Excitation Spectrum of Chrysene.* G. Marconi, P. R. Salvi, and N. Q. Liem.

Electron Densities and Response Properties (T5.2)

T5.2.1 *A Novel Invarience Principle for the Electron Density.* H. Silberbach.

T5.2.2 *Pointwise Comparison of Experimental and Ab Initio Electronic Densities.* Z. Darakjian, and W. H. Fink.

T5.2.3 *Spin Densities in Diatomic First–Row Hydrides.* D. M. Chipman.

T5.2.4 *Accurate Spin Density and Fermi Contact Term for the Lithium Atom.* R. O. Esquivel.

T5.2.5 *Contribution to the Electron Density Analysis.* M. Kohout.

T5.2.6 *Electron Correlation and Electron Density Distributions.* R. J. Boyd and L.–C. Wang.

T5.2.7 *Dynamic Polarizabilities and Hyperpolarizabilities of Polysilanes.* B. Kirtman.

T5.2.8 *Evaluating Response Properties of Quantum Systems with Monte Carlo.* M. Caffarel and O. Hess.

T5.2.9 *Quantum Monte Carlo Applied to Diatomic Molecular Properties.* J. Vrbik, D. A. Legare, and S. M. Rothstein.

T5.2.10 *Ab Initio Coupled–Cluster Calculations of Isotropic Hyperfine Splitting.* I. Carmichael.

Electron Correlation (T5.3)

T5.3.1 *Ab Initio Test of the Pairwise Additivity Assumption of Semiempirical Electronic Structure: Spectator Model of Correlation Contributions.* X–C. Wang and K. F. Freed.

T5.3.2 *Electron Correlation Effects in Simple Molecules: Comparisons between Momentum and Position (Real) Space.* K. E. Banyard and J. Sanders.

T5.3.3 *Limitations in Determining the Lower Bounds to the Ground State Correlation Energy of the Cyclic Polyenes using Optimized Inner Projection Technique.* P. Piecuch, S. Zarrabian, J. Paldus, and J. Cizek.

T5.3.4 *Semi–empirical Studies of the Nonlinear Optical Properties of Molecules and Polymers.* H. A. Kurtz.

T5.3.5 ***Quantum Chemistry by Random Walk: Energies of Helium Dimers and Trimers.*** J. B. Anderson and V. Mohan

T5.3.6 ***MCSCF with the Finite Element Method.*** D. Sundholm and J. Olsen..

Vibrational Studies (T5.4)

T5.4.1 ***Systematic Study of Molecular Vibrational Anharmonicity and Vibration–Rotation Interaction Part ii. Linear Molecules.*** Y. Yamaguchi, R. B. Remington, W. D. Allen, D. A. Clabo, Jr., and H. F. Schaefer III.

T5.4.2 ***Theoretical Studies of the Hydrogen Peroxide Potential Surface: an Ab Initio Anharmonic Force Field.*** L. B. Harding.

T5.4.3 ***The*** HO_2^+ ***Molecular Ion: A Comparison of Methods for the Calculation of Anharmonic Vibrational Frequencies.*** G. E. Quelch, Y. Zie, Y. Yamaguchi, B. F. Yates, and H. F. Schaefer III.

T5.4.4 ***Dynamical and Spectroscopic Study of Non–Rigid Molecules. Application to Thioacetaldehyde.*** Y. G. Smeyers, A. Nino, and D. C. Moule.

T5.4.5 ***Pulsed Laser–Molecule Interactions and the Effects of Permanent Dipoles.*** A. E. Kondo and W. J. Meath.

T5.4.6 ***Hydrogen Atom Tunneling Dynamics and Tunneling Splittings in Polyatomic Molecules.*** V. K. Babamov.

Posters – Vibrational Optical Activity Applications (T6)

Wine and Cheese Reception (courtesy of Nicolet Instruments and IBM Canada)

T6.1 ***Ab Initio Calculations of Infrared Absorption and Circular Dichroism Spectra of Methyl Glycollate and Methyl Lactate.*** R. Bursi, F. Devlin, and P. J. Stephens.

T6.2 ***Vibrational Circular Dichroism Mearurement using a Polarizing Michelson Interferometer.*** N Ragunathan, T. B. Freedman, and L. A. Nafie.

T6.3 ***Gas Phase Vibrational Circular Dichroism of Simple Chiral Molecules.*** T. B. Freedman, K. M. Spencer, and L. A. Nafie.

T6.4 ***Rotational–Vibrational Circular Dichroism.*** P. L. Polavarapu.

T6.5 ***Ab Initio Localized Molecular Orbital Calculations of Vibrational Circular Dichroism.*** P. K. Bose and P. L. Polavarapu.

T6.6 ***Circular Dichroism of the Benzene Group Vibrations and Molecular Stereochemistry.*** P. K. Bose and P. L. Polavarapu.

T6.7 ***Circular Dichroism in the Far–Infrared and Millimeter Wavelength Region: Preliminary Measurements.*** P. L. Polavarapu, P. G. Quincy, and J. R. Birch.

T6.8 ***The VCD Spectrum of 6,8–dioxabicyclo[3.2.1]octane: Comparison of Experimental and Model Spectra.*** T. Eggimann, R. A. Shaw, N. Ibrahim, and H. Wieser.

T6.9 ***The VCD Spoectra of Selected Methyl Substituted Derivatives of 6,8–dioxabicyclo[3.2.1]octane.*** T. Eggimann, N. Ibrahim, and H. Wieser.

T6.10 ***A Systematic Investigation of Charge Flow: Infrared Absorption Intensities of Propane and Dimethyl Ether.*** F. Maurer, R. A. Shaw, and H. Wieser.

T6.11 ***A General Formulation of Raman Optical Activity.*** T. H. Walnut.

T6.12 ***IR and VCD Intensities of Model Systems*** CH_3OH, CH_3NH_2, NH_2NH_2, NH_2OH ***and*** $HOOH$ ***and the Deuterated species,*** ND_2ND_2, $DOOH$ ***and*** $DOOD$***: A Theoretical Study using the Vibronic Coupling Formalism.*** A. Rauk, R. Dutler and D. Yang.

Wednesday, August 30, 1989

8:30 am – Max Bell Auditorium

Quantum and Nonquantum Aspects of Reaction Dynamics (W1)

Organiser – A. Rauk
Chairperson: T. W. Dingle (University of Victoria)

W1.1	8:30 am – 9:15 am	**K. Morokuma** (Institute for Molecular Science, Okazaki): ***Potential Energy Surfaces and Classical Dynamics of Non–adiabatic Processes***
W1.2	9:15 am – 10:00 am	M. E. Mandy (University of Toronto): ***The Calculation of State–to–State Rate Constants for $H + H_2$ (v,J).***

10:00 am – 10:20 am – **Coffee Break**

Chairperson: T. W. Dingle (University of Victoria)

W1.3	10:40 am – 11:00 am	G. K. Schenter and C. B. Duke (Battelle, Pacific Northwest Laboratory): ***Dynamics of Twisted–Intramolecular Charge Transfer in Dimethylaminobenzonitrile.***
W1.4	11:00 am – 11:20 am	S. Fleischman (Convex Computer Corp.): ***Free Energy Simulations of Li^+ and Na^+ Solvation.***

12:00 noon – CLOSE

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The Canadian Society of Chemists

Abstracts

COMPUTERS AND THEORETICAL CHEMISTRY: 1965-1989, A PERSONAL PERSPECTIVE

HENRY F. SCHAEFER III

Center for Computational Quantum Chemistry
University of Georgia
Athens, Georgia 30602

ABSTRACT

From the earliest days of electronic computers, molecular electronic structure theorists have been among the most demanding of users, both in terms of raw cpu power and machine sophistication. This report reviews computer hardware and software developments during what may be called the Second and Third Ages of Quantum Chemistry.

F1.1 1

RECENT DEVELOPMENTS IN CORRELATION THEORY, John A. Pople, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213.

The quadratic configuration interaction method (QCISD) for calculating electron correlation energy is described. A new set of corrections for effects of triple and quadruple substitutions leads to a technique which is fully accurate to fifth order in a Møller Plesset expansion. A preliminary evaluation of the method is described.

F1.2

ELECTRONIC MOTION COUPLED BY MOLECULAR VIBRATION

Tokio Yamabe

Dept. of Hydrocarbon Chem. and Div. of Molecular Engineering,
Kyoto University, and Institute for Fundamental Chemistry,
Sakyo-ku, Kyoto 606, Japan

The electron-phonon coupling often appeared in solid state physics is investigated in molecular system from quantum chemical point of view. The non-adiabatic coupling between electron and phonon induces an effective attractive interaction as a chemical origin of the Cooper pair of superconducting electrons, illustrated in H_2 molecules and $(CH)_x$ with size dependence and coupling rules. We also discuss the process of an electron transfer under the assistance of the molecular vibration.

F1.5

MRCI STUDIES OF ELECTRON AFFINITIES OF ATOMS AND MOLECULES. T. Noro and M. Yoshimine, IBM Almaden Research Center, San Jose, California 95120-6099. Calculations designed to determine reliable electron affinities (EA's) of atoms and small molecules are reported. A selected multi-reference single and double excitation configuration interaction method was used. With large basis sets and manageable numbers of reference configurations, we obtained EA's of 0.268, 1.260, 1.454, 3.367 and 0.604 eV for B, C, O, F, and methylene, respectively, which are in excellent agreement with the observed values to within 0.01-0.03 eV. Energy convergence patterns with respect to systematic expansion of both reference configuration space and one-particle bases were studied to assess the reliability of the results, indicationg that the values given above are most likely within 0.01 eV of the full CI electron affinities.

F1.6

ABSOLUTE HARDNESS AND RELATIVE HARDNESS — MEASURES OF AROMATICITY

Robert G. Parr and Zhongxiang Zhou
Department of Chemistry, University of North Carolina
Chapel Hill, NC 27599

Absolute hardness, which is half the HOMO-LUMO gap in Hartree-Fock or Hückel theory, is shown to be an excellent measure of aromaticity. *Relative hardness* also is defined, and shown to be a good index for identifying aromatic, non-aromatic, and antiaromatic character. Numerical values are given for 216 cyclic conjugated molecules. A principle of maximum hardness is established, and it is demonstrated how the hardness concept incorporates all three aspects of aromaticity: high stability, low reactivity, and sustained ring current.

The Fruitful Interplay between Theory and Experiment.

Paul von Ragué Schleyer, Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen.

Chemistry no longer is an exclusively experimental science. The combination of highly sophisticated quantum mechanics programs and ever more powerful and cost effective computers now enable the chemist not only to help interpret the results of experimental investigations, but also to discover entirely new formulations of matter, and to do so systematically and reliably. Since the vast majority of possible chemical compounds in unknown, calculational investigations can lead to structures which are fundamentally different from those already described. Our predictions of molecules with, e.g., "anti van't Hoff" structures, bridging lithiums, octet-rule violating stoichiometries, and unanticipated geometries, are now being verified experimentally with increasing frequency. This underscores the ability of quantitative theory to lead rather than merely to follow experiment.

Nevertheless, when used in conjunction, theory and experiment are particularly effective. New and impressive examples will be presented. Many of these relate to the detailed structures of carbocations in superacid media, where they can be observed by nmr spectroscopy. ^{13}C nmr chemical shifts in particular are extremely sensitive to very small changes in molecular geometries. Thus, it is possible not only to distinguish between classical and non-classical structural candidates, but even to determine the conformational preference of a methyl group attached to a classical carbocation center. This is achieved by comparing experimental data with that calculated by the IGLO method, developed at Bochum University by Kutzelnigg, Schindler, Fleischer, and their associates (see, e.g., M. Schindler, J.Am.Chem.Soc.,1987, 109, 1020). In collaboration with this group and others, we have explored, and perhaps even solved, many of the outstanding structural problems in carbocation chemistry. Time permitting, the application of the IGLO method to other structural problems will be presented. Carbenoids are an example pertinent to the work of Rudolf Zahradnik, since he was one of the first who investigated the nature of these unusual compounds computationally.

Rearrangements involving carbocation mechanisms were an early interest of Stanly Cristol. The current computational exploration of the potential energy surfaces provides a wealth of details not available experimentally.

F1.7

A NEW LOOK AT ELECTRONEGATIVITY

Leland C. Allen
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Abstract

An extensive search of the literature since 1922 has revealed unexpected and important findings:

(1) The most universally accepted defining concept, bond polarity, is associated with electronegativity difference, $\Delta\chi = \chi_A - \chi_B$, as emphasized in Pauling's 1932 paper, the first quantitative scale of atomic values.

(2) During the past 57 years many scales and definitions have been proposed, but only two, Pauling's and Allred and Rochow's, have been used extensively by practicing chemists to give practical guidance in interpreting chemical bonding. On the other hand, Mulliken's (I+A)/2 has been the definition almost exclusively dealt with by theoretical chemists, in spite of its shortcomings and inconsistencies.

(3) Although textbooks often display electronegativity values in Periodic Table format, several strong correlations indicate a more intimate connection than heretofore realized. This leads to the hypothesis of χ as its third dimension, defined as valence shell energy (the horizontal and vertical dimensions are valence shell occupancy and valence shell size). Average valence shell energy, $(m\,\varepsilon_\pi + n\,\varepsilon_s)/(m+n)$ where ε_p, ε_s are the experimentally known s,p one-electron energies, m,n, their occupancy, is found to closely reproduce the Pauling and Allred and Rochow values and to determine Periodic Table properties such as the diagonal metalloid band and metal to non-metal transition.

The average valence shell energy expression for ground state free atoms can be translated into a rigorous, in situ, quantum mechanical expectation value for bond AB obtainable from any molecular orbital wavefunction. Preliminary results for the Bond Polarity Index so defined supports its chemical utility and promises important applications in organic and inorganic chemistry, materials science, mineralogy and biophysics.

F2.1

FRACTAL REACTION KINETICS

R. Kopelman, Dept. of Chemistry, University of Michigan, Ann Arbor, MI, 48109-1055

Advances in theoretical modeling of many-body reactive processes and in Monte-Carlo simulations have resulted in new formalisms, phenomena and concepts concerning diffusion-controlled reactions. The self-ordering and self-segregation of particles in elementary chemical reactions leads to novel qualitative and quantitative phenomena. These account not only for recent experimental observations but also suggest new experiments involving surface, colloid and solid-state reactions. Specifically, we have established anomalous reaction rate laws, and self ordered particle distribution functions,for diffusion controlled, pulsed and steady-state reactions of the type: $A + A \rightarrow P$, $A + B \rightarrow 0$ and $A + C \rightarrow C$, where P is an inert product and C a catalyst (fixed or moving). The scaling laws, order parameters and segregation parameters show a critical dependence on dimensionality, source-term structure and phase space. The consistency among the simulations, experiments and analytical formulations will be discussed.

F2.2

Immiscible lattice gases

Daniel H. Rothman
Department of Earth, Atmospheric, and Planetary Sciences
Massachusetts Institute of Technology
Cambridge, MA 02139

The lattice gas introduced by Frisch, Hasslacher, and Pomeau [Phys. Rev. Lett., **56**, 1505 (1986)] is a discrete model of molecular dynamics. Identical particles of unit mass traveling with unit speed on a regular lattice propagate and collide according to simple rules. The model, a particular subclass of cellular automata, exhibits the remarkable property that coarse-grain averages asymptotically go over to the incompressible Navier-Stokes equations.

After introducing the lattice gas, I show how an elementary extension of the FHP gas allows the simulation of immiscible mixtures. This *immiscible lattice gas* is composed of two kinds of particles: "red" and "blue." The new collision rule maximizes the flux of color in the direction of the local color gradient, while locally conserving mass, momentum, and color. Surface tension is modeled, thereby making a wide range of problems accessible to study by numerical simulation.

Particular problems of interest emphasized in this talk are spinodal decomposition and the flow of immiscible fluids in micromodels of porous media.

F2.3

Lattice animals and self-avoiding surfaces

Stuart G. Whittington
Department of Chemistry, University of Toronto

The conformation of long linear polymer molecules in dilute solution in good solvents has been studied by theorists for something like 40 years. One of the most popular models is a self-avoiding walk on a lattice. In spite of the apparent simplicity of this model rather little is known rigorously although there is a wealth of information available from numerical studies. Randomly branched polymer molecules have received less attention but there has been a surge of interest since 1979 when Lubensky and Isaacson proposed that such molecules could be modelled by lattice animals, i.e. by connected subgraphs of a lattice. There are strong similarities between lattice animals and self-avoiding walks and the techniques which were useful in deriving rigorous results about self-avoiding walks have also turned out to be useful in the lattice animal problem. A natural extension of these two models is self-avoiding surfaces which, in this context, can be regarded as models of sheet-like polymers. Again the same set of mathematical techniques turn out to be useful and there are hints of a strong connection between the behaviour of self-avoiding surfaces and lattice animals. This lecture will describe some of the basic techniques available and will discuss some recent rigorous results, concentrating on the possible connections between the surface and animal problems.

F 2.4

APPLICATION OF FRACTAL CONCEPTS TO PROBLEMS IN SURFACE CHEMISTRY

Craig Fairbridge, CANMET, 555 Booth Street, Ottawa,
Ontario, Canada K1A 0G1

The properties of typical hydroprocessing catalysts are discussed from the standpoint of fractal geometry. The characterization of heterogeneous catalysts involves the description of an interface. Physical and chemical properties of the interface, such as apparent surface area or active site density, have been quantified by fractal descriptors. Hydroprocessing catalysts are more accurately quantified by a surface fractal dimension, D, rather than by nitrogen BET surface area. The concept of a reaction dimension, D_R, has been demonstrated as a useful parameter for quantifying the structural sensitivity of heterogeneous catalytic systems. This is illustrated by the chemisorption of probe molecules and by the measurement of rates of hydrodesulphurization on hydrotreating catalysts.

F2.5

INTERACTING ANTS ON RANDOM STRUCTURES

W. G. Wilson and W. G. Laidlaw, Department of Chemistry
University of Calgary, Calgary, Alberta T2N 1N4

We present a simulation method for the study of diffusion, in this case on random structures, by the use of interacting, random-walking "ants." The method employs "multi-ant" coding techniques and can be applied to a large variety of problems in a rather efficient manner. In this talk, diffusion through square lattice site percolation structures is examined for the standard percolation problem, and invasion percolation with a trappable defending fluid.

Our simulation may be thought of as a variation of recently introduced lattice-gas cellular automata (LGCA) methods, which directly simulate the movement of fluid particles. The diffusion simulation is carried out by releasing armies of one or more species of random-walking ants into the lattice. These ants carry out their respective walks according to a given set of rules, which can be modified to model effects ranging from simple fields to viscosity to defender fluid trapping.

F3.1

MANY-BODY VALENCE-BOND THEORY OF CONJUGATED SYSTEMS.

D. J. Klein, Department of Marine Sciences, Texas A&M University at Galveston, Galveston, TX 77553-1675.

A key area in the theory of the pi-networks of conjugated systems is the valence-bond (VB) view, which was begun over 50 years ago as a quantum-theoretic realization of classical chemical-bonding ideas. Work in Galveston reveals a heirarchy of several VB-based models including the first VB and resonance-theory models of Pauling and Wheland as well as recent "conjugated-circuit" and "Clar-structure" models. Some useful theorems for these (correlated) models have been established and sometimes show interesting correspondences (or corrections) to predictions obtained from simple Huckel molecular orbital approaches. Systematic many-body cluster expansion techniques for the ground-state wavefunctions of these models are being developed, often as natural extensions of earlier simpler VB approaches. In some cases a novel long-range ordering arises related to bond localization, the possibility of solitonic excitations, and even more speculatively to the possibility of novel superconductive mechanisms. Some work on excited states fore these VB models has been begun.

F3.2

DESIGN OF MOLECULES WITH PRESCRIBED PROPERTIES

Milan Randc
Department of Mathematics and Computer Science
Drake University, Des Moines, Iowa 50010

Using available wavefunction apparatus of quantum mechanics suffices to produce, in principle at least, for a given molecule a desired molecular property. The reverse problem, however has hardly been considered. In this communication we will outline a strategy for finding a molecule or molecules which approach as much as possible a given molecular property.

Our search strategy for molecules of desired property consists in identifying a relevant molecular fragement, if property is local. Subsequently for a subset of molecules with known relative magnitude of the property considered we derive a hierachical ordering and extrapolate in the direction pointed by the molecular descriptors used. The approach is particularly suited for applications in QSAR (quantitative structure activity relationship) studies concerned with design of optimal drugs.

F3.3

ADVENTURES BEYOND THE BORN-OPPENHEIMER APPROXIMATION: EXOTIC MOLECULES

Vedene H. Smith, Jr.
Department of Chemistry
Queen's University
Kingston, Ontario
K7L 3N6

Methods for the treatment of exotic molecular systems such as $e^+e^-e^+$, ppμ, etc., will be discussed, together with calculated properties.

F3.4

SHAPE ANALYSIS OF 3D MOLECULAR BODIES: MOLECULAR SHAPE CODES FROM QUANTUM CHEMISTRY AND TOPOLOGY

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The analysis of shapes of 3D molecular bodies is of major importance both in theoretical chemistry and in applied fields, such as rational drug design. As an alternative to the usual, visual analysis of displays of molecular models on a computer screen, a fully algorithmic approach of 3D shape analysis has been proposed. The nonvisual approach is based on a topological characterization of molecular contour surfaces, such as isodensity contours or electrostatic potential contours obtained from quantum chemical calculations, or fused sphere Van der Waals surfaces, involving only elementary calculations. The topological analysis can be carried out by a computer algorithm, leading to a set of topological invariants, including the shape groups and shape matrices. These invariants provide a series of shape codes that can be used as tools for direct, numerical shape comparisons in sequences of molecules.

F4.1.1

COUPLED-CLUSTER APPROACH WITH APPROXIMATE ACCOUNT OF TRIPLE EXCITATIONS AND ITS APPLICATION TO THE CYCLIC POLYENE MODEL SYSTEMS

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The coupled-cluster theory with double substitutions (CCD) and approximate coupled-cluster theory corrected for connected quadruply excited clusters (ACPQ) are modified to include the effects of connected triple excitations. Detailed equations in an orthogonally spin-adapted form are presented. Resulting approximate approaches, CCDT-1 and ACPTQ, are implemented and applied to the PPP and Hubbard models of cyclic polyenes, C_NH_N, $N=4\nu+2$, $\nu=1$–5, for all values of the coupling constant. Comparisons with approximate account of triexcited clusters as implemented by Bartlett's Florida group and Raghavachari (the CCD+T(CCD) method), as well as CCD, full and limited CI approaches are made. The CCDT-1 method provides excellent results in the weakly correlated region, while the ACPTQ method provides remarkably good results even in the region of intermediate correlation. Contrary to ACPQ, the ACPTQ method breaks down in the highly correlated region, but this is rather connected with the approximate way of including the triples. The CCDT-1 method breaks down not only in the highly correlated, but even in the intermediately correlated, regions, similar to the CCD approach.

An Efficient Formulation of the Analytic Gradient of the Singles and Doubles Coupled Cluster Energy

F4.1.2

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and

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Abstract

A computationally efficient formulation of the analytic energy gradient of the singles and doubles coupled cluster (CCSD) electron correlation method is presented. Particular attention has been given to the cost-effective implementation of the procedure on vector computers. The efficiency and utility of this new method is demonstrated by precisely determining the equilibrium structures and harmonic vibrational frequencies of several polyatomic molecules using large one-particle basis sets.

F4.1.3

A FULL VARIATIONAL METHOD BASED ON A TENSOR PRODUCT DECOMPOSITION

Fredrick A. Senese, Christopher A. Beattie, John C. Schug, Jimmy W. Viers, Layne T. Watson

A new direct full variational approach exploits a tensor (Kronecker) product decomposition of the many-electron Hamiltonian. Explicit assembly and storage of the Hamiltonian matrix is avoided by using the Kronecker product structure to form matrix-vector products directly from the molecular integrals. The wavefunction is expanded in terms of spin-free primitive kets rather than Slater determinants or configuration state functions, and is equivalent to a full CI expansion. The approach suggests compact storage schemes and algorithms which are naturally suited to parallel and pipelined machines.

F4.1.4

CLASSICAL AND NON-CLASSICAL FORMS OF THE VINYL CATION: A COUPLED CLUSTER STUDY

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The energy difference between the classical and non-classical forms of vinyl cation is studied using the configuration interaction (CISD) and coupled cluster methods (CCSD and CCSDT-1). The basis sets employed range from double-zeta to those including f-functions on carbon and d-functions on hydrogen. It is shown that the theoretical energy differences are very sensitive to the inclusion of higher-order polarization functions and the inclusion of triple excitations in the correlated wavefunctions. The results are compared with other theoretical studies in the literature and very recent experimental findings.

F4.1.5

PHYSICAL INTERPRETATION AND ASSESSMENT OF THE GW2 APPROXIMATION FOR MOLECULES

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By using the Green function method, the quantum mechanical problem of n electrons moving in the field of clamped nuclei may be reduced to solving a 1-electron Schrödinger equation with a 1-electron pseudopotential variously known as the "optical potential," "mass operator," or "self-energy." The eigenvalues of the equation are vertical ionization potentials and electron affinities, while the eigenfunctions contain scattering information.

Previous molecular applications have evaluated the self-energy within approximations derived from intrinsically antisymmetrized formalisms. The simplest such approximation beyond the Hartree-Fock level is the second-order (GF2) approximation. It has been shown to be equivalent to Møller-Plesset perturbation theory applied to the parent and daughter wave functions. Unfortunately, the GF2 approximation frequently leads to IPs which are no more accurate than Koopmans' theorem.

We show that it is better to abandon an intrinsically antisymmetrized formalism and use a second-order version (GW2) of Hedin's GW approximation which consists of dropping the exchange and keeping only the direct GF2 Feynman diagram. The result is no longer readily interpretable in terms of wave functions, but the COHSEX approximation provides a physical interpretation in terms of polarization effects. Numerical results are presented for several small molecules and computational efficiency is discussed.

F4.1.6

ELECTRON AFFINITIES REVISITED‡

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The calculation of the electron affinity of an atom or molecular species is notoriously one of the most difficult tasks in Quantum Chemistry. We describe a reliable procedure for calculating the electron affinity of an atom using the multi-reference single and doubles configuration interaction (MRSDCI) methodology. This procedure involves the use of the recently proposed correlation consistent basis sets[1] that have been augmented with functions to describe the anion character of the atom in question coupled with a straightforward uniform expansion of the reference space. Comparisons with previous results and the corresponding (whenever possible) full CI calculations are discussed.

[1] T.H. Dunning, Jr, *J. Chem. Phys.* **90**, 1007 (1989).

‡ This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract No. W-31-109-Eng-38.

F4.1.7

A COMPLETE SHAPE CHARACTERIZATION FOR GAUSSIAN-TYPE, MOLECULAR CHARGE DENSITY FUNCTIONS

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A method for characterizing the shape of molecular charge distributions is implemented and evaluated in detail. The characterization is perfomed by computing a number of topological invariants ("shape groups") associated with a continuum of molecular surfaces: the electronic isodensity contours. In our approach, the electronic charge distribution is modeled by means of Gaussian-type functions. For a given molecule, in a given nuclear spatial configuration, the technique provides a two-dimensional map, displaying the distribution of shape groups as a function of the local curvature on the surface and the density value at the contour surfaces. Several two-dimensional shape maps for simple systems are discussed. The modifications introduced in these maps by a change in the nuclear geometry, as well as nuclear charge values, are also analyzed. The method can be extended easily to molecules, provided an approximate charge density is fitted first to a Gaussian-type function.

F4.1.8

COMPARISON OF POTENTIAL ENERGY MAPS AND MOLECULAR SHAPE INVARIANCE MAPS

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It is well known that many molecular properties are strongly dependent on internal nuclear arrangements. Two possible, independent approaches can be followed while studying changes in molecular characteristics as functions of the nuclear geometry. These are the analysis of potential energy surfaces and the analysis of molecular shape. In this work, we seek to establish relationships between potential energy maps and shape invariance region maps, due to changes in the nuclear configuration. Potential energy is computed at the *ab initio* level, while the shape is described by the shape group method as applied to hard-sphere van der Waals surfaces. It is shown that the shape invariance maps follow closely, but not exactly, the shape of potential energy surfaces. Our findings suggest that a crude hard-sphere model may suffice to describe some of the structural changes in molecular surfaces, as well as their relationships to the electronic energy.

F4.1.9

GAMESS: A PORTABLE AB INITIO PROGRAM

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This descendent of the NRCC program is a relatively robust, full featured package capable of evaluating many types of atomic and molecular wavefunctions (RHF, UHF, ROHF, GVB, MP2, MCSCF and CI) and energies as well as energy gradients and second derivatives with respect to nuclear coordinates (except CI). It can optimize molecular geometries, find transition states, trace intrinsic reaction coordinates and determine normal mode vibrations. Many properties based on electron density can be calculated as well as the electric field and electric field gradient. Vibrational analysis yields frequencies, IR intensities and a variety of thermodynamic properties. The source code can be sent over BITNET (send requests to nu070347@ndsuvml) and easily installed on a large number of machines from Alliant, Amdahl, Apollo, Ardent, Convex, Cray, DEC, ETA, FPS, IBM (mainframe and PS2), NAS, Sun and Stellar.

F4.1.10

STUDY OF ORBITAL TRANSFORMATION IN CONFIGURATION INTERACTION CALCULATIONS OF HYPERFINE COUPLING IN NITROGEN AND THE CH MOLECULE,

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Multi-reference configuration interaction calculations employing various orbital transformations are undertaken to obtain the isotropic hyperfine coupling constant a_{iso} in nitrogen and a_{iso} (H) in the CH molecule. The natural orbital (NO) basis is found to be more effective than the simple RHF-MO basis; the most obvious is a basis of spin natural orbitals (SNO). It is found that a_{iso} is approached from opposite sides in the NO and 2s shell SNO basis if the CI expansion is increased. Both results are within a few percent of the full CI limit for the nitrogen atom (in the given AO basis) and the experimental value for H in the CH radical. Various features of the SNO are discussed.

Core-valence Correlation and the Binding Energy of Mg_2

F4.1.11

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Abstract

The bonding in the Mg dimer is investigated using near-complete one-particle STO and GTO valence basis sets containing up to *h* functions. Using a full CI to calibrate the four-electron correlation treatments, a sequence a of second-order-CI (SOCI) and interacting correlated fragment (ICF) calculations have been performed which are belived to be near the four-electron CI basis set limit. Our best estimate of the valence dissociation energy (D_e) is 471 ± 7 cm^{-1} which is significantly larger than the accurate experimental value of 429.6 cm^{-1}. Core-valence correlation, using the model operator approach suggested by Müller, Flesch and Meyer, is demonstrated to expand the bond length by 0.03 a_o and decrease the D_e by 35 cm^{-1}, yielding spectroscopic constants in reasonably good agreement with the experimental results. Attempts to employ standard *ab initio* methods to accurately compute the core-valence effect were unsuccessful.

F4.1.12

Application of Multi-Reference Spin-Adapted Coupled-Cluster Formalism to the H_4 Model System

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Recently developed explicit form of an orthogonally spin-adapted multi-reference linear coupled-cluster (MRCC) formalism for a two-dimensional model space involving closed-shell configurations [B. Jeziorski and J. Paldus, J. Chem. Phys. 88, 5673 (1988)] has been applied to the H_4 model systems studied earlier by Jankowski and Paldus [Intern. J. Quantum Chem. 18, 1243 (1980)]. These systems have the advantage that the degree of quasi-degeneracy may be varied simply by changing the geometry. In the quasidegenerate region, where the single reference LCCSD approximation breaks down, the two-reference LCCSD method performs very well providing good results for both the ground and lowest excited state. However, in the non-degenerate region, the linear multi-reference approach is plagued with intruder state problems, since the second reference state interacts strongly with other excited configurations. Inclusion of the $T_2{}^2$ quadratic terms [J. Paldus, L. Pylypow, and B. Jeziorski in "Many-Body Methods in Quantum Chemistry, U. Kaldor, Ed., Springer-Verlag, Berlin, 1989. pp156-170] resolves the intruder state difficulty. In addition to the trapezoidal model (H4) discussed there, we have also studied rectangular (P4) and linear (D4) models, and have extended the calculations to larger basis sets. We have found that these MRCC equations including the quadratic terms possess multiple solutions capable of describing not only the two lowest states but also highter excited states, as long as they contain a significant contribution from the reference configurations.

F4.2.1

AB INITIO STRUCTURE CALCULATIONS OF HYDROGEN IONIC CLUSTERS

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Ab initio molecular electronic structure theory has been used in an attempt to characterize the low lying stationnary points on the potential energy hypersurfaces of positive ionic hydrogen clusters. Using triple zeta plus polarization basis sets, self consistent field Hartree-Fock calculations have been carried out for H_n^+, n = 3 to 21 (odd). Configuration interaction calculations with double substitutions have been included for n = 3, 5 7 and 9.

WHAT IS THE MOST STABLE STRUCTURE OF NS_2 MOLECULES ?

F4.2.2

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A paramagnetic (neutral) species has been detected[1] by the millimeterwave spectroscopy in a discharge of a mixture of N_2 and CS_2. Judging from chemistry and isotopic substitution, the species is likely to be NS_2. Detailed theoretical studies on the possible structures of an NS_2 molecule, however, have not been done yet. This study aims to find the most probable structure for the NS_2 molecule detected in the spectrum mentioned above. Among many considerable structures for the NS_2 species, SNS bent (${}^2A_1$), SNS linear (${}^2\Pi_u$), NS_2 ring-1 (${}^2B_1$), NS_2 ring-2 (${}^2A_2$), NSS bent (${}^2A'$), SNS bent (${}^4A_2$), and SNS bent (${}^4B_2$) isomers have been investigated at the SCF and CISD levels of theory with various basis sets. The SNS bent (${}^2A_1$) isomer has been found to be the most stable structure among isomers studied in this research.

Reference 1. T. Amano and T. Amano, Abstract RF1, 44th Symposium on Molecular Spectroscopy, June 12-16,1989, Columbus, Ohio

F4.2.3

A MOLECULAR ORBITAL STUDY OF THE CONFORMATIONAL AND ELECTRONIC PROPERTIES OF SULFAMIDE, H_2N-SO_2-NH_2 .

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Ab initio calculations have been used to study the conformational potential surface of sulfamide, by considering the S-N bond rotations and the nitrogen inversion processes. The lowest energy conformation is found for a cis-trans arrangement of the amino groups, although cis-cis and trans-trans conformers lie close in energy. Nitrogen inversion barriers are very low. The relative stability of the different isomers is governed by interactions between amino protons and between the nitrogen lone-pairs. Our results show that d-π backbonding, involving the d orbitals on sulfur, is responsible of the multiple bond character of the S-O linkage, but is small in the S-N interactions. Although the inclusion of d functions on sulfur is crucial to describe correctly the bonding in sulfamide, the results do not change appreciably if a second set of d functions is centered on sulfur. Nevertheless, only if polarization functions are also included for first row atoms the description of the system is reliable.

Ab initio calculation of the electronic structure and spectra of Cu^+:NaF

F4.2.4

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Relativistic Effective Core Potentials (RECP), a treatment of the crystalline environment, and a carefully chosen double group configuration interaction (dgCI)[1] scheme have been used to obtain the local geometry and d-s spectra of a Cu^+ impurity in a NaF crystal.

F4.2.5

Theoretical d-d spectrum of Cr^{3+}:MgO

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We present a theoretical analysis of the spin-orbit effects on the lower electronic states of the Cr^{3+}:MgO system. Our study is based on the calculation of the electronic structure of the CrO_6^{9-} cluster and includes the effect of the external lattice using an *ab initio* Model Potential formalism. The calculation follows the sequence: (a) The best orbitals and potentials for Mg^{2+} and O^{2-} are obtained by minimization of their effective energy in MgO. (b) Similarly, a basis set is obtained for Cr^{3+}, minimizing it effective energy in MgO. (c) The electronic structure of the cluster CrO_6^{9-} *in vacuo* and embedded in the crystal, is computed at several Cr-O distances. (d) The crystalline spin-orbit coupling constants are determined from the molecular orbitals obtained in (c). (e) Finally, the d-d spectrum is obtained, including ligand-field configuration interaction, spin-orbit coupling, crystal lattice effects and correlacion-energy corrections.

F4.2.6

Theoretical calculation of the electronic structure and d-d spectrum of the MnF_6^{2-} complex ion.

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The electronic structure of the octahedral MnF_6^{2-} complex ion has been computed at several values of the metal-fluoride coordinate R by means of an open-shell Hartree-Fock-Roothaan (HFR) formalism over a Slater-type basis set. The HFR equations have been solved for the $^4A_{2g}$ electronic ground state in order to determine the equilibrium geometry and vibrational constants of the cluster from the curvature of the nuclear potential. Closed- and open-shell covalency parameters and the corresponding spin densities have been determined from the cluster wave functions in order to obtain a measure of the 3d orbital deformation upon cluster formation and the nephelauxetic effects. The HFR solutions corresponding to an average quartet state of the $t_{2g}^2 e_g^1$ configuration have been used to find the energy curves of all the electronic states of the $3d^3$ configuration. These solutions are the starting point for the calculation of the d-d spectrum of this cluster at different levels of refinement. The diagonal or first-order description has been complemented with a configuration interaction calculation limited to the ligand-field manifold. Particular attention has been paid to the analysis of the spin-orbit effects on the lower multiplets of this system.

F 4.2.7 *AB INITIO* CHARACTERIZATION OF THE GASEOUS OXIDES P_2O_x (x=1-5)

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The gaseous diphosphorus oxides P_2O_x (x = 1 - 5) have been characterized by *ab initio* electronic structure calculations. A total of 20 stationary points have been located at the HF/3-21G^* level using analytic gradients and the GAUSSIAN86 program. Vibrational frequencies were calculated from analytic second derivatives at this same level for each stationary point. Ten of these points were found to correspond to local minima. Also found is a transition state for the ring opening isomerization of cyclic P_2O (C_{2v}) to linear P_2O. The energetically preferred structures are: P_2O, linear ($C_{\infty v}$), analogous to N_2O; P_2O_2, *trans* planar (C_{2h}); P_2O_3, non-planar oxobridged (C_2); P_2O_4, non-planar oxobridged (C_s); and P_2O_5, non-planar oxobridged (D_{2d}). Isomerization energies were calculated at the $\text{MP2/3-21G}^*\text{//HF/3-21G}^*$ and $\text{MP4SDTQ/3-21G}^*\text{//HF/3-21G}^*$ levels for P_2O_x (x = 1 - 4); it is found that while correlation lowers the energies of P - P bonded isomers of P_2O_3 and P_2O_4 relative to the energies of their oxobridged isomers, the latter are nevertheless energetically preferred, by approximately 11,500 and 15,750 cm^{-1} for these two molecules, respectively. It is noted that the oxobridged structures of P_2O_3, P_2O_4, and P_2O_5 closely resemble the local structures in the tetraphosphorus oxides P_4O_6 and P_4O_{10}, with the tetrahedral structure of P_4O_6 resolvable into a pair of C_2-symmetry oxobridged P_2O_3 moieties.

F4.2.8 Ab Initio COMPUTATIONAL STUDIES OF C8H6 AND S4N2C2: MAIN GROUP INORGANIC ANALOGUES OF PENTALENE?

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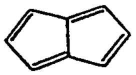

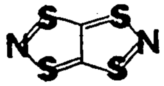

Ab initio calculations at SCF and correlated levels are reported for pentalene, C8H6, and an inorganic heterocycle, S4N2C2. The lowest closed shell singlet state, a lowlying doubly excited state and the corresponding open shell triplet and singlet states were studied computationally. Geometries were optimized with gradient methods and harmonic vibrational frequencies calculated to verify the natures of the stationary points located. Nuclear frameworks of D_{2h} and C_{2h} symmetry were examined in detail.

The relationship between a Second-Order-Jahn-Teller effect which can rationalize the distortion of closed shell singlet pentalene from a D_{2h} to a C_{2h} structure and the stability of the electronic wavefunction to symmetry breaking is considered in light of the ab initio calculations. The SN heterocycle has a closed shell singlet stable to nuclear distortion from D_{2h}. The electron richness of the inorganic heterocycle fills those molecular orbitals which in pentalene are the virtuals involved in a Second-Order-Jahn-Teller rationalization.

F4.2.9 ARYLOXIDE DERIVATIVES OF ACTINIDE(IV) POLYPYRAZOLYLBORATES. STRUCTURAL TRENDS OF URANIUM(IV) BIS[HYDROTRIS-(PYRAZOL-1-YL) BORATE] COMPLEXES.

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Maria José Calhorda, Alberto R. Dias and Adelino M. Galvão
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The complexes $U(HBpz_3)_2(OR)_xCl_{2-x}$ (pz=pyrazol-1-yl; x=1,2; R=Bu^t, C_6H_5, and C_6H_2-2,4,6-Me_3) have been prepared and characterized by variable temperature ^1H-NMR spectroscopy, and/or single crystal X-ray crystallography. ^1H NMR results indicate restricted rotation about the U-O-R bonds for the aryloxide complexes.

Extended Hückel (EHMO) calculations have been used to study the barrier to rotation about the U-O-R bonds, as well as to explain the structural trends shown by X-ray crystallography.

FMO analyses were also made on the model compounds to elucidate the electronic factors responsible for bonding.

F4.2.10 BASIS SET INFLUENCE ON STATIONARY N_4H_2 GEOMETRIES

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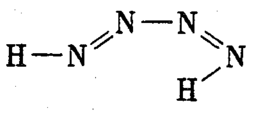
In contrast to other local minima in the potential surface of 1,3-tetrazadiene, the planar cis-E,Z-conformation



shows a drastical basis set dependence at ab-initio SCF level: minimal basis sets and basis sets with polarization functions characterize this geometry as a transition state, split valence basis sets indicate a local minimum. Inclusion of correlation effects does not solve this ambiguity: MCSCF calculations confirm the local minimum, MP results support the transition state.

F4.2.11 THE REACTION OF ALUMINUM ATOMS WITH METHANE. Hengtai Yu+ and John D. Goddard. Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry & Biochemistry, University of Guelph, Guelph, Ontario, CANADA N1G 2W1.

Ab initio SCF and CISD calculations with split valence and larger basis sets have been carried out for several possible reactions of ground state (^2P) aluminum atoms with methane. In particular, the barriers to insertion of Al into a CH bond to give a CH_3AlH intermediate and the abstraction of a hydrogen by Al to give AlH and CH_3 have been studied. At the SCF level, transition state structures have been located and verified by vibrational analyses. In addition, intrinsic reaction coordinates (IRC) have been followed from the transition state geometries down to reactants and to products.

Calculated vibrational frequencies and lowest excitation energy for the CH_3AlH intermediate are in good agreement with matrix isolation experimental results. As anticipated on the basis of MO Natural Correlation symmetry arguments the energy barrier to the insertion reaction is high (~55 kcal.mol^{-1} at the CI level). The energy requirement for the abstraction reaction is similar.

$Al + CH_4 \rightarrow HAlCH_3$ INSERTION
$Al + CH_4 \rightarrow HAl + CH_3$ ABSTRACTION

These SCF and CI results on the ground state surface are necessary prerequisites to ongoing research on the excited state reactivity of Al atoms.

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F4.2.12

ROLE OF SULFURANYL RADICALS IN PRIMARY RADICAL DISPLACEMENT REACTIONS AT SULFUR

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Primary radical displacement reactions at sulfur centers are of particular interest since nucleophilic attack by aryl or alkyl radicals may proceed through a relative energy minimum corresponding to a 9-S-3 intermediate (9 formal electrons about tricoordinate sulfur). Electronic structure calculations performed on a series of model sulfuranyl species, $(H_3C)_3S$, $(H_3C)_2SH$, and H_3S indicate that sulfuranyl radicals conform to the geometric patterns (T-shaped molecular structure) of the phosphoranyl radicals with both the sulfur lone pair and the SOMO assuming equitorial positions. However, for all three cases listed above, the vibrational analysis has indicated sulfuranyl radicals with electropositive ligands are actually transition states for axial-axial displacement rather than the reactive intermediates found with the phosphoranyl radicals.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract DE-AC06-76RLO 1830.

F4.2.13 THE ELECTRONIC STRUCTURE OF HYPERVALENT CHLORINE-OXYGEN COMPOUNDS

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Chlorine and oxygen form an interesting set of compounds of the general formula Cl_xO_y, some of which are thought to be important in ozone destruction chemistry. For $x + y > 2$, more than one isomer exists for each formula. The linear, chlorine terminated, structures such as ClOO and ClOOCl are of normal valency and have electronic structures which are relatively conventional except for some unusually weak bonds. The hypervalent structural isomer of the smaller of these, OClO, also has a relatively conventional (mixed ionic-covalent) representation but the SCF wavefunctions for the (singlet) isomers $ClClO_2$ and OClOCl are "triplet" unstable. That is to say, if an $S_z = 0$ UHF calculation is carried out starting with different alpha and beta orbitals, the expectation value of S^2 for the solution is significantly different from zero and the energy is lower than that of the spin restricted SCF solution. The UHF natural orbital occupation numbers indicate that configurations with one virtual orbital occupied are responsible for the spin symmetry breaking solution in each case. Since the ground states of the latter compounds are poorly represented by a single configuration, treatments such as those of McGrath et. al (Geophysical Res. Let. 15, pp 883-886 [1988]) which depend on single configuration reference functions are not expected to produce reliable results. The results of MCSCF investigations of the ground states of several members of this class of compounds will be represented.

F4.2.14 INTRAMOLECULAR HYDROGEN BONDING IN β-ALANINE AND 3-AMINOPROPANOL

M. Ramek and A.-M. Kelterer, Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010 Graz, Austria.

Both title compounds form an intramolecular H-bond between the $-NH_2$-group and the -OH-group, which have been studied at ab-initio SCF level with the 4-31G basis set. The optimized geometries differ remarkably: the 3-aminopropanol conformation is similar to the chair form of cyclohexane, β-alanine forms an envelope like structure in which the -COOH-group, the N-, and the α-C-atom lie almost exactly in one plane. These geometries and the reaction paths induced by internal rotations of the bonds N-C—C-C, C-C—C-O, and C-C—O-H are discussed in detail.

F4.2.15

COUNTERPOISE CORRECTIONS ON EQUILIBRIUM GEOMETRIES AND INTERACTION ENERGIES OF A SIMPLE H-BONDED COMPLEX: FORMAMIDE + H2O.

D.Dehareng and G.Dive, Service de Microbiologie, Universite de Liege, Belgium.

The determination of the stable conformations of two or more interacting species is one of the most crucial challenges, in particular when big partners are involved, such as an enzyme active site model and its ligand.

Hence, approximations are to be made in the treatment of such big systems and therefore, it is important to know what their implications at a given level are. One of these concerns the basis set superposition error.

We chose a very simplified model to deal with H-bonded interactions: the complex water-formamide. The influence on the equilibrium values of the intermolecular complex coordinates, as well as on the interaction energy has been studied within four basis sets: 3-21G, 4-31G, 6-31G and 6-311G. The most drastic differences are found with 3-21G, namely on the energy. However, the equilibrium geometries are hardly sensible to the counterpoise corrections in all the studied basis sets.

F4.2.16

EXPLORATIONS ON THE POTENTIAL SURFACES OF AH_n-BENZENE COMPLEXES

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Benzene forms weak complexes with small polar molecules, AH_n, where A is an electronegative first- or second-row atom. Gradient search techniques have been employed in conjunction with ab initio molecular orbital theory to locate minima in the potential-energy surfaces of the $AH_n \cdots C_6H_6$ systems. Parameters describing the position of AH_n relative to the benzene ring were treated as variables. The geometry optimizations were carried out using the 3-21G(*) basis set, which has polarization functions only on second-row atoms. In order to reduce the basis set superposition error and include effects of electron correlation, second-order Moller-Plesset theory was used with the larger 6-31G* basis set to determine the energy in a single point calculation at each minimum.

F4.2.17

Abstract

NEW CRITERIA FOR AROMATICITY P.Friedman*, Department of Chemistry . Pratt Institute . Brooklyn , N.Y. 11205 and L.C. Allen , Department of Chemistry , Princeton University , Princeton , N.J.

Several new criteria for "aromaticity" have been developed for heteroaromatic molecules . These criteria are all derived from the coefficients of the lowest π molecular orbital of the molecules as calculated by ab initio MO methods .
A study of 5 membered ring heteroaromatic compounds of the type : [X=O,S,NH ;Y=N,CH :Z=N,CH] was carried out using Gaussian 82 with 3-21G and 3-21G* basis sets and experimental (microwave) geometries to calculate eigenvalues , eigenvectors and RHF energies for this set of compounds . The coefficients of the lowest π molecular orbital of each molecule were used to calculate a number of aromaticity indices , the most useful of which proved to be N and mdq . Both of these criteria correlated very well with experimental measures of aromaticity such as X^{nlcl} and resonance energies. A large number of other aromatics have been successfully studied by these techniques .

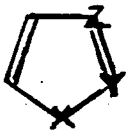

Table 1. Aromaticity Criteria

					nlcl	cmb	
Compound	N	mdm	mdq	Bird A	X	ERE	DRE
Furan	0.6815	0.1022	0.1976	43	-25.3	33.5	18.0
Pyrrole	0.7846	0.061	0.1324	59	-31.9	62.8	22.2
Thiophene	0.8683	0.036	0.041	66	-39.1	66.9	27.2
Oxazole	0.7476	0.0949	0.1699	38	-29.2		
Isoxazole	0.7415	0.1038	0.1682	47	-26.9		
Imidazole	0.8193	0.0670	0.1090	64	-34.7		
Pyrazole	0.7846	0.085	0.121	73	-33.9		
Thiazole	0.8857	0.0263	0.0362	64	-39.6		
Isothiazole	0.8691	0.0446	0.0607	59	-38.1		

F4.2.18

A THEORETICAL STUDY OF THE $-\overset{\ominus}{B}$ C- TRIPLE BOND

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Molecular anions containing the $\overset{\ominus}{B}C$ triple bond have been studied using ab initio molecular orbital theory at the SCF and CISD levels with several different basis sets. The dependence of optimised structures, dipole moments and harmonic frequencies on the inclusion of diffuse functions in the basis set is investigated. The anion $H\overset{\ominus}{B}CH$, which is isoelectronic with acetylene, is found to contain a formal BC triple bond and $H\overset{\ominus}{B}CBH_2$, which is isoelectronic with $H\overset{\ominus}{C}CCH_2$, is found to contain a partial BC triple bond and a partial BC double bond. The x-ray analysis of a system containing the-$\overset{\ominus}{B}CB<$ moiety with large substituent groups yielded experimental bond lengths in good agreement with the theoretically predicted values.

The empty p orbital on boron when it has a valency of 3 dominates its chemistry and the partial bonding in the $H\overset{\ominus}{B}CBH_2$ anion can be interpreted in terms of overlap between an occupied π_{BC} orbital and the empty p orbital on the BH_2 boron atom.

F4.2.19

AB INITIO SEARCH FOR THE STRUCTURE OF THE 4–PROTOADAMANTYL CATION.

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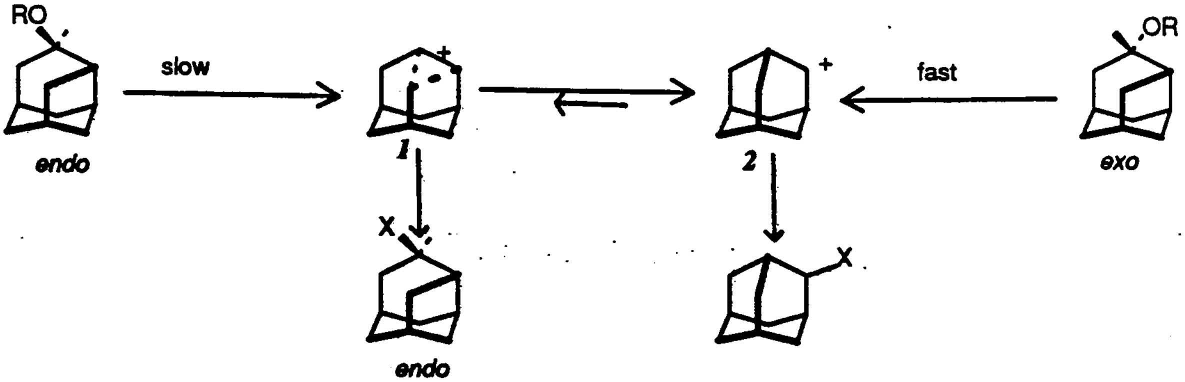
Solvolysis of 4–*exo* and 4–*endo*–protoadamantyl derivatives proceeds with an *exo*/*endo* reactivity ratio of ~10^4. Evidence based on product analysis suggests that different intermediate "4–protoadamantyl" carbocations *1* may be involved. *Ab initio* calculations at the 6–31G and 6–31G* levels suggest that there are local minima corresponding to two



different structures of "4–protoadamantyl" cation. The relative energies, electronic structures and probable reactivities of these two structures, and their relationship to 2–adamantyl cation *2* are discussed.

F4.2.20

STABLE STRUCTURES OF SMALL CATIONS IMPORTANT IN THE INITIAL STAGES OF SOOT FORMATION.

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Two mechanisms have been postulated to be of importance in formation of soot in fuel rich flames. One of these involves small radicals the other small cations. The $C_3H_3^+$ ion is found in quite high abundance in fuel-rich and sooting flames. It has been conjectured that C_3H_3 forms $C_5H_3^+$ and $C_5H_5^+$ by reaction with acetylene. Some results of numerical calculations on various stable structures of $C_5H_3^+$ and $C_5H_5^+$ and possible reactions with acetylene are presented.

F4.2.21

WAVELENGTH DEPENDENCY OF 1,3-CYCLOHEXADIENE TO 1,3,5-HEXATRIENE RING OPENING REACTION

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Diarylethene derivatives show photochromic property which consists of ring opening and closing intramolecular reaction by light. This ring opening reaction has shown remarkable wavelength dependency of quantum yield. In an attempt to understand the mechanism, we have carried out CASSCF calculations on the model system of the titled compounds. Ground states geometries are optimized along the conrotate reaction path at the RHF level by using 3-21G basis set. Then utilizing these geometries, we have obtained even balanced CASSCF solutions for S1 and S2, with six orbitals and six electrons. The crossing of the S1 and S2 potential surfaces has appeared in the reactant 1,3-hexadiene side.

F5.1

THE PIVOT ALGORITHM AND POLYGONS: RESULTS ON THE FCC LATTICE.

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ABSTRACT.

We consider the pivot algorithm, recently proposed by Madras and Sokal for walks and by Madras, Orlitsky and Shepp for fixed endpoint walks on the hypercubic lattice, for polygons on the face-centered cubic lattice. We prove ergodicity of the algorithm on this lattice. A numerical study of the algorithm is carried out, in particular, we look at the acceptance fraction of the elementary moves and find that it goes only slowly to zero as the length of the polygons is increased. The numerical properties of polygons on the fcc lattice are considered and we calculate the exponent (by considering the mean square radius of gyration of the polygons) and compare the result to the expected value (from field theory). We also consider the mean span of the pogons and discuss corrections to scaling and the influence it has on numerical calculation of critical exponents.

F5.2

CHARGE STATE STABILITY OF Ni AND Cu IN MgO.

J.M. Vail*, University of Manitoba, and J. Meng+ and P. Jena+, Virginia Commonwealth University.

Charge states +1, +2, and +3 of Ni and Cu in MgO are investigated for stability against electron transfer and electron capture. The impurity and its six nearest-neighbor oxygen ions are treated as a molecular cluster embedded in a classical shell-model lattice. The cluster is treated in unrestricted Hartree-Fock self-consistent field approximation. Relaxation of the cluster, and distortion and polarization of the embedding lattice, are treated consistently in evaluating the total crystal energy for each defect.

* Supported by NSERC Canada.

+ Supported by U.S. Department of Energy under grant No. DE-FG05-87-ER45316.

F5.3

Ab Initio Studies of the Beryllium Bulk/Cluster Interface.

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The interface between bulk and cluster-like behavior has been investigated via ab inito calculations on large clusters of Be atoms. Calculations are carried out at the Hartree-Fock level of approximation. Systems under study include clusters of up to one-hundred thirty-five Be atoms. The largest cluster corresponds to sixteen coordination spheres of a central Be with internuclear seperations derived from the lattice constants of the bulk metal. Ab initio effective core potentials are employed to replace the effects of the 1s electrons reducing the complexity of the calculations. In addition, the use of full D_{3h} point group symmetry results in a substantial reduction in the number of two-electron integrals that must be computed and processed. Properties calculated for selected states include binding energy, electric field gradient, nuclear-electron potential, diamagnetic shielding constant, second moments, quadropole moment, and Mulliken populations. In addition, density of states diagrams are derived and compared to that of bulk Be metal.

F5.4

VALENCE AND CORE ELECTRONIC STRUCTURE OF THE 90K SUPERCONDUCTOR Y-Ba-Cu-O *

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As an important step toward the justification of cluster calculations for the study of the electronic structure of high-temperature superconductors, the cluster size dependence of results for $YBa_2Cu_3O_7$ is investigated with the relativistic scattered-wave approach. Cluster sizes range from single Cu-O layers with some of the neighboring Y, Ba, and O atoms modeling the Cu-O chains and planes to clusters including up to four Cu-O layers (39 atoms) and a simulation of the ionic crystal environment. The convergence of the results is discussed for the calculated charge distribution, core and valence energy levels, and derived densities of states in comparison with X-ray, UV, and inverse photoemission spectra and other theoretical results. It is shown that already relatively small clusters give a reasonable description of the Cu 3d - O 2p derived density of states between 0 and -8 eV relative to the cluster Fermi level.

* Supported by NASA Lewis Research Center, Cleveland, Ohio.

F5.5 | ELECTRONIC STRUCTURE: MANY-PARTICLE SPECTRUM OF SUPERCONDUCTING $YBa_2Cu_3O_7$. G.A.R. Lima, R. Mota and A. Fazzio, Instituto de Física da USP, Dept. de Física dos Materiais e Mecânica, CP 20516, 01498 São Paulo, SP, Brazil.

We investigate the electronic structure of superconducting $YBa_2Cu_3O_7$ through a molecular cluster approach, using clusters Cu_xO_y simulating different directions within the crystals. The crystalline environment is simulated by inclusion, in place of Ba and Y, of elements from the same column of the periodic table (and not by inclusion of non-interacting point charges) such as Sc and Ca. The calculations are performed selfconsistently through a semiempirical LCAO technique, in which correlation effects are taken into account by a configuration interaction procedure INDO-CI). The spectra for the clusters are obtained using up to 180 Slater determinantal functions, built from the Hartree-Fock ground state function by single and double excitations involving Cu-d and O-p orbitals. We obtain for the ground state a strong p-d covalency, resulting in a width of ~ 7 eV for the valence band which is in good agreement with the experimental data. Also the interaction of Cu 1 and 2 with O 1,2,3 and 4 is analysed in detail showing how hybridization occurs.

F5.6 | HIGH-ORDER INTERACTIONS IN HIGH-PRESSURE MOLECULAR SOLIDS

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Ab initio calculations of interaction energies in solid H_2 at four pressures (3, 1, 0.5 and 0.1 Mbar) will be compared to results from cluster and N-body calculations, performed at equivalent levels of accuracy. For the cluster models, it will be demonstrated that convergence to the asymptotic interaction energies at all pressures occurs very slowly. For the N-body models, calculations including up to 10-body interaction potentials will show that use of few-body potentials alone provides poor representations of solid systems at high pressures.

F5.7

ROVIBRATIONAL DYNAMICS OF ARBITRARY N-BODY SYSTEMS*

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Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

A novel scheme for characterization of the intricate dynamics of nonrigid systems in terms of an overall rotation and internal motions is introduced. Its main merits are that it is applicable to arbitrary N-body systems, irrespective of the degree of their nonrigidity and of the amount of energy in the rotational degrees of freedom. The centrifugal distortions due to the rotation are explicitly taken into account in the analysis of the vibrational dynamics. This analysis is carried out in terms of normal modes which depend on the total angular momentum of the system. The scheme is applied to study the structural and dynamical properties of rotating and vibrating Lennard-Jones clusters.

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*Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

F5.8

RELATIONSHIPS BETWEEN STABILITY, GEOMETRY AND BONDING IN SMALL LITHIUM CLUSTERS : A CHARGE DENSITY TOPOLOGICAL APPROACH

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The study of the electronic structure of planar $Li_n(n=2.6)^1$ and $Na_m(m=2,4)^2$ clusters has led to the discovery of non nuclear maxima (pseudoatoms = *Ps*) in their charge distributions.

This study is here extended to $Li_n(n=6,10)$ 3D-clusters, within the framework of the quantum theory of atoms in molecules[3]. *Pss* are found for each of the examined clusters and they are always linked to one another. Li-Li bonds are never observed. *Pss*' number, location and topological characteristics (including critical point properties, number of other *Pss* linked, number and type of lithium atoms linked) are related with the rate of increase of the binding energy per cluster atom.

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2) W.L. Cao, C. Gatti, P.J. Mac Dougall, R.F.W. Bader, Chem. Phys. Lett., 141,380 (1987)
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A New Quantum Mechanical Description of Solid Neon.

F5.9

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The *ab initio* Perturbed Ion (PI) method is a novel quantum mechanical approach designed to compute the electronic structure of ionic solids. It has been successfully applied to alkali hydride and halides. The mathematical structure of the PI method suggest further applications to materials with different bonding types. We present here preliminary results, limited to solid Neon, of a systematic analysis of the electronic structure of rare-gas crystals in terms of the PI approach.

In the PI calculation the Hartree-Fock-Roothaan equations of a given atom-in-the-lattice are solved for a Fock operator containing nuclear attraction, coulombic and non-local exchange repulsion, and lattice projectors that enforce the atom-lattice orthogonality. The resulting SCF solutions are used to compute the lattice potential and the process is iterated until atom-lattice consistency is achieved. The PI method does not use the LCAO approximation. This means slightly smaller variational freedom but also lack of well-known difficulties like improper dissociation and basis-set superposition error.

F5.10 ON THE ABSTRACTION OF HYDROGEN FROM DIAMOND (111) SURFACES. Steven M. Valone, Materials Science and Technology Division, MS E549, Los Alamos National Laboratory, Los Alamos, NM 87545 USA. A recent proposal by Frenlach and Spear[1] contends that activation of the diamond surface by hydrogen abstraction is a controlling step in the synthesis of diamond films by plasma enhanced chemical vapor deposition. To gain more insight into the behavior of this process, a sequence of semiempirical molecular orbital calculations are used to construct a set of one dimensional potential energy surfaces for the process of abstraction of a hydrogen atom from a hydrogen covered diamond (111) surface by a hydrogen atom. Each potential curve represents an incoming hydrogen atom at a specified angle of incidence relative to the surface normal. The distance of closest approach is selected to allow the formation of molecular hydrogen. The barrier to the abstraction process will be estimated as will the relative importance of quantum effects on the height of the barrier. The degree of tunneling, which influences the height assigned to the barrier, may be estimated from temperature-dependent effective potentials derived from existing quantum path integral techniques.

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[1] M. Frenlach and K. E. Spear, J. Mater. Res. 3(1), 133 (1988).

S1.1

PRODUCTIVITY, GLOBAL SIMULATIONS & EVOLUTION IN SUPERCOMPUTING & SUPERCOMPUTERS, ...Dr. Enrico Clementi

In the last forty years we have witnessed the birth and evolution of computers, minicomputers, personal computers and supercomputers. However, all the available indications point to the expectation that we are only at the beginning of a new socio-economic era, where computing machines and signal processing machines will play a most determinant role.

The global simulation approach is an "assembly line" designed to increase our productivity in generating information. For example in chemistry and related subjects we start with the assumption that molecules are built up of point charge nuclei and electrons, and this is one of the bases of quantum chemistry. With quantum mechanics we can then "assemble" simple molecules, or larger ones. With statistical mechanics we can consider many molecules at a given pressure and temperature, and consider trajectories involving time; finally for even larger systems we can use micro-dynamics and fluid dynamics where viscosity, transport coefficient, convection, turbulence, etc., etc., can be analyzed. Of course all this is well known at the theoretical level, but the novel aspect we have been stressing is how to achieve this at the operational level in such a way that the entire process is self-consistent for computer simulations.

In this lecture we consider in some detail both the relationships between "global simulation modeling" and productivity (as it is known, the latter correlates both to goods and to information), and the relationships between the productivity of goods and information and the evolution of computer's applications.

S1.2

AN EXAMINATION OF THE CONFORMATIONS RESPONSIBLE FOR THE SWEETNESS OF HEXULOSES USING THE SEMI-EMPIRICAL MOLECULAR ORBITAL METHOD, AM1.

Robert J. Woods, Walter A. Szarek, and Vedene H. Smith, Jr., Department of Chemistry, Queen's University, Kingston, ON, K7L 3N6.

The AM1 optimized geometries and energies of two naturally occurring sugars, β-D-fructopyranose and α-L-sorbopyranose, and the synthetic derivatives, 5-deoxy-β-D-threo-hexulose (5-deoxy-fructose) and pseudofructose provide an explanation for the relative sweetness of these compounds. Results are discussed in terms of conformational stabilities and hydrogen bonding. A novel approach to predicting the global energy minima of monosaccharides is presented.

S1.4 I THE USE OF MOLECULAR DYNAMICS IN THE SIMULATION OF FREE ENERGIES OF ASSOCIATION OF MOLECULES. P. A. Kollman. Department of Pharmaceutical Chemistry, University of California, San Francisco, CA 94143, USA.

We review the methodology and results of free energy calculations applied to proteins, nucleic acids, ionophores, and porphyrins. This method has the capability of giving results in excellent agreemnet with experiment leading to new mechanistic insights and making accurate predictions of the results of future experiments.

S1.5 STRUCTURAL EFFECTS ON THE ACIDITY OF ASPARTIC PROTEINASES

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Hebrew University of Jerusalem, Jerusalem, ISRAEL 91120

Eight amino acids form the core of the active site of aspartic proteinases (**AP**): four from the sequence 32-35 (pepsin no. system), and four from the sequence 215-218. Those residues are D-T-G-S/D-T-G-T in the pepsins, D-T-G-S/D-T-G-A in human renin and a dimer of D-T-G-A in AIDS virus (HIV-I and HIV-II) aspartic proteinase. Semiempirical quantum mechanics (**MNDO/H**) was employed to follow the energetics of deprotonation in the active sites of those enzymes- from neutral to mono and to di-anion. On the basis of crystallographic coordinates of endothiapepsin, T-218 was transformed to Ala (for human renin) and both S-35 and T-218 were transformed to Ala for the HIV AP. The results indicate that the active site of endothiapepsin is more acidic than that of human renin, which is itself more acidic than HIV AP. Such results could explain the experimental shift towards less acidic pH of the optimum in the pH activity profile of human renin compared to the pepsins. The results also indicate that it may be possible to design specific inhibitors to each of those enzymes which would exploit their acidity differences.

S2.1 I ALGEBRAIC APPROACH TO MOLECULAR STRUCTURE

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The use of algebraic methods in molecular structure will be reviewed. The relation between the algebra of U(4) and the spectrum of the three-dimensional Morse oscillator will be discussed. It will be shown how, starting from this relation, one can construct a systematic approach to the spectra of polyatomic molecules. Specific examples (HCN, C_2H_2, ...) will be presented.

S2.2

ATOMIC SUPERSYMMETRY

V. Alan Kostelecký

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There is evidence for a phenomenological quantum–mechanical supersymmetry between atomic spectra. The comparison of valence–electron transition probabilities in supersymmetric and hydrogenic schemes suggests that this supersymmetry provides insight into many–body properties of atoms. Quantum defects can be incorporated in a supersymmetry–inspired exactly solvable model. Transition probabilities calculated with the associated analytical wavefunctions show agreement with accepted values. The fine structure naturally incorporates a Landé factor.

Recent developments in the unitary group approaches to the many-electron correlation problem

S2.3

J. Paldus

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University of Waterloo
Waterloo, Ontario, Canada

Abstract:

Several new developments in UGA (Unitary Group Approach) to the many-electron correlation problem will be briefly reviewed. The relevance of Clifford algebras (CA) for many-electron systems and the exploitation of the resulting CAUGA formalism for system partitioning, valence-bond-type methods and coupled-cluster approaches will be discussed. Finally, the role of isoscalar factors for the Racah-Wigner algebras that are relevant in many-electron problems will be outlined, its connection with standard UGA formalism pointed out as well as its exploitation for the description of spin-dependent or particle-nonconserving systems.

S2.4

AB INITIO RELATIVISTIC CALCULATIONS FOR DIATOMICS OF HEAVY AND SUPERHEAVY ELEMENTS, ...

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Ab initio Dirac-Fock (DF) calculations for various diatomics of heavy and superheavy elements will be presented. These calculations have been performed using the RIP program with the chemical basis set(1,2). The effect of relativity on the chemistry of these elements will be discussed.

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2. G. L. Malli, Ab-Initio Relativistic Quantum Chemistry in, Maruani, Jean (ed.), Molecules in Physics, Chemistry and Biology, Vol. II, 85-144, Kluwer Academic Publishers, 1988.

S3.1

MOMENTS AND THE ENERGIES OF SOLIDS

Jeremy K. Burdett, Chemistry Department and James Franck Insitute, The University of Chicago, Chicago, IL 60637, USA

Results from the method of moments are used to understand the energetic preferences associated with molecules on surfaces, and of solids and surfaces of various types. The approach gives a topogeometric viewpoint of electronic stability which is considerably easier to understand than more conventional approaches.

V_{res} $\mu = \sum_i \epsilon_i^n$

S3.2

LDF STUDIES OF TITANIUM HYDRIDE CLUSTERS

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Tunneling-induced cold fusion — enhanced by chemical confinement of deuterons — has been suggested as an explanation of recent reports of the production of neutrons and excess heat in electrochemically-generated metal deuterides. Local-density-functional (LDF) cluster calculations were used to study the the chemical forces between two deuterium atoms in the octahedral and tetrahedral interstitial sites in the titanium lattice as modeled by six and four titanium atoms respectively. The titanium-atom nearest-neighbor distance in these clusters was fixed at 5.58 Bohr. Forces were computed for deuterium-deuterium distances from 0.1 Bohr to the dimension of the model cluster. In no case were the repulsive forces between deuterium atoms less than the replusive forces calculated for molecular D_2. Along directions of lowest total energy, no minimum was found for either interstice. These results are consistent with our earlier calculations on palladium hydride and have implications for possible models of cold fusion in metal lattices.

S3.3 SIMULATION OF MATERIALS; THE THEORY OF HIGH T_C SUPERCONDUCTIVITY.

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To understand the superconductivity in $La_{2-x}Sr_xCu_1O_4$, $Y_1Ba_2Cu_3O_7$, and $Tl_2Ba_2CaCu_2O_8$, we carried out quantum chemical (generalized valence bond) calculations on various clusters to obtain information about the electronic states and magnetic interactions of the oxidized systems. In addition, we developed the valence-bond band method for calculating the energy bands for these systems. This led to the magnon pairing model for high T_c superconductors in which the disordered Heisenberg lattice of antiferromagnetically coupled copper d spins serves a role analogous to the phonons in a conventional BCS system. Magnon pairing theory has been used to solve self-consistently for the superconducting energy gap as a function of temperature, and from the results the critical magnetic fields, the specific heat, and the tunneling as a function of temperature. This model suggests modifications of current materials (replacing Cu and O) to increase T_c and to increase critical current densites.

S3.4 ELECTRONIC STRUCTURE OF COPPER OXIDES: IMPORTANCE OF LOCAL RELAXATIONS AND CHARGE-TRANSFER EXCITATIONS

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The electronic structure of CuO_2 sheets such as present in high Tc superconducting copper oxides is studied by ab initio calculations on small copper oxide clusters. The crystalline environment of the clusters is simulated by point charges and point polarizabilities.
States with intrinsic and induced holes respectively are studied by non-orthogonal CI calculations between relaxed (MC)SCF states. This approach allows for the inclusion of local relaxation effects, as well as oxygen-oxygen and copper-oxygen charge transfer interactions.
The lowest intrinsic hole states are mainly of Cu(d9) character. States with an extra hole are of Cu(d9)O(2p) type. Low lying Cu(d9)O(2pσ) states contain important contributions from Cu(d8) configurations. This effect is largest when the two spins are singlet coupled. For Cu(d9)O(2pπ) states Cu-O charge transfer interactions are much smaller.

S3.5 THE COMPUTATION WITH MINDO/3 OF LOCAL-MODE VIBRATIONAL FREQUENCIES OF CARBON AND OXYGEN DEFECTS IN CRYSTALLINE SILICON, Rongzhi Wu and Lawrence Snyder Chemistry Department, State University of New York at Albany, 1400 Washington Avenue, Albany, New York 12222 U.S.A.

We have employed the MINDO/3 method of Dewar, modified by us for efficient calculation of defect local-mode vibrational frequencies in solids, to predict the local-mode infra-red spectra of carbon and oxygen containing point defects in crystalline silicon.

We will describe applications to the known defects; interstitial oxygen, oxygen in a vacancy, and two oxygen atoms in a vacancy. The use of this program to establish the structure of the Si-G15 defect will be shown.

AN ALGORITHM FOR COMPUTING MOLECULAR VOLUME.

S4.1

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Molecular volume is an important physical property of a molecule. It has been related to properties like solubility, toxicity, scattering intensity, etc. We have developed a numerical algorithm 'ANU' for computing volume enclosed by a van der Waals surface*. The volume is estimated by the volume of cubes enclosed by the surface. The algorithm can compute volume with specified accuracy by subdivision of cubes partly contained within the surface. It converges to the exact volume from below and the upper bound of the error is also computed. ANU has a very low orientation dependence. This method being a numerical method can be easily adapted for surfaces other than of the van der Waals type.

*Master's thesis by Charu Hungenahally, 'Study of Molecular Surfaces and Molecular Volumes', 1989.

S4.2 THEORETICAL STUDY OF SODIUM CHANNEL BLOCKING BY AMILORIDE AND ITS ANALOGS

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Ab initio electrostatic potential surfaces have been used to investigate the sodium channel blocking properties of Amiloride in various epithelial tissue types. Several structural analogs of this novel acylguanidine possess similar blocking properties, though with lower binding affinity than Amiloride itself. The purpose of this study is to look for common features in the electrostatic surfaces for this series of molecules, with the aim of developing a general binding template (pharmacophore) for the interaction of Amiloride with the sodium channel.

S4.3 THE EFFECT OF MOLECULAR CONFORMATION ON THE DETERMINATION OF POTENTIAL DERIVED ATOMIC CHARGES.

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A method of determination of atomic point charges for use in molecular mechanics and dynamics calculations involves fitting atomic charges to the quantum-mechanically determined electrostatic potential of the molecule. This technique results in atomic charges which, relative to Mullikan charges, are basis-set independent and more accurately reproduce molecular dipole moments. The results presented here examine the effect of molecular conformation on the derived charges; in particular, they address the question of how well the atomic point charges determined for a molecular in one conformation represent the quantum-mechanically determined electrostatic surface calculated for the molecule in a different conformation. Electrostatic potential surfaces and derived charges are calculated for 0^o and 90^o inter-ring twist conformations of the 1-, 2- and 4-isomers of phenylimidazole. Charges computed for one conformation are used to test how well they fit to the ab initio potential surface of the other conformation. In addition, molecular modelling results obtained with the 0^o and 90^o conformation charge sets are compared for each isomer of phenyimidazole.

S4.4 USE OF SEMI-EMPIRICAL (AM 1) IONIZATION POTENTIALS TO EXAMINE SINGLE ELECTRON TRANSFER (SET) REACTIONS OF CHEMICAL AND BIOLOGICAL SIGNIFICANCE.

E. Pop[1,2], M. E. Brewster [1,2], D. Doerge[3], J. J. Kaminski [2,4] and N. Bodor[1,2].
[1]Pharmatec, Inc., P.O. Box 730, Alachua, FL 32615; [2]Center for Drug Design and Delivery, College of Pharmacy, University of Florida, Gainesville, FL 32610; [3]Department of Agricultural Biochemistry, University of Hawaii, Manoa, HI 96822; [4]Schering-Plough Corporation, Bloomfield, NJ 07003.

The AM 1 approach, a semi-empirical all valence electron molecular orbital method, was used to study three reactions which are thought to proceed via an initial electron ionization. These included ferricyanide-mediated oxidation of a series of 1-(4-substituted phenyl)-1,4-dihydronicotinamide, oxidation of various sulfur containing compounds by horseradish peroxidase (HRP) and oxidation of a series of para-substituted thioanisoles by chloroperoxidase (CPX). In the first reaction, the energy required to remove an electron from the highest occupied molecular orbital (HOMO) i.e. the vertical ionization potential (I.P.) were calculated (using Koopman's theorem) for a set of seven dihydronicotinamides. The values obtained were highly correlated ($r=0.981$) with the log of the second order rates of chemical oxidation. This result is mechanistically consistent with an initial rate-determining electron loss. Based on the calculated correlation data, the rate constant for three dihydronicotinamides was determined. These were found to be within error of experimental values. In the second study, calculated vertical I.P. were found to be significantly correlated ($r=0.96$) with the log (k_{cat}/k_m) for a series of three sulfur containing compounds which had been subjected to oxidation by HRP. The compounds studied were thioanisole, benzylmethylsulfide and thiobenzamide. In extending this approach, literature values for the oxidation of a series of 4-substituted thioanisoles by CPX was examined. Again, a significant ($p<0.01$) correlation was obtained with vertical I.P. and the data were shown capable of accurately predicting the rate constants for two derivatives. These studies indicate that semi-empirical methods such as AM1 may be very useful in the design of various enzyme inhibition and suicide substrates of therapeutic value.

S4.5 A METHOD FOR THE CHARACTERIZATION OF FOLDINGS IN PROTEIN RIBBONS MODELS

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The ribbon model of chain macromolecules is a useful tool for analyzing some of the large scale shape features that these complex systems exhibit. Up to now the ribbon model has been used mostly to produce graphical displays, which, as a rule, are analyzed by visual inspection. In this communication we suggest a computational method for characterizing automatically, in a concise and algebraic fashion, some of the shape features of these ribbon models. The procedure is based on a graph-theoretical and knot-theoretical characterization of three well-defined projections of a space curve associated to the ribbon. The graphs can be characterized by the handedness of the crossovers in the ribbon that are the vertices of the graph, whereas the knots can be characterized by polynomials. The method can be used to provide a algebraic representation of the changes in the folding pattern of a molecule, such as a protein, undergoing conformational rearrangements, as well as to provide a shape comparison for a pair of related molecular ribbons. Illustrative examples of the method are provided.

S5.1

APPLICATION OF A PADE-APPROXIMATION FORMULA FOR THE KINETIC-ENERGY FUNCTIONAL OF ATOMS.

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A recent kinetic-energy functional of DePristo and Kress [Phys. Rev. A 35, 438 (1987)] is used in variational density-functional calculations of the total atomic binding energy, using the Ne atom as an example. In addition to the kinetic-energy functional, the total-energy functional contains the nuclear-electron interaction functional, the classical electron-electron interaction functional, and the Perdew-Wang [Phys. Rev. B 33, 8800 (1986)] exchange-energy functional. Two-parameter and three-parameter calculations are carried out with an electron (number) density that is modeled by using hydrogen-like one-electron wave functions (with the 2s function orthogonalized to the 1s function) containing two and three variational parameters, respectively. The results, -127.18 a.u. and -129.94 a.u., respectively, are compared with the Roothan-Hartree-Fock single-zeta energy value of -127.81 a.u., as obtained by Clementi and Roetti [At. Data Nucl. Data Tables 14, 177 (1974)].

BORN AND BORN-MAYER POTENTIALS AS ANTIANNIHILATION BARRIERS IN ATOM-ANTIATOM INTERACTIONS, WITH REFERENCE TO COLD FUSION.

S5.2

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The potential energy (PE) curve of H2 is calculated using the atom-antiatom scheme introduced previously. Only electrostatic Coulomb hydrogen-antihydrogen interactions are thereby considered but, in order to obtain an extremum, Born or Born-Mayer type repulsive potentials are introduced, in order to avoid collapse of the bond just like in ionic anion-cation interactions.

The results are in satisfactory agreement with experiment, especially if the simplicity of the calculation is considered, and illustrate therefore the usefulness of the atom-antiatom scheme in theoretical chemistry.

The potential of this scheme for cold fusion experiments is discussed briefly.

S5.3

FINITUDE OF THE NUMBER OF ELEMENTS

ORIADE, J O O
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We first prove that the universe is finite. We then prove that the universe has at most 18 roots or elements. Our current universe is then compared to the new found universe. The agreement for the biological and chemical universes are excellent.

S5.4 AN ANALYSIS OF REACTION SPHERES AND REACTION TORI

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The global analysis of potential energy surfaces based on the Oppenheimer approximation is important in studying chemical reaction mechanisms. In the topological model of molecular structures, each critical point on the potential energy surface corresponds to a possible chemical structure. If one finds all the critical points on the potential energy surface, then all the corresponding chemical structures and reaction mechanisms will be known. Similarly to the 3-polytopes in the three dimensional space, some simple reaction systems can be modelled by reaction spheres and reaction tori for which a complete analysis can be given.

S5.5

AN APPROXIMATION TO $E \otimes \varepsilon$ VIBRONIC STATES.

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An approximation method is introduced to describe linear as well as linear-plus-quadratic $E \otimes \varepsilon$ vibronic states. It is found in this method that for the linear coupling case, the two Born-Huang (and Born-Oppenheimer) potential curves for the nuclear radial motion are non-degenerate, in contrast to the conventional Born-Huang and Born-Oppenheimer methods. For the lowest internal angular quantum number 1/2, the lower potential curve is attractive. For linear as well as linear-plus-quadratic coupling, evident improvement has been achieved.

S5.6

INDUCED S_n-SYMMETRY SCHEMES FOR SPIN-1/2 CLUSTERS: LIOUVILLE SPACE CONTRASTS BETWEEN DIAGRAMATICALLY DERIVED KOTANI FORMS AND THE EXACT IRs DEFINING THE S_n/SO(3) CARRIER SPACES FOR $(k_i=1)$-SPIN CLUSTERS.#

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Extended Kotani-augmentation schemes for clusters of identical one-half spins under the S_n groups are considered within Liouville space formalisms of NMR spin dynamics. Use of the rank partitional form under S_{n-1}, set out as a simply reducible (SR) initial space, allows one to derive the $[\lambda]^k$ (S_n) forms over the correct augmented space; the precise statistical frequencies associated with the degenerate IRs require an algebraic approach.

An exact description of S_n/SO(3) Carrier Spaces is given in a Mathematical Lemma for $\{\tilde{\Gamma}(S_n)|D^k(\tilde{U})\}$ duality over Liouville space, which extends the Hilbert space formalisms of Louck and Biedenharn[1] and generalizes some recent work[2] on the Liouvillian quantum mechanics of the $\sigma(S_n)$ density operators for spin cluster NMR problems.

Outline of MS submitted to Chem. Phys. Letters, Apr. 1989, and revised June '89.

1. J.D. Louck and L.C. Biedenharn, in 'The S_n- group in Physics and Chemistry (LN:12) 1979, pp 121-163. 2. F.P.T. Chem. Phys. 132 (1989) 9-31.

S5.7 | S_n-ADAPTED LIOUVILLE SPACE IX: ROLE OF SCALAR INVARIANTS AND LEXICAL COMBINATORICS OVER A FIELD IN DERIVING EXPLICIT $|KQ(k_1-k_4):[\lambda]S_4\rangle\rangle$ TENSOR BASES.#

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Combinatorial arguments derived from lexical sets and 'Invariants over a field' are utilized to form the dual-group spin tensors; these are inherent in formulations of the $\sigma(S_4)$ density operators for the $[A]_4^{I_i}$ and $[AX]_4^{I_i}$ multiquantum NMR problems in quantum-Liouville Generalized-torque formalisms. Both the $S_n/SO(3)$ operator bases and related scalar invariants are associated with descriptions of the spin dynamics and relaxation of n-fold spin clusters; we reconsider a number of their many-body spin aspects. In particular, the graphical (i=2->n) propagation of cluster spins within the context of Cayley Algebra of Scalar Invariants[1] (now over Liouville space) proves to be more general than the Levy-Leblond viewpoint[2] that used S_n-Automorphisms of few-body democratic recoupling.

F.P.T. Physica A (in press); 1. P. Doubilet, G.C. Rota & J. Stein, Stud. Appl. Maths. 53 (1974) 185. 2. J.M. Levy-Leblond & M. Levy-Nahas; J. Math. Phys. 6 (1965).

S5.8 |

ELECTROSTATIC CALCULATIONS WITH THE MAXWELL INVARIANT REPRESENTATION OF SPHERICAL HARMONICS; GENERAL RESULTS FOR HARMONICS DEFINED BY A CYLINDRICALLY SYMMETRIC DISTRIBUTION.

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The representation has been shown to be convenient for problems requiring the electrostatic potential and its derivatives. For any harmonic defined by a cylindrically symmetric distribution of order $N=4Q+K$, $0\leq Q$, $0\leq K\leq 3$, K characteristic directions lie along the symmetry axis. There are Q sets of 4 each. Each set is determined by the solution of a quadratic equation with one variable parameter. An algorithm has been given for their determination. For any order ≤ 19 the complete solution can be obtained by closed form calculations.

S6.1

THE PROBABILITY OF OCCURRENCE OF KNOTS IN RANDOM RING CLOSURE IN DILUTE POLYMER SOLUTIONS

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Random ring closure can be investigated by studying structures such as self-avoiding polygons on a regular lattice such as Z^3 (the simple cubic lattice). We are concerned with questions about the knottedness of a closed curve of given length embedded in Z^3. What is the probability that such an embedding is knotted? What is the probability that the embedding contains a particular knot? What is the expected complexity of the knot? To what extent can these questions also be answered for a graph of a given homeomorphism type?

We use a pattern theorem due to Kesten (1963) to prove that almost all embeddings in Z^3 of a sufficiently long closed curve contain any given prime knot. We introduce the idea of a good measure of knot complexity. One good measure of knot complexity is crossover number. We prove that the average value of the crossover number diverges to infinity as the length (n) of the embeddings goes to infinity, at least linearly in n.

Finally we consider similar questions for embeddings of graphs. We show that for a fixed homeomorphism type, as the number of edges n goes to infinity, almost all embeddings are knotted if the homeomorphism type does not contain a cut edge. We prove a weaker result in the case that the homeomorphism type contains at least one cut edge and at least one cycle.

S6.2

A Computer Algorithm and Examples for Reaction Globe Generation

Imre Bálint , Paul G. Mezey

For an upper bound of energy, the number of possible reaction mechanisms of a molecular system is related to the topological characteristics of a well-defined region of the potential surface . By an appropriate transformation, one can convert this region into a reaction globe or a reaction polyhedron [1]. In this report, we describe an algorithm and computer program for the generation of reaction globes, using a spherical map of a bounded region of the reaction surface. Illustrative examples of analytic model surfaces and actual quantum-chemical potential surfaces are presented .

[1] P.G. Mezey : Potential Energy Hypersurfaces, Elsevier, Amsterdam, 1987

S6.3

The Exact One-Electron Model of Molecular Structure.

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One-electron (orbital) models of atoms and molecules have dominated theoretical chemistry since the 1920's. Yet quantum theorists have believed that such one-electron models are essentially approximate; i.e. the Hartree-Fock approximation. In 1985 I formulated a wave-mechanical, one-electron model of a many-electron atom or molecule that is, in principle, exact. This is an application of the conditional/marginal factorization of a wavefunction, which I introduced into quantum mechanics in 1974 in order to remove the approximation from the Born-Oppenheimer Separation.

The model partitions the 3-dimensional space of a single electron into classically allowed and forbidden regions. In atoms these regions are spherical shells, the allowed regions being the traditional "electron shells". In ionically bonded molecules there is a forbidden region (i.e. a barrier) between the two ions, while in covalently bonded atoms an allowed region (the valence shell) extends around both nuclei. The surface between the outermost allowed region (the valence shell) and the forbidden region that extends to infinity defines the size and shape of the molecule. This surface has been appropriately named the "molecular envelope" by R.F.W.Bader. The poster will summarize the algebra of the Exact One-Electron Model and illustrate allowed and forbidden shells and the molecular envelope by graphical results from calculations on several small molecules.

S6.4

HALF-BOUND STATES
by

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For a gas in which there is chemical equilibrium between monomers and dimers, the existence of states *other than free monomer and bound dimer states* is examined. An equilibrium estimate of a term in the reduced pair density matrix $\rho^{(2)}(ij)$, denoted by

$$P_{bij}\rho^{(2)}(ij)(I - P_{bij})$$

is given for a model separable potential, where P_{bij} is the projector onto the bound states of the pair (ij). This is referred to as the "halfbound" state. In addition, its role in the kinetic theory of monomer-dimer recombination reaction is investigated along the lines of previous work by Lowry and Snider[1].

[1] J. T. Lowry and R. F. Snider, J. Chem. Phys., **61**, 2320 (1974); ibid., 2330 (1974).

S7.1 ·

GENERALIZED COHERENT STATE ANALYSIS OF DAVYDOV SOLITONS.

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A time-dependent variational principle (TDVP) is used to provide equations of motion for the evolution of a molecular exciton which interacts with lattice vibrations on a molecular chain. The dynamics of the system is described by a Davydov Hamiltonian with dimensionless lattice constant a and dimensionless exciton-phonon coupling constant α. The trial state for the TDVP is taken as a linear combination of generalized coherent states with variational parameters given by a set of time-dependent exciton probability amplitudes ϕ_n, lattice displacement amplitudes d_{kn}, and phonon pair amplitudes $g_{kk'n}$ (n labels the exciton site and k labels the phonon mode). The equations of motion are numerically integrated on a 49-site lattice using a = 2.7 (value for an α-helix) and several values of α for three cases of increasing generality:

(1) $d_{kn} = d_k$ and $g_{kk'n} \equiv 0$ (standard Davydov theory)
(2) d_{kn} unrestricted and $g_{kk'n} \equiv 0$
(3) d_{kn} unrestricted and $g_{kk'n} = g_{kk'}$.

Soliton formation and stability are discussed in light of the numerical analysis.

S7.2

A MODEL OF UNIMOLECULAR REACTIONS WITH SLOW IVR

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A model of thermal unimolecular reactions was analyzed. The model allows not only for reaction but also for unimolecular interconversion of two groups of states of the reactive molecule. This interconversion may be regarded as intramolecular vibrational energy redistribution (IVR). A solution valid at long time was obtained for the kinetic equations which characterize the model. Said solution consists of a weighted sum of two exponentials. A sufficient condition for relatively rapid decay of one of these exponentials was shown to be that the threshold energy for IVR is lower than that for reaction by several kT. In this case the time evolution of the system may be characterized by a rate coefficient. The rate coefficient as a function of collision frequency ω was found, when plotted logarithmically, to have an upward concave segment provided that both the fraction of reactive states and the IVR frequency are sufficiently small. It was found from a crude analysis that the effect of weak collisions is to shift the falloff curve parallel to the log ω axis in the direction of higher ω, and to make the upward concave feature somewhat less pronounced.

S8.1

SPIN-ORBIT COUPLING IN THE LOCAL SPIN DENSITY-SCATTERED WAVE METHOD.

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The spin-orbit coupling has been introduced into the multiple scattering -local spin density method. The spin-orbit splitting is obtained by diagonalization of the spin-orbit operator matrix for the valence orbitals, which are obtained by solving the secular problem of the quasi-relativistic (SW) formalism. All atomic orbitals, outersphere excepted, are taken into account so that the procedure is not limited to monometallic complexes.

Test calculations have been performed on small platinum clusters and the results are compared with Dirac-scattered wave calculations. Excellent agreement is obtained with reduced computational effort(factor 3 or more).

S8.2

VARIATIONAL PRINCIPLE FOR OBTAINING APPROXIMATE SOLUTIONS OF THE THOMAS-FERMI EQUATION FOR ATOMS IN A STRONG MAGNETIC FIELD

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Abstract: An approximate analytical solution of the Thomas-Fermi differential equation for atoms in superstrong magnetic fields is obtained by making use of an equivalent variational principle. The trial solution, depending on several parameters, is chosen in such a way that it satisfies the boundary conditions imposed on the TF equation together with the subsidiary condition that the electron density be normalized. The numerical values of the parameters are determined by extremalizing the variational expression with respect to the parameters. Using the approximate variational solution, ground-state binding energies for several atoms are calculated and the results are compared with other theoretical results.

S8.3

RESPONSE COEFFICIENTS FOR ATOMS AND MOLECULES

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In the spin polarized version of density functional theory, there are, in addition to the well known indexes (electronegativity, hardness and fukui function), new quantities that are also first or second derivatives of the energy functional. These new response coefficients are related with the relaxation of local and global polarization of spin during chemical events. By using Khon-Sham theory we calculate spin polarized reactivity criteria for atoms, and by using ab-initio methods, we calculate them for molecules. Our results allow us to conclude that the response coefficients derived from spin polarized DFT are able to help in the analysis of charge and spin transfers during chemical interactions.

S8.4

The Application of the Hartree Fock Slater method to the optimization of Transition State Structures

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The Hartree-Fock-Slater(HFS) method was applied to optimize the transition state structures by the gradient method for the first time, The reaction systems studied were RNC→RCN (R=H,CH_3) and H_2N_2→HNNH(trans)→HNNH(cis). The transition state structures obtained in the HFS calculations were similar to those reported by other authors in the electron correlation calculations. After the zero-point energy correction, the energy barrier of CH_3NC→CH_3CN was 40.1 kcal/mole which was in good agreement with the experimental value of 38.4 kcal/mole. The barriers obtained for the other reactions are incomparable with experiments since the later are not available, but our results are close to those predicted by the electron-correlation calculations. The vibrational frequencies obtained were in very good agreement either with the experiments for the stable molecules or with the high level ab inition calculations for the transition states.

The success of the HFS method in optimizing transition state structures makes it possible to apply the method to the studies of the reaction mechanisms. We shall later on report the applications of the method to some reaction systems involving transition metal compounds.

M1.1

CALCULATIONS OF ENERGY PROFILES OF METAL-SURFACE REACTIONS: A BOND-ORDER CONSERVATION APPROACH

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The talk will concentrate on realistic calculations of reaction energy profiles on metal surfaces comprising heats of adsorbate chemisorption Q and activation barriers ΔE^* for adsorbate dissociation and recombination. The framework is the "back-of-the-envelope" BOC-MP (bond-order conservation Morse-potential) model providing the analytic formalism to calculate the values of Q and ΔE^* for both diatomic and polyatomic admolecules (1). As examples, the BOC-MP projections concerning CO hydrogenation, C_2 hydrocarbon transformations, and HCOOH decomposition on transition metal surfaces will be discussed in detail, particularly the relative preference of various conceivable reaction pathways. We will demonstrate the basic consistency of the BOC-MP results with experiment. It appears that the BOC-MP modeling provides a practical means for understanding and projecting surface reactivity.

(1) E. Shustorovich, Surf. Sci. Rep., 6(1986) 1-63; Acc. Chem. Res. 21(1988) 183-189; Adv. Catalys., 37(1989), in press.

M1.2

COADSORPTION ON TRANSITION METAL SURFACES

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One of the outstanding features observed during the coadsorption of alkali metals on CO covered transition metal surfaces is a further lowering of the CO vibrational frequency by about 300 cm^{-1}. Many experimental data confirm the weakening of the carbon-oxygen bond, but there is still no generally accepted explanation of the mechanism involved in the alkali-CO interaction. Indirect charge transfer, direct orbital interactions, and polarization due to the surface dipole field have been suggested. A unified discussion will be presented based on LCGTO-LDF chemisorption cluster models of increasing complexity: COK_2, Ni_2CO, Ni_2COK_2, Ni_8CO, Ni_8COK_2. It is found that electrostatic interaction and indirect charge transfer from the alkali metal to the CO via the substrate contribute about equally to the lowering of the CO frequency. Direct orbital interaction seems to be negligible.

M1.3 THEORETICAL STUDIES OF SMALL COPPER OXIDE CLUSTERS*

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ABSTRACT

Ab initio molecular orbital computations indicate that in a $[CuOH_2]^{3+}$ complex oxygen hole ($p\pi$ type orbital) formation is favored over Cu^{3+} formation. In contrast it is found that in a $[Fe(H_2O)]^{3+}$ complex oxygen hole formation is much less favorable, thus, suggesting a reason for the depression of T_c upon Cu substitution by Fe in $YBa_2Cu_3O_{7-x}$. Computations on a symmetrical $[Cu(H_2O)_4]^{3+}$ cluster indicate that it has a degenerate unrestricted Hartree Fock (UHF) ground state in which the oxygen hole is strongly coupled adiabatically to nuclear motions. The electronic repulsion energy of the ground state is, as a result, lowered by a combination of vibrational and electronic correlation effects. The relevance of these observations to the existence of high temperature superconductivity in cuprates is discussed.

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M1.4 SILVER CATALYZED ETHYLENE EPOXIDATION; on the rôle of Pauli repulsion and the Fermi surface in chemisorption and catalysis. E.J. Baerends, P. van den Hoek. Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands.

The interaction of small molecules with metal surfaces is determined by attractive and repulsive forces. Attraction is due to charge-transfer type of interactions between empty molecule levels and occupied metal states en vice versa. Also polarization, particularly of the metal, will play a rôle. There are, however, also important repulsive interactions. The Pauli repulsion, related to the antisymmetry requirement, is responsible for the inner repulsive wall of the interaction energy curve. It depends on details of the electronic structure of the interacting systems, and is often responsible for (part of) the activation energy for reactions.
We will discuss the effect that the presence of a Fermi-level in extended substrates has on the Pauli-repulsion component of the interaction and activation energy in the cases of an ethylene molecule reacting with an adsorbed O atom on a silver catalyst.

Specific Character of Chemical Bonds in Elemental Clusters

M1.5

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Characteristic features of the electronic structure of small neutral and charged clusters composed of Ia, IIa, IIIa and IVa atoms are analyzed and explained. Surprising similarities among some properties of clusters of different elements (e.g. cluster shape) are mainly due to the presence of "dangling" bonds which causes peculiar bond characteristics (e.g. electron deficient bonds, many-center bonds). The differences in the properties of clusters with the same nuclearity but built from different elements can be be caused by different numbers of valence electrons available and by the resulting Jahn-Teller effect or pseudo-Jahn-Teller effect. Other important factors are the compactness of the agglomerate and the electronegativity differences in mixed elemental clusters.

General rules governing the electronic and geometric structure of clusters are formulated and the extrapolation of these rules on agglomerates of other elements is attempted.

M2.1 | THE MAXWELL SCHROEDINGER EQUATION AND PULSE PROPAGATION IN MOLECULAR MEDIA

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The Maxwell Schroedinger equation describing ultrashort laser propagation in multilevel molecular media are shown to be analytically solvable and to reduce to nonlinear multisine-Gordon equations for certain models of field-molecule interactions. Special cases of level schemes are shown to lead to soliton propagation. Numerical studies are presented to examine the effect of nonresonant (virtual) transitions on pulse propagation as a function of field intensity and frequency detuning.

M2.2 | LOCAL MODES IN MOLECULES

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Although it requires symmetry breaking, energy can become localized on a single bond in a system of identical coupled molecular bond oscillators. This is known from experimental evidence for example for the CH stretch oscillators of benzene and the dihalomethanes. While linear oscillator models have been very successful at describing the fundamental spectral lines of such systems, nonlinear models appear necessary to fit the overtone spectrum and explain the phenomenon of energy localization. A simple coupled-anharmonic-oscillator model is presented called the Discrete Self-Trapping Equation (DST). It is shown to have the following properties:

1. It is a nonlinear model that can be quantized without approximations and with the ease of quantizing a system of harmonic oscillators.
2. It gives a good fit to experimentally determined spectra, overtones as well as the fundamental levels, and explains the extensive success of linear theories at fitting the fundamental levels.
3. It yields a simple analytical formula that shows how the mechanism of energy localization in systems of identical oscillators depends on the excited level.

Ongoing research into a driven and damped DST model is discussed.

"Bifurcations and Homoclinic Chaos in Classical Dynamics of Two Coupled Anharmonic Oscillators."

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The problem of describing chaotic dynamics in high excitation states of ABA triatomics using the Darling–Dennison Hamiltonian is essentially equivalent to the classical mechanical problem of two identical coupled anharmonic oscillators. Here we use recently developed nonlinear methods to investigate this problem as a classical Hamiltonian system. Invariance of the Hamiltonian function under changes of phase of the two-component complex oscillator modes reduces the modal phase-space to the two-sphere, $\mathbb{S}^2$, on which the problem is completely integrable. The fixed points (corresponding to local modes, normal modes, and their generalizations) are identified, and the complete bifurcation diagram is presented describing how the phase portraits on $\mathbb{S}^2$ change as the orbits deform and reconnect when the Darling–Dennison parameters are varied. (These bifurcations include the local–normal mode transitions.) Homoclinic and heteroclinic orbits on $\mathbb{S}^2$, are identified in each parameter domain. By using the Melnikov method, homoclinic chaos is analytically shown to develop when the Darling–Dennison parameters are periodically perturbed. The perturbed orbits then show sensitivity to initial conditions, even in the absence of resonance island overlap. The mechanism for this sensitivity to initial conditions is shown to be a Smale horseshoe in the Poincaré map for the perturbed oscillator system.

M2.4

RECENT SYMMETRY REDUCTION ANALYSES FOR MULTIDIMENSIONAL PDE'S AND PATTERN FORMATION

A. TUSZYNSKI

In this paper we discuss recent developments in the area of multidimensional dynamical critical phenomena. Starting from a most general Hamiltonian for strongly interacting many-body systems near criticality, a connection is made to the Landau-Ginzburg type of Hamiltonian. Subsequently, the results of the symmetry reduction method applied to the nonlinear partial differential equations describing the dynamics of physical system near criticality will be reviewed. Both the allowed geometries and the functional forms of the order parameter structure will be demonstrated. Depending on the particular physical situation the governing equations to be analyzed are: the complex and real nonlinear Klein-Gordon equations, the nonlinear Schrödinger equation and the time-dependent Landau-Ginzburg equation. Special emphasis will be placed on the role of anisotropy of interactions which leads to a variety of new classes of solutions. A new aspect of the method is the possibility of restoring the full symmetry of the Hamiltonian in the solution space by applying complementary symmetry operators to the reduced order parameter structures. A number of the obtained solutions exhibit the very interesting properties of multivaluedness, bifurcation and transition from regular to ergodic behavior. Examples of such solutions will be given and illustrations will be provided which will range from crystal growth to fluid flows to magnetic structures and which demonstrate pattern formation.

M2.5

A LATTICE-GAS CELLULAR AUTOMATON FOR A CHEMICALLY REACTING SYSTEM.

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A probabilistic lattice-gas cellular automaton, where space, time and particle velocities are discrete, is used to model the dynamics of a specific nonlinear chemically reacting system, the Schlögl reaction. The reduction of the dynamics to a simple cellular automaton form will be described, and microdynamical equations of motion for the system will be presented. The system will be shown to exhibit the phase separation and wave propagation phenomena expected in the macroscopic domain, and the role of internal fluctuations in determining this macroscopic structure will be discussed. Scaling transformations allow one to pass to the kinetic regime where a lattice-gas Boltzmann equation applies, and this will be reduced to a reaction-diffusion equation with molecular expressions for the reaction rate and diffusion coefficients.

M3.1

SINGLE- AND MULTI-PHOTON ABSORPTION FOR MOLECULES UNDERGOING FREE AND HINDERED ROTATIONS INCLUDING PERMANENT MULTIPOLE MOMENTS AND CHIRAL EFFECTS.

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Allowing a molecule to rotate, either freely or in a hindered manner, can markedly affect its single- and multi-photon absorption spectra. A number of spectral calculations will be presented to illustrate this, including an example involving the use of both continuous wave and pulsed lasers to probe surface adsorbed molecules. In general the effects of permanent moments (as well as transition dipoles), the temporal behaviour of the absorbing molecule, and chiroptical aspects associated with the absorption spectra, will be discussed in some detail using two- to five-level molecular models. The calculations are carried out using Riemann product integral methods to solve the time-dependent wave equation. Modifications of the original approach, needed to evaluate the time-dependence of the molecular states for very long times, will be discussed briefly. The exactly calculated spectra, and the underlying temporal population of the states of the absorbing molecule, are often complicated. Analytic molecular rotating wave approximations for these quantities can often be used to advantage in their interpretation.

M3.2

LINEAR RESPONSE CALCULATIONS OF MOLECULAR PROPERTIES

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Many molecular properties arise as responses of the ground state molecular wavefunction to an external time-dependent or static perturbation. Examples include electronic absorption intensities (UV and CD), static and dynamic dipole polarizabilities, and nuclear magnetic shielding tensors. To the extent that the Hartree-Fock wavefunction is an adequate representation of the molecular ground state, the Time-Dependent Hartree-Fock (TDHF) or Random-Phase Approximation (RPA) method provides the correct linear response properties for that wavefunction. This lecture will focus on results for NMR shielding tensors that we have obtained with our Localized-Orbital/Local Origin (LORG) variant of the RPA, with particular emphasis on the nature and display of the tensor at low-symmetry molecular sites. The localized orbital framework also allows an analysis of the results into molecular structural contributions. The relation of this approach to optical activity calculations will also be discussed.

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M3.3

THE ACCURATE DETERMINATION OF NON-LINEAR POLARIZABILITIES

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Abstract

There is considerable interest in non-linear optical materials because of their application in areas such as fibre optics, optical signal processing and optical computing. In recent years, studies of conjugated organic polymers have demonstrated the potential utility of these materials. From a theoretician's point of view, one of the advantages of organic materials is that the solid phase is generally held together by weak Van der Waals' forces ('condensed phase approximation'), and thus the molecular properties can play a decisive role in the determination of the bulk properties. We consider here the accurate evaluation of non-linear polarizabilities for some conjugated organic molecules using *ab initio* methods which include the effects of electron correlation.

M3.4 AHARANOV-BOHM EFFECT: INTERACTING MAGNETIC FIELDS AND QUANTUM MECHANICS. Gordon R. Freeman*† and Larry D. Coulson†. *Department of Chemistry, and †Radiation Research Center, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

In 1959 Y. Aharonov and D. Bohm (henceforth AB) proposed that the magnetic vector potential has an effect in quantum mechanics that it does not have in classical mechanics. In classical mechanics all magnetic effects are due to field-field interactions. AB proposed that an electron beam that was split in two, the two halves passed on opposite sides of a confined magnetic flux (for example, in an infinitely long solenoid) and then rejoined would display an interference effect without a force having been exerted on the electrons. In 1985 two kinds of experiment (coherent electron transport through a μm split conductor, and electron split beam in an electron microscope) verified the effect to the satisfaction of the general physics community. However, the moving electrons generate their own magnetic fields which overlap the applied magnetic field and exert forces on the electrons. The AB effect must be force-free, and has therefore never been observed. No direct effect can be attributed to the magnetic vector potential in the absence of fields. The use of the vector potential in conventional quantum mechanical formulations is a convenience and should not mask the fact that observed effects are due to potential gradients, not to the absolute magnitudes of the potentials.

T1.1

THEORETICAL MODELS AND APPROACHES TO VCD CALCULATIONS

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The earliest theoretical models of VCD intensity were based on the use of fixed charges on moving nuclei to simulate the generation of vibrational electric and magnetic dipole moments in molecules. Another early approach was the coupled oscillator model in which electric and magnetic moments are generated from in- and out-of-phase combinations of local electric moments situated on identical, chirally-oriented chromophores. In both approaches detailed descriptions of the motion of electron charge density (electron current density) were avoided due to the vanishing of the electronic contribution to the magnetic dipole transition moment within the Born-Oppenheimer approxiamtion. In subsequent years a number of models of VCD intensity were proposed which, through various approximations, took into account these vanishing electronic contributions. They are the localized molecular orbital model, the charge flow model, the dynamic polarization model, the bond dipole model, the atomic polar tensor mode, the non-localized molecular orbital mode, and the ring current model. In 1983, the first complete, theoretical description of VCD through the lowest order correction to the Born-Oppenheimer approximation was published. The theoretical approach to VCD calculations required a summations over all allowed electronic excited states (SOS). In 1985, an alternative calculational approach, employing the overlap of two different ground state wavefunctions (WFO), but based on the same non-Born-Oppenheimer vibronic coupling expressions for the magnetic dipole moment, was published. Since then, the WFO approach, as well as more recently the SOS approach, have been employed to carry out *ab initio* calculations of VCD intensity which are in excellent agreement with available experimental VCD spectra. Recent refinements to the theory including choice of gauge, the use of the random phase approximation and floating atomic basis functions have given rise to further improvements in the calculation of VCD intensity and our understanding of this new phenomenon.

T1.2

AB INITIO CALCULATIONS OF VCD SPECTRA

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The fundamental theory of vibrational absorption spectra is well-known. Within the harmonic approximation, prediction of vibrational absorption spectra requires the molecular geometry, the harmonic vibrational force field and the atomic polar tensors ($P^{\lambda}_{\alpha\beta}$). Ab initio methods currently permit geometries, force fields and $P^{\lambda}_{\alpha\beta}$ tensors to be calculated. Vibrational absorption spectra predicted thence can be of considerable accuracy.The theory of vibrational circular dichroism (VCD) spectra has recently been developed [1]. In addition to the geometry, force field and $P^{\lambda}_{\alpha\beta}$ tensors, prediction of a VCD spectrum also requires the atomic axial tensors, $M^{\lambda}_{\alpha\beta}$. The technology for the ab initio calculation of these new molecular tensors has also been developed [2], permitting prediction of VCD spectra.Examples of calculations of vibrational absorption and VCD spectra of several chiral molecules will be presented. Particularly thorough studies have been carried out of propylene oxide, trans-1,2-dicyanocyclopropane-d_0 and -d_2 and 4-methyl-2-oxetanone. When ab initio calculations are carried at the SCF level of approximation using the 6-31G** basis set, and when the SCF force field is scaled, predicted absorption and VCD spectra are in excellent agreement overall with experimental spectra. It can be concluded that VCD spectra can now be calculated as efficiently and accurately as vibrational absorption spectra. A number of approximate approaches to the calculation of VCD spectra have been proposed. The Fixed Partial Charge (FPC), Atomic Polar Tensor (APT) and Coupled Oscillator (CO) theories can be shown to be approximations to the general theory [1b]. Calculations show that these specific approximations are generally very inaccurate.

1. a) P.J.Stephens, J.Phys.Chem. 89 748 (1985). b) P.J.Stephens, J.Phys.Chem. 91 1712 (1987). 2. a) R.D.Amos. N.C.Handy, K.J. Jalkanen and P.J.Stephens, Chem.Phys.Lett. 133 21 (1987). b) K.J.Jalkanen, P.J.Stephens, R.D.Amos and N.C.Handy, J.Phys.Chem. 92 1781 (1988). c) R.D.Amos, K.J.Jalkanen and P.J.Stephens, J.Phys.Chem. 92 5571 (1988).

T1.3 LOCAL MODES, NORMAL MODES, AND VIBRATIONAL CIRCULAR DICHROISM

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Simple Theoretical arguments show that XH bond anharmonicities dominate over interbond couplings, beyond the first or second overtone (X=C,O,N,etc.). This leads to the interpretation of overtones' absorption spectra in terms of local modes (B.R. Henry, in "Vibrational Spectra and Structure, X, 1981).

Recent VCD experiments in the second and third CH stretching overtone regions for some monoterpenes have shown band patterns, which are most easily interpreted assuming the existence of normal modes (S. Abbate *et al.*, JACS,111(1989)836). Through the use of classical mechanics methods, both numerical and analytical, we studied the resonances between vibrational degrees of freedom in the relevant molecular fragment. In particular we will discuss the importance of torsional motions in generating indirect couplings between CH stretchings.

T1.4 The Vibrational Circular Dichroism of α-Deuterioethanol.

R.Dutler, A.Rauk., R.A. Schaw and H. Wieser, Department of Chemistry, The University of Calgary, Calgary Alberta, T2N 1N4

α–Deuterioethanol exists in three distinct conformations, one in which the CH_3-group is located in a trans position, and two where the CH_3-group is gauche relative to the hydrogen on oxygen. We report here the calculated *ab initio* vibrational circular dichroism (VCD) spectra of these isomers obtained with the Vibronic Coupling formalism by Nafie and Freedman, as well as a comparison of the calculated VCD bands with the experimental data in the frequency range of approximately 800-1500 cm^{-1}.

In the experimental system, the low barriers of rotation around the CO-bond preclude the optical resolution of the three conformers of α-deuterioethanol. The experimental, mid inrared VCD spectrum of this system, and the calculated VCD data of the equilibrium mixture, 0.382 CH_3-trans, 0.301 H-trans and 0.316 D-trans relative to the hydroxy hydrogen, compare very well. In particular, the main features in the measured gas phase spectrum, namely two relatively intense negative differential absorption bands just above 1000 cm^{-1}, followed by a strong positive band at approximately 1130 cm^{-1} and two medium strength negative intensities above 1250 cm^{-1} agree favorably, and are useful to determine the relative populations of the three conformers at the experimental temperature, and the origin of the individual bands in the observed spectrum of α–deuterioethanol. The temperature effect on VCD intensities is found to be negligible in this system.

T1.5

[1]VIBRONIC COUPLING FORMULATION OF VCD INTENSITIES WITH FLOATING BASIS SETS

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A vibronic coupling formulation of vibrational circular dichroism intensities will be presented that employs atomic orbital basis sets that float with nuclear position and velocity. With this formulation, the electronic contributions to vibrational rotational and dipole strengths that perfectly follow the nuclear motion are determined from the equilibrium ground state electronic wave function. The electronic contributions arising from charge flow are calculated from vibronic summations that can be restricted to valence transitions. With this method, polarized basis sets with derivative basis functions are not required for the SCF calculation. In addition, terms in this formulation can be directly correlated with the expressions for approximate models for VCD.

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[1] Freedman, T. B.; Nafie, L. A. *J. Chem. Phys.* **1988**, *89*, 364.

T1.6

Abinitio Raman optical Activity calculations

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Abstract

Raman optical activity (ROA) refers to the differential Raman scattering for right versus left circularly polarized incident light by chiral molecules. ROA is the Raman counterpart for infrared vibrational circular dichroism (VCD). ROA spectra are governed by the normal coordinate derivatives of electric dipole-electric dipole polarizability, electric dipole-magnetic dipole polarizability and electric dipole-electricquadrupole polarizability tensors. The evaluation of the former derivatives is now widely known. However the evaluation of latter two derivatives is more involved. Recently we have carried out the first abinitio ROA calculations using the CADPAC program. In this presentation we will summarize the status and reliability of these calculations.

T1.7

THE VCD SPECTRUM OF 2-METHYLOXETANE: EFFECTS OF CONFORMATIONAL MOBILITY AND CHARGE FLOW

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The mid-infrared vibrational circular dichroism spectrum has been measured for 2-methyloxetane and compared with spectra calculated for the FPC and APT models. For the optimized 3-21G (planar) structure, the FPC model reproduces the experimental VCD signs for nearly all observed bands, and major discrepancies in the absorption intensities occur only for the very intense ring stretching modes. In contrast the APT calculation reproduces qualitatively the observed absorption intensities, however the VCD features are generally not reproduced even in sign. We have extended this work to investigate the effects of i) changing the assumed ring conformation, and ii) including charge flow terms to reduce the errors in the ring stretching intensities. The results of these investigations will be presented and discussed in the context of previous applications of both models.

T2.1

ELECTRONS ON THE MOVE IN LIQUIDS.

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Excess electrons in liquids exhibit a wide variety of behaviors manifesting extended and localized states of electrons. The theory for these different electronic states is discussed. The theory for the transition between extended and localized states is related to the theory for the folding or crumpling of transition polymers.

T2.2

SYMMETRY-BASED ALGORITHMS TO LINEARIZE PARTIAL DIFFERENTIAL EQUATIONS

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ABSTRACT: Simple and systematic algorithms are presented for linearizing nonlinear PDE's. The local symmetries admitted by a given nonlinear system of PDE's lead to necessary and sufficient conditions for the existence and construction of an **invertible mapping** of the nonlinear system to **some** linear system of PDE's. Examples include the hodograph and Legendre transformations, and the linearization of a nonlinear telegraph equation, a nonlinear diffusion equation, and nonlinear fluid flow equations.

An algorithm is presented to linearize nonlinear PDE's by **non-invertible mappings**. This algorithm depends on finding nonlocal symmetries of a given system which are realized as appropriate local symmetries of a related auxiliary system of PDE's. Examples include the Hopf-Cole transformation and the linearizations of a nonlinear heat conduction equation, a nonlinear telegraph equation, and the Thomas equations.

COMPETING INTERACTIONS AND COMPLEXITY IN CONDENSED MATTER

T2.3

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Nonlinear partial differential equations and coupled nonlinear ordinary differential equations arise in many condensed matter contexts(1), where both spatial and temporal aspects are important. Furthermore, condensed matter provides controlled, bench-top scale experiments. Thus, pattern formation and complex dynamics in condensed matter and materials science are an increasing focus, both because of the information they can provide for extended dynamical systems generally and their importance for specific materials.

After briefly introducing some of the materials contexts, we discuss our current understanding of several typical model problems based on the perturbed sine-Gordon equation and generalizations: (1) AC-, DC-, and wave-vector-dependent driving in the 1 + 1 and 2 + 1 dimensional, damped sine-Gordon equations(2); and (2) Ground states and dynamics in the discrete sine-Gordon equation with <u>nonconvex</u> interparticle interactions(3).

We use the above problems to emphasize the importance of: (1) <u>Competing interactions</u> -- both of spatial length scales and temporal frequencies -- as the fundamental source of "complexity"; (2) <u>Mappings</u> of nonequilibrium space-time problems to effective equilibrium Hamiltonian systems with competing length scales and associated inhomogeneous (e.g. incommensurate) ground states; (3) Nonlinear "collective" (e.g. solitary wave) <u>mode reduction</u> as a basis for describing low-dimensional dynamics and attractors in many-degree-of-freedom systems; (4) Generalized homoclinic orbits as sources of temporal sensitivity and spatial instability; and (5) "<u>Defects</u>" controlling large-scale flow and response in competing interaction nonlinear problems.

(1) See "Competing interactions and microstructures: statics and dynamics" (Springer-Verlag 1988).

(2) A. Bishop et al., Physica <u>23D</u>, 293 (1986); Phys. Lett. <u>119A</u>, 273 (1986); Phys. Lett. <u>127A</u>, 335 (1988); Phys. Rev. B <u>35</u>, 3207 (1987); Phys. Rev. B <u>38</u>, 4853 (1988).

(3) S. Marianer et al., Phys. Rev. B <u>37</u>, 9893 (1988).

T2.4 Vapour-liquid equilibrium for model molecular fluids

P.A. Monson (U. of Massachusetts, Amherst), S.F. O'Shea (U. of Lethbridge), and D.J. Tildesley (U. of Southampton)

The conditions determining liquid-vapour coexistence have been known for more than a century, but the accurate prediction of the properties of the coexisting fluids has proved an extremely difficult computational problem. Until recently reliable computer simulation results for fluid phase diagrams have been limited to the Lennard-Jones 12-6 potential. The recently developed Gibb's ensemble (Monte Carlo) method permits direct calculation of coexistence properties, and promises to expand the range of reliable data to include molecular models having non-spherical cores and polar interactions.

We report calculations for a series of well-known realistic models. In the case of the Stockmayer model we have studied the sensitivity of the results to details of the implementation of the long-ranged interactions. We have compared the coexistence curve and critical conditions determined in this way with those obtained by other methods. Lennard-Jones diatomics have been studied as a function of bond length, and results are in remarkable agreement with those of a recent optimized cluster theory. Lennard-Jones diatomics with point-charge dipoles also yield results in agreement with theory. The results as a whole furnish strong support for the method (when it is implemented carefully) and for the optimized cluster theory.

T2.5 MULTIPARAMETER BIFURCATIONS IN REACTION - DIFFUSION SYSTEMS.

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Multiple steady state solutions for two kinds - isothermal and non-isothermal reaction-diffusion systems will be compared. A crossover between two kinds of bifurcation diagrams obtained by various boundary conditions will be analyzed. The problems of thermal runaway and selective permeability and phase separation by active membranes will be discussed. Instability of homogeneous solutions leads to spontaneously formed fluxes of mass end energy across the boundaries. Relative signs of fluxes at different boundaries depend on the membrane thickness. As an extension of the results for one-dimensional models, patterns in two and three dimensions will be discussed in the context of Ginzburg - Landau theory of phase transitions. Recent observations of patterns formed by the photoproduction of Fe^{2+} and its subsequent reaction to form Turnbull's Blue will be analyzed as an example of commensurate phase transitions.

T3.1 BASIS-SET-FREE DENSITY-FUNCTIONAL QUANTUM CHEMISTRY.

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We have recently developed new numerical (i.e. non-basis-set) computational methods for application to polyatomic molecular systems. A multicentre numerical integration scheme and an algorithm for numerical computation of multicentre Coulomb potentials have already been reported (Becke, J. Chem. Phys. 88, 2547, 1988: Becke and Dickson, J. Chem. Phys. 89, 2993, 1989). These methods have now been extended to the calculation of multicentre molecular orbitals in the framework of Kohn-Sham density-functional theory. Basis-set-free quantum chemistry, in coordinate space, is thus possible for the first time on polyatomic systems. An overview of our methodology will be provided, as well as discussion of recent applications to selected small polyatomic molecules.

T3.2 EXCHANGE AND CORRELATION IN DENSITY FUNCTIONAL AND *AB INITIO* METHODS

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Theoretical investigations on molecular systems by *ab initio* techiques are affected by the unsatisfactory results often obtained at the Hartree-Fock level, and the slow convergency of Configuration Interaction calculations.

Alternative, and computationally inexpensive computational schemes based on Density Functional Theory have been widely applied to the study of molecular systems. The aim of this seminar is to justify the success achieved by Density Functional calculations by showing that these computational methods, unlike the Hartree-Fock scheme, include[1] part of the correlation energy obtained by computationally expensive Configuration Interaction calculations.

Recent improvements[2] to Density Functional Theory will also be outlined and corresponding results[3] on bond energies of numerous molecular systems, including transition metal complexes, will be presented and compared with experimental values.

[1] V. Tschinke and T. Ziegler, in progress.
[2] a) A.D. Becke, *J. Chem. Phys.* **1986**,*84*, 4524.
  b) V. Tschinke and T. Ziegler, *Can. J. Chem.* **1989**, *67*, 460.
[3] a) V. Tschinke and T. Ziegler, in *Density Matrices and Density Functionals*, R.M. Erdahl and V.H. Smith Jr. (Eds.), D. Reidel, Dordrecht, 1987.
  b) T. Ziegler, V. Tschinke and A. Becke, *Polyhedron*, **1987**, *6*, 685.
  c) T. Ziegler, V. Tschinke and A. Becke, *J. Am. Chem. Soc.*, **1987**, *109*, 1351.
  d) T. Ziegler, V. Tschinke and C. Ursenbach, *J. Am. Chem. Soc.*, **1987**, *109*, 4825.

T3.3

ELECTRON CORRELATION AND DENSITY-FUNCTIONAL METHODS

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Most discussions of correlation in density-functional theory have focused on correction terms to the simple $\rho^{1/3}$ ($X\alpha$) exchange potential, derived from analyses of correlation in an electron gas. However, in molecular systems the $X\alpha$ potential itself often gives results superior to Hartree-Fock, even without the addition of explicit correlation terms. In a number of cases for which HF yields an incorrect electronic ground state, $X\alpha$ produces the correct one. $X\alpha$ calculations are often more accurate than Hartree-Fock with respect to the energetic spacing of different molecular electronic states, as well as for the shapes of the individual potential curves.

This behavior has been analyzed;[1] it is found to be a consequence of the fact that density-functional methods, unlike Hartree-Fock, are not sensitive to artifactual differences of ionic character among determinantal molecular wavefunctions.

[1] M. Cook and M. Karplus, J. Phys. Chem. 91: 31 (1987)

DENSITY FUNCTIONALS FOR THE CORRELATION ENERGY

T3.4

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Hartree-Fock energies can be improved by using density functionals for the correlation energy. [1] Although this approach is computationally advantageous over the configuration interaction method, it does not include the possiblity of a systematic improvement.

Progress can be made by combining the density functional and the configuration interaction method. Such a procedure must avoid - at least in principle - a double counting of the correlation energy. [2]

Results obtained with both approaches are presented.

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[1] see, e.g., B.Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Letters *157*, 200, 1989

[2] see, e.g., A. Savin, Int. J. Quantum Chem. *S22*, 59, 1988

T3.5

RECENT PROGRESS WITH THE LCGTO-MP-LSD METHOD.

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Density Functional Theory provides an alternative way of treating electron correlation which has known considerable success in handling complex systems such as transition-metal clusters and adsorption complexes. It will be necessary , for several properties, to go beyond the local density approximation. The way to do this is not yet firmly established. One hope is that comparisons of DF results with those of more conventional ab inito theory will provide clues. I will discuss a few such comparisons in order to help situate the method in proper perspective. Time, and the advancement of the projects permitting, I will mention recent progress with non-local functionals, analytical gradients, faster integrals and relativistic calculations.

T4.1

THEORETICAL MODELS OF AMPHIPHILIC SELF-ASSEMBLY

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We present methods that we are investigating to model the self-assembly into complex phases of systems containing amphiphilic molecules, water, and oil. Molecular dynamics simulations have been performed for a simple model of a phospholipid and water mixture in a bilayer phase, and the forces that determine the stability of the phase investigated. Also, the structure of the phase and its transport properties have been studied over a range of temperatures, up to the point where the system undergoes phase transitions. Current research includes the development of dynamical mean-field potentials to more accurately represent the interactions of complex molecules in different phases as well as the development of a method to use normal-mode accelerated Langevin dynamics to simulate the large scale changes in structure that accompany phase transitions. A lattice model has also been proposed which can represent all the components of these systems as well as the spatial orientation of the amphiphilic molecules. Mean-field and perturbation theories are being used to determine the global properties and phase diagram of this model.

T4.2

SPONTANEOUS ISOMERIZATIONS AND DYNAMICAL PROPENSITIES OF SOME SF_6-$(Ar)_n$ CLUSTERS

Mary Ann Kmetic , *John C. Shelley** and *Robert J. Le Roy*, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

As part of our effort to understand the structural and dynamical properties of heterogeneous van der Waals systems, molecular dynamics simulations of SF_6-$(Ar)_n$ clusters ($n = 7$-12) have been carried out at total energies corresponding to effective temperatures ranging from 6 to 40 K. Various dynamical properties and the predicted frequency shift of the ν_3 band of the perturbed SF_6 chromophore were examined as a function of time. Abrupt changes in the frequency shift and in certain dynamical properties were found to occur in single trajectories for cluster sizes $n = 7$, 8, 9 and 10. We interpret this as evidence for the occurrence of spontaneous iso-energetic isomerizations between structures consisting of a liquid-like monolayer of Ar atoms coating the SF_6, and others in which a solid-like bilayer "cap" of $(Ar)_n$ sits on one face of the "substrate" SF_6 molecule. Configurations sampled during these trajectories are used to illustrate the nature of this isomerization process , and the generality and physical considerations underlying this type of "phase coexistence" behaviour will be discussed.

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T4.3

HYDRODYNAMIC MODE SELECTION DUE TO THE ELECTROCAPILLARY EFFECT

(The "Mercury Beating Heart" in Neutral and Basic Solutions)

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The Mercury Beating Heart, or MBH, system has been something of a laboratory curiosity, occasionally used as a classroom demonstration, but not widely studied. In the usual procedure, a drop of mercury is placed on a watchglass, then covered with a strongly oxidizing, acidic solution. When an iron nail is brought up against the side of the drop, the drop begins to oscillate, moving alternately in and out of contact with the nail. Under some circumstances, the drop will assume a triangular (or heart) shape at the extremes of the oscillation. We have investigated the electrocapillary mechanism driving the oscillatory hydrodynamic modes of a mercury drop in the absence of oxygen and in neutral and basic solutions. The electrocapillary driver can be mimicked by imposition of an external field oscillating with frequency ν_{max} and amplitude ΔV about an appropriate voltage V_0. The hydrodynamic mode selection for a given V_0 is controlled in a reproducible and reversible manner by adjustment of the driver frequency ν_{max} and the voltage ΔV.

~~56.5~~

T4.4

Finite Difference Simulation of Foam Generation

William Laidlaw & *Fred Wassmuth*; Chemistry Dept. U. of Calgary

The foam system (liquid/gas) is governed by a set partial differential equations, the hydrodynamic conservation equations (mass, momentum and energy). However the majority of partial differential equations can not be integrated analytically. In such cases it is necessary to apply some method of approximation, one of these is the method of finite differences.

We plan to model the foam generation using the finite difference technique. This route allows one to model systems under many different physical constraints and conditions. Also the physical variables such as temperature, velocity and pressure can be determined at any point in the system, allowing for detailed monitoring of the systems progress. To treat the problem of a constantly deforming surface, a second coordinate system was introduced, that moves along with the surface and has coordinates parallel and normal to the interface. The important interactions between liquid and gas phase take place in this moving coordinate system. The advantages of having a moving coordinate systems are twofold. The interfacial equations reduce to their simplest form and the interphace is treated consistently throughout.

The program is employed so that it can monitor the movement of a bubble front through a straight capillary. The next step is to built a constriction into the pipe to model the snap of processs.

T5.1.1

LASER EXCITATION AND QUANTUM CHEMICAL STUDIES OF THE FIRST EXCITED STATES OF FORMIC ACID

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A laser excitation spectrum of formic acid monomer, has been recorded in the 267 - 250 nm region and has been attributed to an $n \to \pi^*$ electron promotion in the trans conformer.The activites of the antisymmetric aldehyde wagging and hydroxyl torsional modes in forming progressions is central to the analyses in that they demonstrate that the two hydrogens are distorted from the O-C=O molecular plane in the upper S_1 state. The result is that while the lower S_0 state possesses trans and cis planar conformations, the S_1 state has four stable molecular configurations. The equilibrium structures and the geometries of the saddle points of formic acid in the S_0 and T_1 states were explored by ab initio SCF theory using the Gaussian 86 package of MO programs. In the upper T_1 state, the potential surface which describes the OH torsion and the CH wagging motions was found to be complex. The OH and CH bonds were calculated to be twisted with respect to the O-C=O plane of the molecule by 67.99 and 45.87 degrees respectively. The calculations predicted a second stable conformer which is 464 cm^{-1} above the equlibrium configuration with OH and CH angles displaced from the plane by -58.29 and 40.71 degrees.

Rydberg States of the Ethynyl Radical*

T5.1.2

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Abstract:

Ab-initio CAS-MCSCF/MRSDCI calculations, employing a correlation-consistent p-VDZ basis set augmented with Rydberg s and p functions, have been made on several Rydberg states of the ethynyl radical. The emphasis of the study was to re-examine the excitation energies as reported by Shih et al, to explore in some detail the potential energy surface of these states and reconcile these results with the most recent experimental findings. We will report various schemes aimed at reducing the number of CI configurations while maintaining a relatively accurate description of the different states of interest. The "largest" of the CI calculations is used to establish the vertical excitation spectrum of CCH while the most reliable of the "smallest" CI calculations is used to describe the potential surfaces.

**Acknowledgment.* This work was supported by the U.S.Department of Energy, Office of Basic Energy Sciences,Division of Chemical Sciences, under contract W-31-109-ENG-38.

T5.1.3

MOLECULAR ORBITAL THEORY FOR EXCITED STATES

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Michael J. Frisch

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This work reviews the methodological and computational considerations necessary for the "ab initio" determination of the energy and wavefunction of a molecule in an electronically excited state. Configuration interaction among all singly substituted determinants using a Hartree-Fock reference state is used to deduce a zeroth order approximation. Second-order Moller-Plesset perturbation theory is then employed to correct these energies for the effects of correlation. We present excitation energies and optimized geometries for a number of standard chromophores as well as the results from several large systems of interest in optical spectroscopy.

T5.1.4 | HUND'S RULE AND SINGLET-TRIPLET ENERGY DIFFERENCES FOR MOLECULES.

Katherine V. Darvesh, Paul D. Fricker, and Russell J. Boyd, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3 Canada

A series of molecular systems has been studied using the configuration interaction method, with the aim of examining pairs of states for each molecule where each state arises from the same orbital occupancy but the multiplicities differ. These systems of two open-shell electrons obey Hund's rule whereby the state of higher multiplicity lies lower in energy. A greater understanding of Hund's rule for molecular systems is gained through energy component difference plots for a series of molecules at various geometries. The molecular virial theorem and the molecular geometries are found to be very important in describing the behaviour of the energy component difference curves.

T5.1.5 | DIATOMIC ANIONS WITH NINE VALENCE ELECTRONS

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Diatomic anions of the first row, such as C_2^-, have a maximum of three bound states lying below the ground state of the neutral diatomic. Since second- and higher-row diatomic molecules have electron affinities even smaller than first-row diatomics, fewer such bound states are expected. However, Li_2^-, Ge_2^-, $A\ell P^-$, $GaAs^-$ and other diatomic anions with nine valence electrons have more than three bound states below the ground state of the neutral molecule. For example, $A\ell P^-$ has seven. Most low-lying excited states are characterized by $\pi \rightarrow \pi^*$ transitions, and the reason for the larger number of low-lying states can be seen in the decreasing $\pi - \pi^*$ separation for higher-row diatomics. The above-named anions, as well as BN^- and BP^-, were studied by CI methods, and results for their ground as well as low-lying excited states will be presented.

T5.1.6

EXTRACTION OF MEAN EXCITATION ENERGIES FROM OSCILLATOR STRENGTH MOMENTS.

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The dipole oscillator strength distribution of an atom or molecule is approximated by functional forms constrained to have the correct asymptotic behavior at both large energies and in the vicinity of the lowest transition energy. These forms are fitted to moments of the distribution which can be obtained by electronic structure calculations using sum rules.
Differentiation of the forms then yields mean excitation energies pertinent to Lamb shifts, and also to the stopping and inelastic scattering of fast charged particles by the target molecule. Approximately 80 variants of this method are tested on the hydrogen atom for which exact results are known. The "best" variants are then applied to the hydrogen molecule and its cation as a function of bond length.

T5.1.7

LOW-LYING SINGLET STATES IN THE TWO-PHOTON EXCITATION SPECTRUM OF CHRYSENE.

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P.R.SALVI,N.Q.LIEM, Università di Firenze,Italy

The two-photon fluorescence excitation spectrum and polarization ratio of chrysene have been measured in the spectral region 370-230 nm. Totally-symmetric electonic transitions have been observed which give direct evidence of A_g $\pi\pi^*$ states in the near UV. Comparison with MO-SDECI calculation of TP properties offers strong support to our experimental assignement.The vibronic activity of the most important b_u normal modes has been also calculated in the orbital following framework. The main mechanisms of vibronic borrowing are discussed.

T5.2.1

A NOVEL INVARIANCE PRINCIPLE FOR THE ELECTRON DENSITY

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A reevaluation of the mathematical foundations of Berlin's Theorem for diatomic molecules yields the result that the notions of "binding" and "anti-binding" regions cannot be maintained. Instead, a new invariance property is found for the integral expression that connects the (exact) electron density and the intramolecular force.

T5.2.2

POINTWISE COMPARISON OF EXPERIMENTAL AND *AB INITIO* ELECTRONIC DENSITIES. Zareh Darakjian and William H. Fink. Department of Chemistry, University of California, Davis, California 95616, USA. Deformation densities obtained with a hierarchy of successive basis sets in the RHF approximation are compared on superimposable grids with those obtained from refinement of extremely high quality, low temperature X-ray intensity measurements for a series of views of the molecules dimethyl- γ-pyrone, triazine trichloride, and diiminosuccino(di)nitrile. The convergence toward quantitative agreement between the experimental results and the more sophisticated basis sets is particularly gratifying. The resulting electron distributions show features illuminating the interpretation of extensive pi-electron delocalization in these molecules.

T5.2.3

SPIN DENSITIES IN DIATOMIC FIRST-ROW HYDRIDES

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Fermi contact spin densities have been theoretically determined for the ground state π radicals CH, OH and NH. MCSCF wave functions include the dominant configuration and single excitations from it describing the most important spin and orbital polarization effects. Optimization of the orbitals by precise numerical grid methods shows that this simple wave function model is capable of providing spin densities in satisfactory agreement with experiment. Gaussian basis sets suitable for use with this wave function model are determined by comparing to the precise numerical spin density results. Popular primitive Gaussian bases designed for Hartree-Fock calculations provide a good starting point if augmented with diffuse and polarization functions and with a tight (high exponent) *s* function at hydrogen. Only the innermost few primitive functions may be contracted. Contraction coefficients may be determined on the basis of free atom Hartree-Fock calculations. These studies lead to economical contracted Gaussian basis sets that should be useful for spin density calculations in larger polyatomic radicals.

T5.2.4

ACCURATE SPIN DENSITY AND FERMI CONTACT TERM FOR THE LITHIUM ATOM

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An accurate analytical spin electron density for the lithium atom is obtained by using a systematic and reliable method recently developed and already tested.[1] The density convergence is analyzed in terms of well-defined improvements in the corresponding configuration-interaction wave functions. The convergence process turns out to be very sensitive to the orbital basis parameters as long as they are properly optimized. The stability of the spin electron density yields a value of 2.90957 ± 0.00005 a.u. at the nucleus, for the Fermi contact term of lithium , which is in excelent agreement with the experimental value of 2.9096 ± 0.0001 a.u.

[1] R.O. Esquivel and A.V. Bunge, Int. J. Quantum Chem. 32, 295 (1987)

T5.2.5

CONTRIBUTION TO THE ELECTRON DENSITY ANALYSIS

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Relativistic spherically averaged numerical all-electron densities ρ were computed for the atoms Be-Ba, B-Tl, C-Pb, Cu-Au, and Zn-Hg. The Laplacian of these densities is not able to separate the valence shell from the core in case of heavy atoms, starting with the 4th row [1, 2]. The distribution of the local kinetic energy E_{kin} [3] shows a valence maximum even for these heavy atoms, unfortunately in a region of negative kinetic energy.

Test with pseudopotential densities reveal that for pseudopotential calculations it is advisable to use at least the two outermost shells in order to reproduce the all-electron values of $\nabla^2\rho$ and E_{kin} in the valence region. Molecular results are also shown. The above mentioned behaviour of $\nabla^2\rho$ and E_{kin} leads to difficulties in their interpretation.

The quantity $-|\nabla\rho|/\rho$ was also investigated. For all computed atoms the $-|\nabla\rho|/\rho$ diagrams are capable of describing the complete shell structure. $-|\nabla\rho|/\rho$ is sensitive to basis set quality: poor Gaussian basis sets exhibit 1) spurious oscillations, 2) a premature onset of the Gaussian decay. The $-|\nabla\rho|/\rho$ for the dimers and hydrides of Li - F was analysed. Attemps were made to link the shape of the $-|\nabla\rho|/\rho$ diagrams to bond properties.

[1] R. P. Sagar, A. C. T. Ku, V. H. Smith, Jr., A. M. Simas, J. Chem. Phys. 88, 4367 (1988)
[2] Z. Shi and R. J. Boyd, J. Chem. Phys. 88, 4375 (1988)
[3] G. Hunter, Int. J. Quantum Chem. 29, 197 (1986)

T5.2.6 |

ELECTRON CORRELATION AND ELECTRON DENSITY DISTRIBUTIONS

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Two methods for including the effects of electron correlation on the electron density distributions of molecules are compared. Second-order MΦller-Plesset perturbation theory (MP2) is shown to give electron density distributions in good qualitative agreement with much more time-consuming configuration interaction calculations. The latter include all single and double substitutions from the Hartree-Fock reference configuration. The two methods are compared by means of difference density maps calculated with large basis sets for a few representative molecules. From an analysis of the relative importance of single and double substitutions, it is shown that double substitutions are dominant near nuclei, but in other regions of space the single substitutions are more important. The MP2 method is shown to provide a practical method for calculating the correlation corrections to the electron density distributions of molecules of intermediate size. The formaldehyde molecule is used to illustrate the effect of electron correlation on the topological and atomic properties of electron density distributions.

T5.2.7

DYNAMIC POLARIZABILITIES AND HYPERPOLARIZABILITIES OF POLYSILANES

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Ab initio coupled perturbed Hartree Fock (CPHF) calculations of dynamic polarizabilities and hyperpolarizabilities are carried out for the polysilane oligomers $SiH_3-(SiH_2)_n-SiH_3$. Various choices for the basis set are examined along with the effect of using a core pseudopotential. We also compare the *ab initio* results to those obtained from a semiempirical treatment.

T5.2.8 | EVALUATING RESPONSE PROPERTIES OF QUANTUM SYSTEMS WITH MONTE CARLO

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Within the framework of the Pure Diffusion Quantum Monte Carlo (PDQMC) method (1), response properties of quantum systems may be expressed in terms of suitably defined n-time correlation functions along stochastic trajectories. Starting from theoretical expressions, it is shown how to perform practical calculations of such quantities. Results for some response properties of the Helium atom (dipole dynamic polarisability, C_6 Van der Waals coefficient) are presented. By using the same formalism, some preliminary results concerning exact evaluation of components of the interaction energy between two Helium atoms within the framework of Symmetry-Adapted Perturbation Theories (SAPT) are also presented (2). It is emphasized that by using QMC it is possible to evaluate contributions which are known to be particularly difficult to calculate with standard ab initio perturbation theory (e.g. intramonomer correlation or high-order perturbational contributions).

Ref. (1) M. Caffarel and P. Claverie, J.Chem.Phys. 88,1088 (1988).
(2) M. Caffarel and O. Hess, "Evaluating Interaction Energies using Monte Carlo. The Helium Dimer" (in preparation).

T5.2.9 QUANTUM MONTE CARLO APPLIED TO DIATOMIC MOLECULAR PROPERTIES[a)]

Jan Vrbik[b,c)], Daniel A. Legare[b,d)], and Stuart M. Rothstein[b)], Brock University, St. Catharines, Ontario L2S 3A1, Canada.

We show how to estimate, for a given molecule, the first and higher derivatives of the expected value of an operator with respect to one or more physical parameters. This is done with high accuracy achieved by sampling to within a certain approximation from the exact electron distribution, compatible with the Hellmann-Feynman Theorem. Finite difference approximations are avoided. The required derivatives of the unknown exact wavefunction are determined by averaging expressions involving only the total serial correlation of known quantities. The operator is not restricted to the case of the molecular Hamiltonian. This allows for computation of virtually all ground state properties of a molecule by a single, relatively trivial computer program. Our formulas are presented and applied in the context of a diatomic molecule (LiH), but they can be readily extended to polyatomics.

[a)] Work supported in part by grants from The Natural Sciences and Engineering Research Council (NSERC)
[b)] Department of Chemistry.
[c)] Department of Mathematics.
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Ab Initio COUPLED-CLUSTER CALCULATIONS OF ISOTROPIC HYPERFINE SPLITTING.

IAN CARMICHAEL
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Isotropic hyperfine coupling constants for a number of small radicals have been determined by means of *ab initio* molecular orbital theory.

An augmented coupled-cluster doubles technique, which partially incorporates the effect of amplitudes due to single and triple replacements in the (UHF) reference determinant, is used, in conjunction with finite (Fermi-contact) field perturbation theory, to calculate the required spin densities.

Using moderately large contracted gaussian basis sets, results, in good agreement with experiment, are reported for the first-row atoms B-F, for their diatomic hydrides and for the electronic ground state of diboron, $[^3\Sigma_g^-]$.

Some analysis is made of basis set requirements and of the contribution from various levels of excitation.

The research described herein has been supported by the Office of Basic Energy Sciences of the United States Department Energy

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AB INITIO TEST OF THE PAIRWISE ADDITIVITY ASSUMPTION OF SEMIEMPIRICAL ELECTRONIC STRUCTURE: SPECTATOR MODEL OF CORRELATION CONTRIBUTIONS

T5.3.1

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ABSTRACT

The effective valence shell Hamiltonian (H^v) formulation of quasidegenerate many-body perturbation theory is applied to the CH_2 molecule and its positive ion to investigate the ability of the method to describe large valence spaces having a wide range of orbital energies and patterns of quasidegeneracy that vary greatly with molecular geometry. Sensitive tests are provided by the adiabatic singlet-triplet energy difference, by the lowest singlet excitation energy, by the ionization potentials to a series of ion states, and by the question of whether accurate energies emerge simultaneously for a whole set of valence and ion states from a single H^v computation. Computations assess the dependence of H^v calculations on the choice of orbitals and orbital energies, the only degrees of freedom available to the H^v method once the valence space has been prescribed. H^v calculations of CH_2 are also used to test the pairwise additivity assumption of semiempirical electronic structure methods in which it is assumed that the one- and two-center semiempirical integrals in an atomic basis are independent of the molecular environment (except for the one-electron, one-center Coulomb integral). Computed ab initio H^v matrix elements are transformed into a molecule independent atomic basis and are analyzed as a function of bond length and bond angle. The computed behavior is well represented by a spectator model for the influence of molecular enviroment on correlation contributions to individual H^v matrix elements.

T 5.3.2

ELECTRON CORRELATION EFFECTS IN SIMPLE MOLECULES: COMPARISONS BETWEEN MOMENTUM AND POSITION (REAL) SPACE.

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For the examples H_2 and H_3^+, existing ground-state correlated and HF wavefunctions are used to examine (i) one-particle densities and (ii) changes in the interparticle distributions (Coulomb holes) in position space (for specific molecular planes) when a 'test' or 'reference' electron has various fixed locations. Wavefunction transformation into momentum space allows a complementary examination to be made of the Coulomb shifts in the interparticle momentum distributions. A natural expansion of the correlated wavefunction for H_2 assists the interpretation of the results in each space.

The use of these 'partial planar' Coulomb holes and shifts is also applicable to an understanding of electron correlation effects in larger many-electron systems.

T 5.3.3

LIMITATIONS IN DETERMINING THE LOWER BOUNDS TO THE GROUND STATE CORRELATION ENERGY OF THE CYCLIC POLYENES USING OPTIMIZED INNER PROJECTION TECHNIQUE

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Optimized inner projection (OIP) method is used to determine lower bounds to the exact correlation energy for both the PPP and Hubbard models of the cyclic polyenes, C_NH_N, N=4ν+2, ν=3--5, for the entire range of the coupling constant. Orthogonally spin-adapted OIP equations, as derived by graphical methods of spin algebras, are presented. To make extensive OIP studies possible,a special-purpose program, exploiting all symmetries of the PPP cyclic polyene model, was written and implemented. Comparisons with the exact full CI as well as approximate coupled-cluster and limited CI approaches are carried out. Contrary to six and ten membered rings, the OIP lower bounds to the ground state correlation energies of cyclic polyenes with more number of sites are very poor and cannot serve as a meaningful source of information. As the eigenvalues of intermediate hamiltonian, in terms of which the OIP technique is defined, are highly degenerate, even for the weakly correlated region, and because of the irregularities of shapes of branches of the OIP bracketing function, the OIP method, when applied to fourteen and more membered rings,. becomes computationally very intensive. In most cases, simple iterative procedure employing the DCI correlation energy as a starting guess is divergent. Even if it is convergent, there is no guarantee that the result is an OIP lower bound to the ground state correlation energy. Similar difficulties appear when Newton's method for convergence or more sophisticated root searching procedures are applied.

T 5.3.4 | SEMIEMPIRICAL STUDIES OF THE NONLINEAR OPTICAL PROPERTIES OF MOLECULES AND POLYMERS, Henry A. Kurtz, Department of Chemistry, Memphis State University, Memphis, TN 38152

Finite-Field procedures based on both energy and dipole moment expansions for calculating polarizabilities (α) and hyperpolarizabilities (both β and γ) have been implemented within the MOPAC program. Results of this method will be discussed using MNDO, AM1, and PM3 Hamiltonians.

First hyperpolarizability (β) results have been obtained for several substitutent benzenes and related compounds. Comparisons are made to the experimental EFISH results.

Second hyperpolarizabilities (γ) for extended π systems such as polyacetylene and polythiophene oligomers have been obtained. Of particular interest is the behavior of γ as the π system grows. Studies have also been performed on smaller systems to help develop an understanding of the molecular effects which lead to increased hyperpolarizabilities.

T 5.3.5

Quantum Chemistry by Random Walk: Energies of Helium Dimers and Trimers

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We have used the random walk method to calculate total electronic energies for the ground states of helium dimers and trimers in several configurations. The importance-sampling functions for the calculations were antisymmetric combinations of Hylleraas-type functions for each atom multiplied by Jastrow terms to account for the electron-electron and electron-nucleus correlation in adjacent atoms. The energies obtained are estimated to be accurate to within 1.7×10^{-6} au (0.001 kcal/mole) for the dimers and within 1.0×10^{-5} au (0.006 kcal/mole) for the trimers. The usual assumption of pairwise-additivity is tested by results for the trimers.

T5.3.6

MCSCF WITH THE FINITE ELEMENT METHOD

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A numerical multiconfigurational self-consistent field method (MCSCF) for atoms and diatomic molecules is reported. Lagrange interpolation polynomials are used as local basis functions. The orthonormality of the occupied orbitals is built into the parametrization and, since the element functions are non-orthonormal, a generalization of the exp(κ) technique from normal basis function techniques has been developed. The occupied orbitals are optimized using a quasi-Newton method. The configuration interaction (CI) eigenvalue problem is solved using a direct Slater determinant CI program. Atomic MCSCF calculations on He with 140 active orbitals and, on Be with up to 200 000 configuration state functions, and molecular calculations on H_2 and LiH will be presented.

SYSTEMATIC STUDY OF MOLECULAR VIBRATIONAL ANHARMONICITY AND VIBRATION-ROTATION INTERACTION
PART II. LINEAR MOLECULES

T5.4.1

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Recently developed analytic third derivative techniques for SCF wavefunctions have been used to theoretically determine a number of anharmonic molecular properties, including vibration-rotation interaction constants, vibrational anharmonic constants, fundamental vibrational frequencies, sextic centrifugal distortion constants, and *l*–type doubling constants. In this study the applications will be extended to several small linear molecules. The formulas employed for the various spectroscopic constants are those derived from standard spectroscopic perturbation theory. For linear molecules the anharmonic molecular constants which are available from experiments are found to be satisfactorily reproduced theoretically using double zeta plus polarization and/or better basis sets.

T 5.4.2

THEORETICAL STUDIES OF THE HYDROGEN PEROXIDE POTENTIAL SURFACE: AN AB INITIO ANHARMONIC FORCE FIELD*

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Ab initio, GVB+1+2 calculations, employing a (4s3p2d1f/3s2p) basis set have been used to characterize the ground state potential energy surface of hydrogen peroxide. An anharmonic force field that is quartic in the non-torsional degrees of freedom and higher order in the torsion is reported. A second-order perturbation theory calculation of the vibrational energy levels using the ab initio force field yields fundamental frequencies which are within 25 cm^{-1} (3%) of experiment. A reaction path analysis of the torsional mode is also presented in which tunneling splittings for ground and excited vibrational states for both H_2O_2 and D_2O_2 are calculated.

**Acknowledgement*. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

T5.4.3

THE HO_2^+ MOLECULAR ION. A COMPARISON OF METHODS FOR THE CALCULATION OF ANHARMONIC VIBRATIONAL FREQUENCIES

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Four distinct methods for the evaluation of anharmonic vibrational frequencies have been used to study the frequencies of the, as yet, unobserved molecular ion, HO_2^+. Three methods are variational with the other being based upon second-order vibrational perturbation theory. Results will be presented for two potential energy surfaces: a) an SCF surface utilizing up to 4th derivatives of the energy and b) a CI surface formed by replacing the SCF second derivatives by the appropriate CI second derivatives. All calculations were performed with DZ, DZP and TZ2P basis sets.

T5.4.4

DYNAMICAL AND SPECTROSCOPIC STUDY OF NON-RIGID MOLECULES. APPLICATION TO THIOACETALDEHYDE.

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The methyl torsion and aldehydic hydrogen wagging modes are studied theoretically in thioacetaldehyde, in both singlet ground and first triplet excited states. In this aim, the potential energy surfaces are determined resorting to ab initio RHF and UHF calculations with 4-31G basis set + d orbitals on the sulfur atom. It is found that both electronic states present different preferred conformations: The singlet ground state exhibits a planar eclipsed conformations, whereas the triplet state a pyramidal anti-eclipsed one. These surfaces are fitted to a symmetry adapted funcional form.

The two-dimension Schrödinger equations for the torsion and wagging motions are solved for both singlet and triplet states, taking into account the internal symmetry and using appropriate basis. From the eigenvalues and eigenvectors, the relative band locations and intensities (Franck-Condon factors) are deduced, and the absorption spectrum drawn. The theoretical spectrum is compared favorably with the experimental one. A new assignment for the torsional and wagging modes is proposed.

T5.4.5

PULSED LASER-MOLECULE INTERACTIONS AND THE EFFECTS OF PERMANENT DIPOLES

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The interaction of a Gaussian pulsed electric field with a molecule that has a nonzero difference between the permanent dipole moments of the energy levels involved in a transition is studied. The observation of the spectral effects due to the presence of permanent dipoles, including increased periods of the excited state population and negative Bloch-Siegert shifts, will often require the intense fields associated with pulsed rather than purely continuous wave electric fields. However the exact continuous wave analogs can be used to interpret the "permanent dipole" molecule-pulse interaction, with the help of analytic Rotating Wave Approximation results. The increased period of the excited state population for these dipolar molecules can be probed by sampling the time-dependent population using pulses of ultrashort duration. The Riemann product integral method is used to determine the evolution operators for the model two-level problems studied. The symmetry of sine or cosine pulses about the centre of the pulse permits a significant decrease in computational effort as the evolution operators need only be determined for one half of the pulse.

T5.4.6 HYDROGEN-ATOM TUNNELING DYNAMICS AND TUNNELING SPLITTINGS IN POLYATOMIC MOLECULES.

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The hydrogen-atom tunneling dynamics and the splitting of hydrogen-atom vibrational levels due to tunneling in polyatomic molecules and in hydrogen-bonded systems is analyzed. The coupling of the hydrogen-atom vibrational mode to the heavier particle modes (skeleton modes) is considered using adiabatic and near-adiabatic approximations. The tunneling splitting is governed by the barrier to hydrogen-atom transfer at the skeleton configuration most favorable for tunneling rather than the barrier at the equilibrium skeleton configuration. Simple analytical formulas that include the effect of the skeleton-mode dynamics are derived. The theory is tested by comparisons with numerical multidimensional tunneling calculations. The theory can be used to interpret experimental data and is capable of predicting the observed isotope effects.

Abstract: T6.1

"Ab initio calculations of infrared absorption and circular dichroism spectra of methyl glycollate and methyl lactate."

Ab initio SCF calculations of the molecular structure and vibrational spectra of methyl glycollate ($CH_2OH.COOCH_3$) and methyl lactate ($CH_3.CHOH.COOCH_3$) have been carried out at the 6-31G* basis set level.
The structures and energies of several conformational isomers of these molecules, both internally-hydrogen bonded and without H bonding, have been obtained.
The lowest energy structure of each molecule is found to be internally-hydrogen bonded to the carbonyl oxygen. The ester methyl is cis.
The 5-membered ring is very nearly planar.
Vibrational frequencies and absorption intensities have been calculated for each conformational isomer and compared with experimental spectra (in dilute solution), both before and after scaling of the _ab initio_ force field using the methodology of Pulay.
Vibrational circular dichroism (VCD) spectra have been also calculated for methyl glycollate-d_1 and methyl lactate.
The results are compared to available experimental data for methyl lactate.
The ability of _ab initio_ SCF calculations of vibrational absorption and circular dichroism spectra to discriminate among the conformational structures of methyl glycollate and lactate is analysed.

In the case of predictions of VCD spectra, the results obtained are compared to the expectations of the ring current hypothesis.

T6.2

VIBRATIONAL CIRCULAR DICHROISM MEASUREMENT USING A POLARIZING MICHELSON INTERFEROMETER

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The first measurements of vibrational circular dichroism (VCD) using a polarizing Michelson interferometer (PMI)[1,2] have been obtained for neat (-)-α-pinene in the midinfrared region between 1400 and 900 cm^{-1}. These are the first VCD spectra to be measured without the use of a photoelastic modulator. VCD spectra at 4 cm^{-1} resolution were obtained from 60,000 double-sided interferometric scans of a Bomem DA3 Fourier transform infrared (FTIR) spectrometer equipped with a PMI accessory consisting of a second source mounted on the sample chamber, a BaF_2 wire grid polarizing beamsplitter, and an optical plate equipped with mirrors to redirect and focus the infrared beam. In a PMI-FTIR spectrometer, the beam is modulated in polarization, and not in intensity as is customarily the case. Circular dichroism is obtained from the imaginary (sine) Fourier transform of the complex interferogram. The final VCD spectrum is the difference between the VCD of (-)-α-pinene relative to that of its optical isomer. Normalization was achieved using 6000 scans with a properly oriented polarizer placed before the sample.

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T6.3

GAS PHASE VIBRATIONAL CIRCULAR DICHROISM OF SIMPLE CHIRAL MOLECULES

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Vibrational circular dichroism (VCD) spectra of two exceptionally simple chiral three-membered ring molecules with C_2 symmetry, (*S*,*S*)-oxirane-2,3-$^2H_2$ and (*S*,*S*)-cyclopropane-1,2-$^2H_2$, have been obtained in the gas phase at 1 and 4 cm^{-1} resolution. (*S*,*S*)- and (*R*,*R*)-Oxirane-2,3-$^2H_2$, synthesized by J. A. Moore and J. M. Schwab (Department of Medicinal Chemistry and Pharmacognosy, Purdue University)[1] and (*S*,*S*)- and (*R*,*R*)-cyclopropane-1,2-$^2H_2$, synthesized by S. J. Cianciosi and J. E. Baldwin (Department of Chemistry, Syracuse University)[2] were obtained with >95% deuteriation and >92% enantiomeric excess. The signs and relative intensities of the prominent VCD bands can be understood in terms of coupled C*H or C*D motions. The experimental results can be compared with the reported results of VCD intensity calculations based on *ab initio* approaches.[3,4]

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T6.4

Rotational-Vibrational Circular Dichroism

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Abstract

Experimental rotational-vibrational circular dichroism (RVCD) spectra are presented for methyloxirane. These spectra were obtained at 1 cm^{-1} resolution in the ~1500-650 cm^{-1} region. It is found that the circular dichroism sign associated with the Q branch is opposite to those of the P and R branches for some vibrational bands. These unusual RVCD features are explained by developing the necessary theoretical analysis. It is found that the CD associated with the central Q branches of the rotational-vibrational bands in accidental symmetric top chiral molecules provides a unique source for determining the signs of electric dipole and magnetic dipole moment derivatives.

T6.5

Abinitio Localized Molecular Orbital Calculations of Vibrational Circular Dichroism

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Abstract

Vibrational circular dichroism (VCD) can now be predicted using different theoretical formulations. A localized molecular orbital (LMO) approach using CNDO wave functions was developed several years ago. The absence of LMO-VCD calculations using the abinitio wave functions prevented a proper evaluation of the reliability of LMO-VCD calculations. To fill this gap we have developed the necessary algorithm and performed the first abinitio LMO-VCD calculations. Calculations were carried out for trans-1,2-dideuteroethyleneoxide and trans-1,2-dideuterocyclopropane using several different basis sets. The results are found to be in satisfactory agreement with the experimental observations.

T6.6

CIRCULAR DICHROISM OF THE BENZENE GROUP VIBRATIONS AND MOLECULAR STEREOCHEMISTRY.

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Abstract

Circular dichroism (CD) in the vibrational transitions of three different series of molecules namely; phenylcarbinols, carboxylic acids and oxiranes containing the benzene group is measured. It is found that a benzene group vibration, where the hydrogen atoms in the meta and para positions vibrate in a concerted semi-circular path, gives rise to CD that is consistent with the molecular stereochemistry. This observation provides a practical approach to the use of the benzene group as a probe of molecular chirality.

T6.7

Circular dichroism in the far infrared and millimetre wavelength regions: Preliminary measurements.

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Abstract—Preliminary spectroscopic measurements in the near millimetre wavelength region are presented which demonstrate that the study of circular dichroism at those wavelengths should be readily achieved using existing Fourier transform instrumentation.

T6.8

THE VCD SPECTRUM OF 6,8-DIOXABICYCLO[3.2.1]OCTANE: COMPARISON OF EXPERIMENTAL AND MODEL SPECTRA

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The vibrational circular dichroism (VCD) spectrum in the region of 800 to 1500 cm^{-1} of the (+)-(1R,5S)-enantiomer of the title compound is reported. The majority of VCD bands were assigned on the basis of a complete vibrational analysis with the aid of a 3-21G *ab initio* harmonic force field which was scaled in an overlay refinement including the 6-oxa, the 8-oxa, and the unsubstituted hydrocarbon analogs and several deuterated derivatives.

Infrared absorption and VCD intensities were calculated with the fixed partial charge (FPC) and atomic polar tensor (APT) models. The former adequately reproduces the observed signs for most of the observed VCD bands, although absolute intensities are low for both VCD and the absorption intensities. One charge flow parameter, transferred from 2-methyloxetane, is introduced into the FPC expression. It is shown that this term drastically improves the calculated intensities. The FPC and CF models are compared to the corresponding APT calculations.

T6.9

THE VCD SPECTRA OF SELECTED METHYL SUBSTITUTED DERIVATIVES OF 6,8-DIOXABICYCLO[3.2.1]OCTANE

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The VCD and infrared absorption spectra of the exo-7-methyl, the endo-7-methyl, the exo-5,7-dimethyl, the endo-5,7-dimethyl, and the 1,5-dimethyl derivatives of 6,8-dioxabicyclo-[3.2.1]octane are presented in the spectral region 820 to 1500 cm^{-1}. Certain VCD chromophores are identified which give rise persistently to characteristic VCD features recurring in these analogs and in the parent molecule. Selected assignments and intensities are shown from preliminary calculations based on harmonic scaled *ab initio* force fields at the STO-3G and 3-21G levels of theory.

T6.10

A SYSTEMATIC *AB INITIO* INVESTIGATION OF CHARGE FLOW: INFRARED ABSORPTION INTENSITIES OF PROPANE AND DIMETHYLETHER

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Complete sets of charge flow parameters of propane and dimethylether were calculated by a numerical *ab initio* method using the STO-3G, 3-21G and the 6-31G* basis sets. These charge flow parameters, calculated with respect to local symmetry coordinates, were introduced in infrared absorption intensity calculations and compared to the corresponding Fixed Partial Charge and Atomic Polar Tensor intensities. Differences in magnitude as well as direction of the electric molecular dipole moment changes are shown with respect not only to the different empirical intensity models, but also to the different basis sets introduced in the Charge Flow Parameter calculations.

T6.11

A GENERAL FORMULATION OF RAMAN OPTICAL ACTIVITY

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A general formulation of Raman scattering, including the effects of wave length, is presented. The formulation treats the scattering of photons directly. In an application of these results, it is found that, under certain, very general conditions, the ratio of the intensities of Stokes and anti-Stokes scattering is given solely by the ratio of the fourth powers of the frequencies.

Rotationally averaged intensities are obtained for Raman optical activity in terms of photon scattering. Rotationally averaged intensities are also obtained for magnetic Raman activity.

T6.12

IR and VCD INTENSITIES of MODEL SYSTEMS CH3OH, CH3NH2, NH2NH2, NH2OH, and HOOH and the DEUTERATED SPECIES ND2ND2, DOOH and DOOD: a THEORETICAL STUDY using the VIBRONIC COUPLING FORMALISM.

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We have implemented at the *ab initio* level the Vibronic Coupling formalism for infrared and vibrational circular dichroism (VCD) intensities of Nafie and Freedman. We report here the results of a series of calculations on model systems. Hydrazine and Hydrogen peroxide exist in chiral conformations. Although low barriers to racemization preclude the possibility of optical resolution of the parent compounds, the local gauche configuration at the heteroatom bond is preserved in substituted hydrazines and peroxides and these chiral fragments may contribute significantly to the vibrational chiroptical properties of the molecules in which they appear. The calculated VCD rotational strengths for the chiral gauche forms of both molecules suggest that the torsional mode is very intense in the VCD spectrum. In gauche hydrazine of P chirality, the in– and out–of–phase umbrella motions of the nitrogen atoms, ν6 and ν12, respectively, give rise to an intense CD couplet with negative rotational strength to the long wave length side. In hydrazine, all combinations of NH stretches are relatively weak in the IR but the highest frequency mode of b symmetry, ν8, has moderate positive strength. The in– and out–of–phase OOH bends and OH stretches of HOOH are coupled oscillator systems. The former yields a strong bisignate CD pattern whereas the nearly degenerate stretches result in a single band arising from the more intense negative rotational strength of the antisymmetric mode ν5. Significant changes in the VCD patterns due to deuterium substitution are discussed.

W1.1

POTENTIAL ENERGY SURFACES AND CLASSICAL DYNAMICS OF NONADIABATIC PROCESSES

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Chemical reactions of excited state molecules usually involve two or more potential energy surfaces and transitions among them. A quantum chemistry calculation has to give these potential energy surfaces and the seams of crossing or avoided crossing among them, as well as non-adiabatic coupling and transition dipole functions. We have recently studied with the ab initio MO method several of such reactions. In some cases surface-hopping classical trajectory calculation has been carried out on fitted potential functions. The systems studied include 1. The charge transfer reaction $F^+(^3P)+CO \rightarrow F(^2P)+CO^+(A2\pi)$, 2. Transition state spectroscopy in $K+NaCl \rightarrow Na^*+KCl$ and its reverse, 3. Photofragment trapping in NaX*, 4. Photodissociation of CH_3I and ICN and 5. Electronic enhancement of reactivity in Na(3s,3p)+HCl. In the present talk, some of these topics will be discussed.

W1.2

THE CALCULATION OF STATE-TO-STATE RATE CONSTANTS FOR $H + H_2(v,J)$.

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The macroscopic behaviour of a bulk system, in this case, H_2 in H atoms, depends on the results of individual collisions. In order to use the master equation to simulate a particular system of interest, such as excitation and dissociative cooling of hydrogen in interstellar shocks, rate constants for all pertinent processes are necessary. Cross sections obtained from quasi-classical trajectory studies on the Lui-Siegbahn-Truhlar-Horowitz potential energy surface are used to calculate state-to-state rate constants for the possible categories of outcomes of $H + H_2$ interactions including exchange, collision induced dissociation, and non-reactive energy transfer. Classical results are compared with other quantum calculations on the same system in order to assess the suitability of the classical treatment. Interpolation and extrapolation of rate constants to and from other (v,J) states of H_2 are discussed.

W1.3

Dynamics of twisted-intramolecular charge transfer in dimethylaminobenzonitrile

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A detailed dynamical model of the twisted-intramolecular charge transfer (TICT) in dimethylaminobenzonitrile (DMABN) has been developed. The potential energy surfaces are based on the molecular orbital calculations of the excited state energies by LaFemina et. al.[1] for DMABN as modified by the dielectric relaxation about a dipole in a dielectric medium described by a single Debye relaxation with the parameters characteristic of alcohol solvents[2] in the temperature range 218°K ≤ T ≤ 273°K. The time dependence of the twist angle θ, in DMABN is described by two coupled Langevin equations for θ and the local electric field at the DMABN molecule. Friction parameters are taken from a hydrodynamic model[3] of the alcohol solvent using the Debye relaxation time as the time required to develop the full hydrodynamic rotational friction. The trajectories for θ(t) were obtained by solving the resulting Langevin equations numerically. From the resulting distributions of θ(t) the time dependent fluorescence yields are defined as integrals over appropriate regions of θ. This model is used to interpret the nanosecond and picosecond duel fluorescence behavior occurring in various polar solvents over a broad range of temperatures. Our explicit account of the interrelation between the twisting motion of the molecule and the response of the solvent to a dynamical dipole moment allows us to reproduce the observed time dependent fluorescence and Stokes shift. It also allows us to extend the model of Marcus and coworkers[4,5] to a situation in which the twisting dynamics controls the dual fluorescence yields. Moreover, the observed scaling of the yields as functions of solvent polarity and temperature is predicted. From comparison to experiment, we conclude that the rotational dynamics of DMABN in a polar solvent with fluctuations due to solvent hinderance adequately describes the resulting dynamics of the TICT process.

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FREE ENERGY SIMULATIONS OF Li^+ AND Na^+ SOLVATION

W1.4

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Free energy simulation with molecular dynamics is used to calculate relative free energies of solvation of Li^+ and Na^+ in water and methanol. A comparison is made to the experimental observations of Marcus, Kamlet and Taft[1] and a theoretical study by Honig and Coworkers.[2]

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