Second Canadian Computational Chemistry Conference

Queen's University at Kingston
Kingston, ON, Canada

21-25 May 1994

C^4

Program
Poster Schedule
Collected Abstracts
List of Participants

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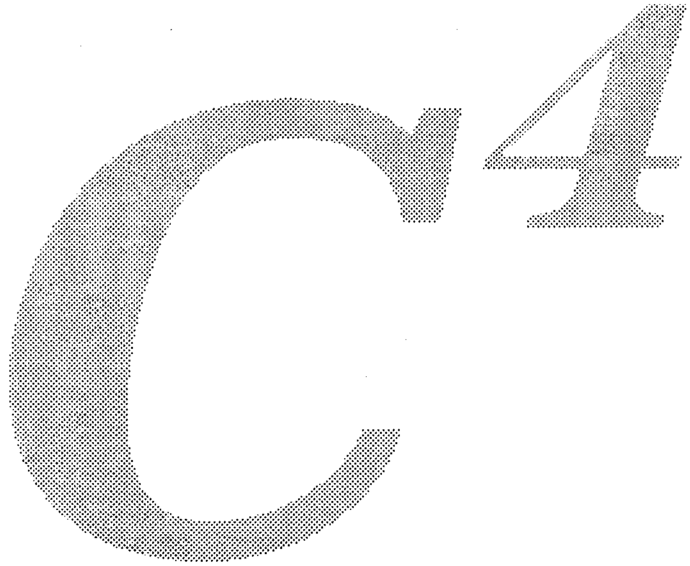
Second Canadian Computational Chemistry Conference

Program



2^{nd} Canadian Computational Chemistry Conference

Queen's University at Kingston
Kingston, Ontario
May 21-25, 1994

Saturday, May 21

2:00PM	Registration desk opens Main Common Room, Victoria Hall
8:00PM –12:00PM	Opening social (cash bar) Lower Common Room, Victoria Hall

Sunday, May 22,1994

Morning	Electronic Structure Chair: R. J. Boyd Lecture Theatre D, Stirling Hall	
8:45AM	Opening remarks D. H. Turpin, Dean, Faculty of Arts and Science, Queen's University	
8:50AM	E. Carter	New ab initio Alogorithms for Solving the Electronic and Geometric Structure Problems
9:35AM	S. Fortier	Molecular Scene Analysis: Application of a Topology-based Procedure for the Automated Interpretation of Protein Electron Density Maps at Medium Resolution
10:05AM	Refreshment Break, Lower Common Room, Victoria Hall	
10:30AM	R. Bartlett	Excited States in Coupled-Cluster Theory: Valence, Rydberg and Core Excitations
11:15AM	P. Piecuch	Orthogonally Spin-Adapted Hilbert-Space Coupled-Cluster Formalism. Importance of the High-Order Coupling Terms
11:40AM	J. D. Goddard	Applications of Computational Quantum Chemistry: Ab initio Theoretical Studies of Group 16 Compounds
12:05PM	Lunch, Lower Common Room, Victoria Hall	

Sunday, May 22, 1994

Afternoon	Applications Chair: M. A. Whitehead Lecture Theatre D, Stirling Hall	
1:30PM	P. Kollman	Molecular Dynamics and Free Energy Perturbation Calculations on Complex Molecular Systems
2:15PM	J. Tirado-Rives	MD Simulations of Protein Dynamics and Unfolding
3:00PM	Refreshment Break, Lower Common Room, Victoria Hall	
3:25PM	P. Mezey	High-Resolution Shape Analysis of Macromolecules
4:10PM	G. Arteca	Scaling Behavior of Entanglement Descriptors of Compact and Noncompact Protiens
4:35PM	End of Afternoon Session	

Sunday, May 22, 1994

Poster Session

5:00PM –7:00PM	Lower Common Room, Victoria Hall Wine and Cheese Social Sponsored by Cray Research Canada

Monday, May 23, 1994

Morning	Reactions and Dynamics Chair: T.T. Nguyen-Dang Lecture Theatre D, Stirling Hall	
8:30AM	G. Patey	Ion Solvation Dynamics
9:15AM	J. Tse	The Structure and Dynamics of Protonated Methane and Acetylene
9:40AM	M. Bramley	Lanczos or Householder Diagonalization? Contracted or Product Basis Sets? What is the Most Efficient Combination for Calculating Triatomic Vibrational Eigenstates?
10:05AM	Refreshment Break, Lower Common Room, Victoria Hall	
10:30AM	P. Brumer	Phase Incoherent Laser Control of Molecular Photodissociation
11:15AM	R. Wyatt	Quantum Dynamical Studies of Energy Transfer in Molecules
12:00AM	Lunch, Lower Common Room, Victoria Hall	

Monday, May 23, 1994

Afternoon	Electronic Structure Chair: A. Thakkar Lecture Theatre D, Stirling Hall	
1.30PM	D. Salahub	Using Density Functional Theory and Other Tools to Model Complex Systems and Processes
2:15PM	W. Yang	A Divide-and-Conquer Method and Its Applications to Large Molecules
3:00PM	Refreshment Break, Lower Common Room, Victoria Hall	
3:25PM	C. Bunge	Large-Scale Atomic Configuration Interaction
4:10PM	A. St-Amant	Gaussian Density Functional Calculations on Systems of Biochemical Interest
4:35PM	Break	

Monday, May 23, 1994

Poster Session

5:00PM –7:00PM	Lower Common Room, Victoria Hall Wine & Cheese Social Sponsored by Molecular Simulations

Tuesday, May 24, 1994

Morning	Applications Chair: D. M. Bishop Lecture Theatre D, Stirling Hall	
8:30AM	D. Dixon	Density Functional Theory Predictions of Molecular Properties and Applications of Computational Chemistry to Atmospheric Chemistry
9:15AM	A. Chaka	A Quantum Mechanical Study of the Friedel-Crafts Mechanism for the Alkylation of Arylamines
9:40AM	F. van Veggel	The Mechanism of Conformational Interconversion of Calix[4]arenes: a Theoretical Study Using the Conjugate Peak Refinement
10:05AM	Refreshment Break, Lower Common Room, Victoria Hall	
10:30AM	P. Saxe	Force Fields and Massively Parallel Computers
11:15AM	H. Carlson	Computational Investigations into the Stereochemistry of Cyclophane-Steroid Complexes
11:40AM	D. Ortwine	Use of Molecular Modeling in the Design of NMDA Antagonists
12:05AM	Lunch, Lower Common Room, Victoria Hall	

Tuesday, May 24, 1994

Afternoon	Reactions and Dynamics Chair: R. Kapral Lecture Theatre D, Stirling Hall	
1:30PM	T. Ziegler	Density Functional Theory as a Practical Tool in Studies of Molecular Energetics and Dynamics
2:15PM	G. Scuseria	Density Functional and Hartree Fock Theories Applied to Large Systems: The Mechanisms of Fullerene Annealing, Fragmentation and Window Opening
3:00PM	Refreshment Break, Lower Common Room, Victoria Hall	
3:25PM	A. Bandrauk	Molecular Multiphoton Transitions: Computational Methods from Perturbative to Nonperturbative Regimes
4:10PM	P. Kusalik	Structure in Molecular Liquids and Its Dynamical Implications
4:35PM	End of Session	

Wednesday, May 25, 1994

Morning	Current and Future Trends Chair: M. Klobukowski Lecture Theatre D, Stirling Hall	
8:30AM	M. Dupuis	Advances in Parallel Processing: Prospectives and Results
9:15AM	C. Johnson	Crystallographic Orbifold Atlas
9:40AM	A. Wong	Large-Scale Parallel SCF
10:05AM	Refreshment Break, Lower Common Room, Victoria Hall	
10:30AM	G. Diercksen	Intelligent Software: The OpenMol Project
11:15AM cancelled	R. Poirier	OSIPE: A Tool for Scientific Programming in FORTRAN
12:00AM	Lunch and END, Lower Common Room, Victoria Hall	

Second Canadian Computational Chemistry Conference

Poster Schedule

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Sessions and locations available at registration time.

Presenter:	Title:
E.E. Aubanel	Intense-Field Molecular Spectroscopy: Vibrational and Rotational Effects in Harmonic Generation by H_2^+
M. T. Banh	On the Interpretation of Unimolecular Decay Lifetime
Angela Barkley	Comparative Conformational Analysis of Sarafotoxins -b and -c: A Molecular Dynamics Study
Christopher I. Bayly	Optimally Sampling the Electrostatic Potential for Potential-Derived Atomic Charges
Attila Berces	Force Fields and Vibrational Frequencies of Organic Molecules Complexed to Transition Metals. A Density Functional Study
Attila Berces	Internal Coordinate Representation for the Skeletal Degrees of Freedom in Coordination Compounds. Applications in Normal Coordinate Analysis and Geometry Optimization
F. Bohr	Study of cycloaddition reaction mechanisms by Density Functional Theory
Pablo J. Bruna	Search for the $\sigma \rightarrow \pi^\star$ and $\pi \rightarrow \sigma^\star$ states of H_2CO
P. Bündgen	Sum rule calculations for moments of the dipole oscillator strength distribution
Patrizia Calaminici	A Density Functional Study of Small Copper Clusters, Cu_n ($n \leq 5$)
Mark E. Casida	Assessment of Kohn-Sham Density-Functional Orbitals as Approximate Dyson Orbitals for the Calculation of Electron Momentum Spectroscopy Scattering Cross-Sections
D. Chartrand	Quantum Effects on the Dynamical Behavior of SF_6 - (Rare-Gas)$_n$ Clusters
Kelly A. Dakin	Antioxidant Activities of Natural and Unnatural Thiol Amino Acids: Implementing Ab initio Calculations to Investigate Factors Affecting Antioxidant Activity

William M. Davis	The Cations, Radicals, and Radical Dimers of Ditelluradiazolyl [HCN_2Te_2]
Ross M. Dickson	Two-Electron Integrals for Multiplet Splittings in DFT
Gino DiLabio	Ground State PoO_2. A Trend Breaker
M. Dory	Conformations of a Cyclohexapeptide Related to the Nerve Growth Factor: a Molecular Dynamics Analysis and NMR Spectroscopy
Liangyou Fan	An Intrinsic Reaction Coordinate Analysis of the Competitive Ethylene Insertion and Chain Termination Reactions of Ziegler-Natta Polymerization by Density Functional Theory
Liangyou Fan	A Density Functional Study of Ethylene Dimerization by Acetylacetonate Nickel Hydride
R. Fournier	Kohn-Sham Study of the Association and Insertion Complexes of Nickel with Water, Methanol and Ammonia
Luc Girard	EHMO Investigation of Haptotropic Shifts in Metal (Fe, Cr, or Mn) Complexes of 4H-Cyclopenta-[def]- Phenanthrene: Are Napthalene-Like Transition States Involved?
Nathalie Godbout	Density Functional Theory Calculations of the Nuclear Quadrupole Coupling Constants of Deuterium and Other Nuclei
F. Grein	Potential Energy Surfaces and the UV Spectrum of H_2CS
Jingang Guan	A Case Where a Better Grid was Needed: Geometry Optimization of Na_4 with the LCAO-Gaussian DFT Program deMon
Hong Guo	Performance of Density Functional Theory on Medium Sized Organic Molecules
I. P. Hamilton	Ab Initio Vibrational Levels for HO_2 and Vibrational Splittings for Hydrogen Atom Transfer
M. Hô	Measures of Distance for Position and Momentum Densities for Atomic and Molecular Systems

Geoffrey Hunter	The Exact One-Electron Model of Molecular Structure: the Molecular Envelope- a Well-founded Basis for Molecular Graphics
Christine Jamorski	Ground State Structures of Fe_n, Co_n and Ni_n $(n \leq 5)$ Clusters
Christine Jamorski	Kohn-Sham Response Theory: Formulation and Implementation for an Auxillary Function-Based Numerical Method
Beiyan Jin	Approaching the Ground State with the Lower Bound Method of Reduced Density Matrix Theory
Martin Kaupp	Relativistic Effects in Mercury Chemistry
S. T. Kim	A Molecular Model of an Ion-Channel of the Amyloid β-Peptide: A Conformational Study
R. A. Kirby	A Conformational Analysis of Serotonin Uptake Inhibitors
Mariusz Klobukowski	Systematic Sequences of Well-Balanced Gaussian Basis Sets
Dennis D. Klug	Ab Initio Dynamical Studies of Li_7 and K_7 Microclusters
Jing Kong	Re-examination of the Hyperfine Structure of $^{14}NH_2$
Andreas M. Köster	Approximation of MOlecular Electrostatic Potentials in Density Functional Theory
Mangala S. Krishnan	Energy and Angular Momentum Dependent Transition Probabilities in Unimolecular Kinetics
Mimi E. Lam	Dehydrogenation of C_2H_4 to C_2H_2 on the Ni(111) Surface
Martin Leboeuf	Electronic Structure Analysis in Density Functional
Xiangzhu Li	Implementation of State-Specific Spin-Adapted Open-Shell Coupled-Cluster Methods
Jaime M. Martell	Ab Initio Studies of the Reactions of OH with Fluorinated Ethanes

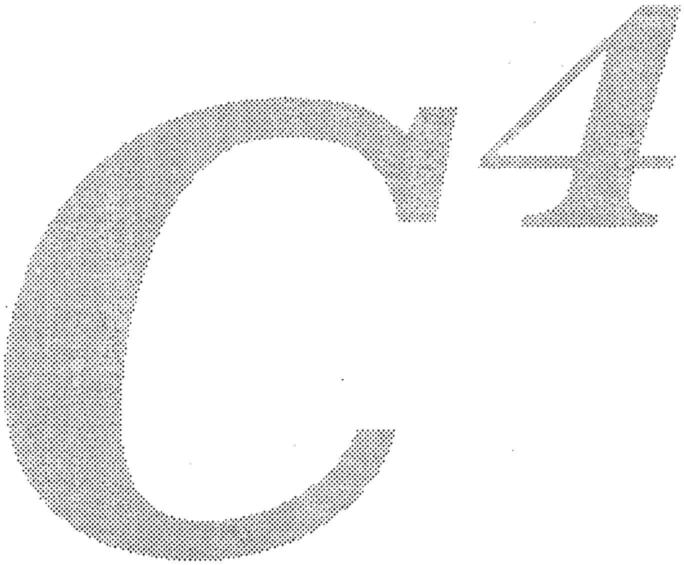
Saba M. Mattar	Electronic Structure, Effective Spin Hamiltonian Expressions and Experimental Evidence for the Parallel Paramagnetic Resonances of the Matrix-Isolated $(\eta^6\text{-}C_6F_6)V$ and $(\eta^6\text{-}C_6F_6)_2V$ Half- and Full-Sandwich Complexes
Saba M. Mattar	Interpretation of the Electronic and Vibrational Spectra of the Neutral 4,5-Bis(Trifluoromethyl)-1,3, 2-Diazolyl Radical
S. Marone	Molecular Structure Analysis of Tricyclic Psychomimetic Drugs
Robert C. Mawhinney	Stability of the BN Bond, From BN^{2-} to BN^{3-}
André McNichols	A 6-Dimensional Calculation for the Vibrational Bands of the HF Dimer
J. Nagy	Critical Evaluation of Molecular Mechanics Nonbonded Interactions for Saturated Alkanes
T. T. Nguyen-Dang	Time-Resolved Laser Control of Vibrational Excitations in Molecules
Shahul H. Nilar	Computational Studies on the Active Site of Papin
Y. S. Park	A Conformational Study of Four Membered Ring and Nine Membered Ring Compounds
José M. Pérez-Jordá	Automatic Numerical Integration Techniques for Polyatomic molecules. Backward Trimming
M. Martin Poulin	Vibrational Band Intensities of Polyatomic Molecules Without Wavefunctions via the Lanczos Algorithm
E. I. Proynov	Nonlocal Correlation Functional Involving the Laplacian of the Density
Cory C. Pye	π-Facial Diastereoselectivity in the Diels-Alder Reaction of the Plane-nosymmetric Dienes
A. V. Raja	Conformational Study of Substituted Poly(thionylphosphazenes) Molecular Models using Density Functional Theory

Pierre-Nicholas Roy	A Time-Energy Resolution Iterative Method for the Direct Calculation of High-Lying Bound Energies and Wavefunctions
I. Rozas	Structure-Activity Relationships in a Family of Anticonvulsant Arylsemicarbazones. Between 2D and 3D QSAR Studies
Eliseo Ruiz	Intercalation of Halogen Molecules in Alkalifluorides Lattices: A Theoretical Study
Hartmut Schmider	Local Speed Distributions Based on Electronic Husimi Functions
F. Senese	Theoretical Studies of Nitric Acid Monohydrate and its High-Energy Isomers
Ting-Hua Tang	A Study of the $H{-}X\cdots\pi$ Hydrogen-Bonded Complexes Using the Theory of Atoms in Molecules
F. P. Temme	Semi-topological NMR Spin Clusters
Mark Thachuk	Dissociation of Diatomic MOlecules in Intense Laser Fields: Stormy Separation or Peaceful Parting?
Ajit J. Thakkar	Accurate Calculation of the Hyperpolarizability of Li
W. T. Thompson	Facility for the Analysis of Chemical Thermodynamics
Chang-Sung Tung	Nucleic Acid MOdeling Tool (NAMOT): An Interactive Graphic Tool for Modeling Nucleic Acid Structures
F. C.J.M. van Veggel	Molecular Mechanics and Molecular Dynamics in Solution of Well-Shielded Eu(3+)-complexes: A Critical Note to Observed Life-Times
A. Vela	Permanent Electric Moments in Density Functional Theory
Jiahu Wang	The Hyperfine Structures of Al_3 and Ga_3 by Density Functional Theory
Jian Wang	The Effects of Flexible Charges in Molecular Dynamics Simulations

Hua Wei	Discrete Variable Representations of Complicated Kinetic Energy Operators
M. A. Whitehead	Correlation in Molecules
James S. Wright	Rydberg Dimer Cations: $(H_2)_2^+$ and $(H_3)_2^+$
Hengtai Yu	Application of the Finite Element Method to Time-Dependent Quantum Mechanics: II-H_2^+ in a Laser Field
V. I. Yukalov	Calculation of Spectra by Method of Self-Similar Approximations

Second Canadian Computational Chemistry Conference

Abstracts



Late or revised abstracts to be distributed later.

Scaling behaviour of entanglement descriptors of compact and noncompact proteins

Gustavo A. Arteca
Département de Chimie et Biochimie, Laurentian University, Ramsey Lake Road,
Sudbury (Ontario), Canada P3E 2C6.

Abstract:

Our goal is to analyze whether global macromolecular folding features are relatively independent of molecular size in real polymers. To this purpose, we employ a novel group of descriptors which convey the complexity of self-entanglements in a moleculear chain. The descriptors we use are derived from one notion: the probability of observing N double points or *overcrossings* when a rigid placement of a polymer backbone is projected onto two dimensions [1,2]. The approach combines the information provided by the three-dimensional molecular geometry and the atomic connectivity. In this work, we deal with protein backbones, which appear always as (folded) linear polymers. Nevertheless, the methodology can be applied to any other type of polymer architecture.

We have studied the asymptotic behaviour of the entanglement descriptors as a function of the number of amino acid residues. A set of 373 proteins, containing a large variety of structural features, has been used. It is found that the configurational averages of the mean number of overcrossings, $\overline{N}$, and the largest probability of overcrossings, A*, obey power laws in terms of the number of monomers [3]. We have compared this behaviour with the scaling observed in the radius of gyration. As well, by specializing in the group of smallest proteins for a given chain length, we have analyzed the effect of the chain's compactness on the type of entanglements observed. The results indicate that the scaling is little affected by the configurational state of the proteins, since virtually the same exponents are obtained for both "swollen" and "compact" structures. The consequences of this finding, and its possible applications in the analysis of protein folding, are discussed with some detail.

[1] G.A. Arteca, J. Comput. Chem. **14**, 718-727 (1993).
[2] G.A. Arteca, Biopolymers **33**, 1829-1841 (1993).
[3] G.A. Arteca, Phys. Rev. E **49** (3), (1994), in press.

Intense-Field Molecular Spectroscopy: Vibrational and Rotational Effects in Harmonic Generation by H_2^+.

E. E. AUBANEL, T. ZUO, AND A. D. BANDRAUK
Laboratoire de Chimie Theorique, Faculte des Sciences
Universite de Sherbrooke, Sherbrooke, Quebec J1K 2R1

We present results of a complete treatment of electronic, vibrational, and rotational motion in numerical calculation of harmonic generation (HG) of 1064 nm laser radiation by the hydrogen molecular ion for intensities $10^{13} < I < 10^{14}$ W/cm^2. We show that efficient HG can be enhanced by suppression of photodissociation, a phenomenon which results from vibrational trapping in laser field-induced potential wells. The HG spectra exhibit peaks clustered around even and odd harmonic orders. All peaks can be assigned to Raman-like transitions between dressed eigenstates of the field-molecule system. Rotational excitation is shown to compete with HG. Thus harmonic generation and photon scattering in molecules holds the promise of a potential diagnostic for molecular stabilization by intense laser fields.

Molecular Multiphoton Transitions – Computational Methods from Perturbative to Nonperturbative Regimes

A. D. BANDRAUK, E. AUBANEL AND H. YU

Laboratoire de Chemie Théoretique, Faculté des Sciences
Université de Shebrooke, Shebrooke, Que, J1K 2R1

The total Schrödinger equation for an electromagnetic field interacting with a molecule leads to time independent coupled elliptic differential equations for CW laser excitation, and to time dependent parabolic partial differential equations for short pulse excitation. The time independent equations result from using a quantized representation, i.e. photon number states, of the electromagnetic field. The stationary states of such a quantized field-molecule system are called dressed states. The relationship between the quantized time independent approach and the time dependent semiclassical field method follows from the consideration of the coherent states of the quantized radiation field.

Examples of appropriate numerical methods for each approach will be presented where one treats radiative and nonradiative interactions simultaneously for any coupling strength. Example of time-independent (CW laser) and time-dependent (laser pulse) calculations of laser coherent control of molecular photochemical processes will be discussed. High intensity processes, such as photoionization, high order Harmonic Generation and its control in molecules have been calculated exactly for H_2^+ by using unitary propagation schemes whereas Finite-Element time-dependent Hartree-Fock methods have been developed for H_2 and H_3^+. Finally we will illustrate from numerical simulations the intriguing possibility of suppressing and hence controlling photodissociation and photoionization at high intensities ($I > 10^{13} W/cm^2$).

On the Interpretation of Unimolecular Decay Lifetime

M. T. BANH AND D. M. WARDLAW

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A particular realization of variational transition theory, known as flexible transition state theory was applied to obtain unimolecular decay lifetime for hydrogen peroxide. A new treatment of the density of reactant states, which takes advantage of the availability of the ab-initio based potential energy surfaces, was tested for hydrogen peroxide. Compared to the traditional rigid-rotor harmonic-oscillator treatment of density of states, the new treatment yields a larger density of states, and statistical lifetime predictions that are in better agreement with a spectroscopy experiment and classical trajectories. Three different potential energy surfaces were used. These give decay lifetimes between 3 and $14ps$ for reactants excited to the $6\nu_{\mathrm{OH}}$ vibrational level, consistent with the lower bound established by the experiment.

ABSTRACT

Comparative Conformational Analysis of Sarafotoxins -b and -c : A Molecular Dynamics Study. Angela Barkley[*] and Donald F. Weaver[*,#], Departments of Chemistry (*) and Medicine (#) (Neurology), Queen's University, Kingston, Ontario, Canada, K7L 3N6.

The sarafotoxins (snake venom toxins-SRTXs) are potent vasoactive peptides. These partially constrained 21-amino acid peptides are both structurally and functionally similar to the human endothelins. A number of hypotheses have been presented to account for the marked variation in activity among the sarafotoxin/endothelin family of peptides based primarily on structure-activity relationships. In this study, theoretical conformational analysis was applied to the study of conformational preferences of sarafotoxins-b and -c. Both high and low temperature molecular dynamics (MD) simulations were used to screen the conformational space of the two SRTXs in an aqueous environment. The AMBER molecular mechanics force field was used for energy minimization. The results were compared to the previously studied conformational analysis of endothelin-1 by Weaver *et al.* (1993). Like endothelin-1, these peptides exist in a number of low energy conformers. The difference in reactivity between SRTX-b and -c and endothelin-1 was rationalised not only in terms of amino acid differences but also on conformational preferences imparted by the different amino acids. Such theoretical studies will contribute to further understanding the diverse activity of this class of peptides, especially with respect to their potential role as neuromodulators of the central nervous system.

Excited States in Coupled-Cluster Theory: Valence, Rydberg and Core Excitations

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Quantum Theory Project
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Abstract

Coupled-cluster theory has been demonstrated to offer a highly accurate description of the general states of molecules, via $\Psi_{cc} = e^{T}\Phi$. To obtain excited states of the same symmetry as a lower state requires some generalizations. One approach is multi-reference CC, either in a Hilbert or Fock (value universal) space framework. The other, the equation-of-motion (EOM) CC method, is conceptually single reference, but provides a spectrum of excited states, associated oscillator strengths and properties. EOM-CC also permits the facile treatment of ionized (IP-EOM-CC) and electron attached (EA-EOM-CC) states. The latter, in particular, permits an alternative treatment of excited states by adding an electron to a cation. The above methods are described and illustrated by application to various types of excited states, with the EA-EOM-CC being particularly appropriate for core excitations.

References

1. A. Balkova and R.J. Bartlett, "Coupled-Cluster Method for Open-Shell Singlet States," Chem. Phys. Lett. **193**, 364 (1992).
2. D.C. Comeau and R.J. Bartlett, "The Equation-of-Motion Coupled-Cluster Method: Applications to Open- and Closed-Shell Reference States," Chem. Phys. Lett., **207**, 414 (1993).
3. J.F. Stanton and R.J. Bartlett, "The Equation of Motion Coupled-Cluster Method — A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition Probabilities and Excited State Properties," J. Chem. Phys. **98**, 7029 (1993).
4. J.D. Watts and R.J. Bartlett, "Triple Excitations in Coupled-Cluster Theory: Energies and Analytical Derivatives," Int. J. Quantum Chem. **S27**, 51 (1993).
5. M. Nooijen and R.J. Bartlett, "Equation of Motion Coupled Cluster Methods for Electron Attachment," to be published.

Optimally Sampling the Electrostatic Potential For Potential-Derived Atomic Charges

Christopher I. Bayly* and Claude Dion, Merck Frosst Center for Therapeutic Research, P.O. 1005, Pointe-Claire Dorval, Québec H9R 4P8

A new criterion is suggested for use in sampling the quantum-mechanical (QM) electrostatic potential (ESP) around a molecule for purposes of fitting atomic charges. The objective of the new scheme is to get as close as possible to the molecule without penetrating the "van der Waals envelope". This is desirable because previous work suggests that (a) improving the description of buried atomic centres will decrease the problem of excessive and fluctuating potential-derived charges on these centres, and (b) in order to best reproduce specific, localized intermolecular electrostatic interactions such as hydrogen bonds, it is important to retain characteristics of higher-order electric moments of the molecule. Sampling the QM ESP closer to the molecule will yield more information about the higher order electric moments (since they decrease faster with distance) and the buried atomic centres.

Force Fields and Vibrational Frequencies of Organic Molecules Complexed to Transition Metals. A Density Functional Study

ATTILA BERCES AND TOM ZIEGLER
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Calgary, Alberta, T2N 1N4 Canada

Density functional theory (DFT) has been successfully applied to calculate geometries, force fields, and vibrational frequencies of a large variety of molecular systems, including transition metal compounds. We have started a systematic investigation based on this technique, of harmonic force fields of benzene and cyclopentadienyl anion and their complexes with transition metals. We studied how the calculated force field reproduces vibrational frequencies and eigenvector related quantities. Further, this study investigates how the force fields of free ligands change upon coordination to transition metals. Our calculated geometries, and harmonic frequencies for benzene, $C_5H_5^-$, and LiC_5H_5, ferrocene, dibenzene chromium, and chromium-benzene- tricarbonyl are in very good agreement with experimental data. The average deviation between the calculated and the empirical frequencies is 17 cm-1.for benzene, and about 30 cm-1 for organometallic complexes. We suggest alternative frequency assignments for organometallic complexes. Further, we compared the force constants of free and coordinated ligands, and found that the metal–ligand interaction makes significant difference in the values of out-of-plane force constants.

Internal Coordinate Representation for the Skeletal Degrees of Freedom in Coordination Compounds. Applications in Normal Coordinate Analysis and Geometry Optimization

ATTILA BERCES AND TOM ZIEGLER
Department of Chemistry, The University of Calgary,
Calgary, Alberta, T2N 1N4 Canada

A set of molecules in a unit cell of a single crystal possesses some vibrational modes that are the result of intermolecular interactions, and that originate from the rotational and translational motions of the free molecules. The vibrational degrees of freedom of transition metal complexes, containing a central metal atom and organic molecules as ligands, can be considered in a similar manner. The modes arising from the translations and rotations of ligands are called skeletal vibrations. In order to facilitate comparison of force constants between related molecules, one needs a physically meaningful set of internal coordinates. Since the skeletal modes originate from translations and rotations, usual internal coordinates, like bond stretches, bending angles etc. do not provide an appropriate representation. We introduced a set of local symmetry coordinates, that represent these modes. We found that these coordinates are suitable for comparing the force constants of free and coordinated ligands, and that they also produce close to diagonal force fields. Due to the small coupling between coordinates, these coordinates are appropriate optimization variables in geometry optimization. These coordinates are compared to other representations.

Study of cycloaddition reaction mechanisms by Density Functional Theory.

F. Bohr[1,2], X. Assfeld[3], M.F. Ruiz-López[3] and D.R. Salahub[1,2]

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3. Laboratoire de Chimie théorique, URA CNRS 510,
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FRANCE

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Various algorithms are available to locate reaction transition states with Density Functional Theory calculations [1,2]. However, at present time, there are still few reactivity studies in organic chemistry by this approach. Since many ab initio studies have been devoted to the study of cycloaddition processes, which are among the most important reactions in organic synthesis, it appears interesting to investigate them at the DFT level.

Calculations on Diels-Alder reactions have been already carried out [2,3]. In this work, we consider some [2+2] cycloadditions. The mechanism of these reactions may be either diradical, zwitterionic or concerted and depends a lot on the system studied and on the reaction medium. For instance, the ketene+imine, or Staudinger reaction, that is a widely used method in the synthesis of β-lactams, seems to proceed through a zwitterionic mechanism in solution [4] although theoretical studies for isolated species predicted a concerted one.

We study some model [2+2] cycloaddition processes by DFT methods and compare the results with available experimental data and other theoretical works. Since medium effects can be substantial, solute-solvent electrostatic interactions have been taken into account by a recently developped SCRF continuum model [5]. The influence of the solvent on the reaction mechanism is discussed.

[1] L. Fan and T. Ziegler *J. Chem. Phys. 92 (1990) 3645*; Y. Abashkin and N. Russo *J. Chem. Phys.* (submitted)

[2] R.V. Stanton and K.M. Merz *J. Chem. Phys. 100 (1994) 434*

[3] M.F. Ruiz-Lopez, X. Assfeld, J.A. Mayoral, J.I. Garcia, L. Salvatella and F. Bohr (to be submitted)

[4] X. Assfeld, J.A. Sordo, J. Gonzalez, M.F. Ruiz-Lopez and T.L. Sordo, J. Mol. Struct., Theochem, 287 (1993) 193

[5] M.F. Ruiz-Lopez, F. Bohr, M.T.C. Martins-Costa and D. Rinaldi *Chem. Phys. Letters*, in press

Lanczos or Householder diagonalization? Contracted or product basis sets? What is the most efficient combination for calculating triatomic vibrational eigenstates?

Matthew J. Bramley and Tucker Carrington Jr.
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Three-dimensional exact quantum calculations of triatomic vibrational eigenstates (energy levels and wavefunctions) are now routine. Such calculations require a model nuclear potential energy surface (PES) as input. Being dynamically exact, they provide in principle the definitive means of refining the PES, an important goal since the latter is the key to all quantitative understanding of molecular spectra. But PES refinement requires the calculations to be repeated very many times — a compelling reason for the most efficient methods be established. Another reason lies in the obvious interest in extending these calculations to larger molecules. Some of the most promising techniques, such as the Lanczos algorithm, are only just beginning to be fully explored. We have put novel Lanczos methods together with other state-of-the-art approaches in a single optimized computer program capable of answering the questions posed in the title. Results will be presented both for H_2O, a relatively rigid molecule, and HCN/HNC, which is floppy and isomerizing.

Quantum Interference Control of Photodissociation at High Fields

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Control over product probabilities and channel specific line shapes in molecular photodissociation is shown to result from quantum interference effects which can be manipulated by varying the frequencies of two intense laser fields. The laser fields, whose relative phase need not be well defined, have frequencies centered around two transitions: one between the continuum and an initially populated state and the second between the continuum and an initially unpopulated molecular bound state. Computations on Na_2 photodissociation show that control over product yields is extensive, with the branching ratio changing by a factor of ten as the frequencies are tuned over a convenient range.

Search for the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states of H_2CO.

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The CO-stretching potentials of low-lying singlet states of H_2CO in C_{2v} symmetry, resulting from *ab initio* multireference CI calculations, are reported. Within the Franck-Condon region, the valence states ${}^1B_1(\sigma,\pi^*)$ and ${}^1A_1(\pi,\pi^*)$ cross all members of the n → Ryd series as well as $\pi \rightarrow 3s({}^1B_1)$. The structures of the absorption bands are therefore extensively altered by vibronic mixing, intensity borrowing and predissociative interactions. In fact, experiments show that the n → Ryd bands are vibrationally more complex and of higher intensity than expected.1) Predissociation appears to be the main cause preventing detection of $\pi \rightarrow 3s\ ({}^1B_1)$. The diabatic ${}^1A_1(\pi,\pi^*)$ potential, of repulsive nature and crossing all electronic states from X^1A_1 (H_2CO) up to X^2B_2 (H_2CO^+), plays an unique role in the electronic spectrum by coupling the ground state with the whole n → Ryd manifold. These predissociating interactions leading to CH_2 + O fragments are responsible for the absorption continuum in the spectrum above 7.5 eV. Vertically, the $\pi \rightarrow \pi^*$ excitation lies at 9.6 eV and mixes strongly with the doubly-excited configuration $n^2 \rightarrow \pi^{*2}$. The large quantum defect and other anomalies reported for the n → "3d" experimental band at 8.88 eV, assigned here to the $3^1A_1 \leftarrow X^1A_1$ transition, are due to a heavy mixing in the upper state between π,π^* and both Rydberg excitations $n \rightarrow 3d_{yz}$ and $n \rightarrow 3p_y$.

1) M. Hachey, P.J. Bruna, and F. Grein, *Faraday Transactions*, 1994, in press.

Sum rule calculations for moments of the dipole oscillator strength distribution

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Moments of the molecular dipole oscillator strength distribution are defined by

$$S(k) = \sum_b (E_b - E_0)^k f_{0b} + \int (E - E_0)^k \frac{df}{dE} dE \ ,$$

where f_{0b} is the oscillator strength for a bound state transition and $\frac{df}{dE}$ is the density of the dipole oscillator strength for transitions into the continuum. The $k = 0$ moment is given by the Thomas-Reiche-Kuhn sum rule as the number of electrons in the system. For $k = 2, 1$ and -1 other sum rule expressions are available that allow these moments to be expressed as ground state expectation values[a]. These sum rule expressions have been used to calculate moments of the isotropic and anisotropic molecular dipole oscillator strength distribution for a series of small molecules. All sum rule expressions are evaluated at various levels of theory. Basis set requirements are analysed for each dipole sum and correlated multi-reference CI wavefunctions are employed to study the effect of electron correlation on the moments and their anisotropies. Results will be presented for O_2,NO,CO,N_2,HF and HCl. The anisotropy data obtained are hoped to provide a useful source of constraints in recently developed anisotropic dipole oscillator strength distribution techniques[b].

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[a] J.O.Hirschfelder,W.Byers Brown, S.T.Epstein Adv.quant.Chem. 1,255 (1964)

[b] W.J.Meath,A.Kumar Int.J.Quant.Chem.:Quant.Chem.Symp. 24,501 (1990)

Large-Scale Atomic Configuration Interaction

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Large-scale atomic CI is needed to account for valence and core-valence correlation even at a qualitative level of accuracy. We have developed a carefully optimized open-ended suite of programs for relativistic and nonrelativistic atomic CI running on RISC workstations (DEC Alpha, HP, IBM and SG). The efficiency of the codes will be illustrated with fine grained profiles of selected applications.

Accuracy is limited by four factors: (i) the extent to which Slater-type orbitals can reliably be optimized, which is user- dependent but has, nevertheless, its ultimate limits, (ii) a loss of accuracy in the evaluation of symmetry eigenfunctions by means of projection operators when high ($l > 6$) angular momentum orbitals occur, (iii) the approximation to the full CI by multireference singles and doubles CI or similar methods, and (iv) the computer resources available. Each of the above will be illustrated with calculations on He, Li, Be, Ne, Ca and negative Ca.

An outline of strategies for relativistic atomic CI will also be given, in particular the implementation of MCSCF-CI using Brillouin's theorem and a new variational principle for atomic relativistic states.

A Density Functional Study of Small Copper Clusters, $Cu_n(n \leq 5)$.

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Density Functional calculations were done for small copper clusters, $Cu_n(n \leq 5)$. using the Linear Combination of Gaussian-Type Orbitals (LCGTO-DF) approach implemented in the deMon program. The calculations were of the all-electron type and local and nonlocal functionals were used. For each case, we have tried several candidates in order to determinate the lowest energy structures. Our results show that the introduction of non local corrections is crucial for a right assignment of the ground state for a given cluster. A vibrational analysis was done for the calculated ground states. The obtained results show that these structures are minima, since there were no imaginary frequencies. Our results of bond lengths, adiabatic ionization potentials and binding energies are in reasonable agreement with experimental data as well as with other theoretical results.

Computational Investigations into the Stereochemistry of Cyclophane-Steroid Complexes

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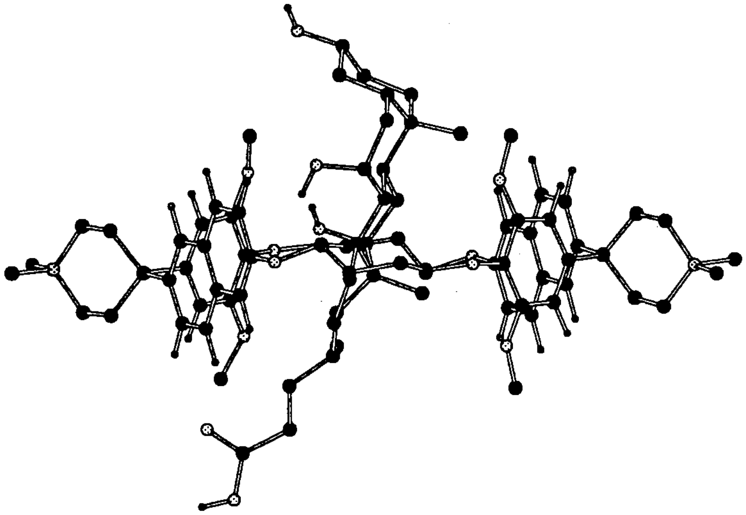
Abstract: Monte Carlo calculations have been used to determine the relative change in free energy of binding for steroid-cyclophane complexes in four different conformations. Statistical perturbation theory provided changes of free energy for the mutation of the C12αOH in excellent agreement with the experimental data; however, the C7αOH mutation provided only one stereoconformer which agreed with experiment. Therefore, one of the guest binding orientations in the inversion symmetric host conformer has been chosen as the over-all best representation for further studies. Analyses of hydrogen bonding and energetic contributions to the free energy changes provided insight into the interaction of the steroid with the cyclophane and with the mixed methanol/water solvent; this information should prove useful to future steroid host design. Furthermore, the binding patterns in the gas phase and the orientational variations in the solution phase provide a model for the interpretation of the two NMR binding patterns for hydrophilic vs. hydrophobic steroids.



New Ab Initio Algorithms for Solving the Electronic and Geometric Structure Problems

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We will present an overview over our work in two areas: (i) new numerical algorithms for the *ab initio* treatment of electron correlation and (ii) new methods for unbiased predictions of both potential energy surface minima and saddle points. For the first topic, we will discuss our pseudospectral (combined grid/function space) methods for both configuration interaction (including full[1], double excitation[2], and multi-reference single and double excitation CI[3]) and many-body perturbation theory (MP2 MP3)[4]. By evaluating the time-consuming terms involving two-electron integrals on a grid rather than analytically, we are able to efficiently reduce the scaling by typically one power of the number of basis functions used in the problem. For example, we have shown that we obtain an order of magnitude speed-up in MP2 calculation relative to Gaussian 92. For the second topic, we will discuss: (i) our Ridge method for finding saddle points on potential energy surfaces, which only requires input about the reactant and product geometries and no initial guess for the saddle-point structure;[5] (ii) out *ab initio* molecular dynamics/simulated annealing method for finding geometry minima[6,7]; and (iii) our modified quasi-Newton method for finding geometric minima that reduces the scaling of the two-electron integrals computation to $O(N^3)$, where $N =$ the number of basis functions[8]. Examples will be provided in each case. With these methods in hand, and work in progress, we expect that accurate predictions of reaction paths for large molecules will be feasible.

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[3] T. J. Martinez and E. A. Carter, *to be published (1994)*.
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[6] B. Hartke and E. A. Carter, *J. Chem. Phys.*, **97** (6569)1992
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ASSESSMENT OF KOHN-SHAM DENSITY-FUNCTIONAL ORBITALS AS APPROXIMATE DYSON ORBITALS FOR THE CALCULATION OF ELECTRON MOMENTUM SPECTROSCOPY SCATTERING CROSS-SECTIONS.

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Electron momentum spectroscopy is a binary (e,2e) knockout experiment in which the experimental momentum profile is proportional to the spherically averaged momentum distribution (MD) of the Dyson orbital of the ionized electron. Accurate comparisons between theory and experiment require the inclusion of correlation and relaxation effects in the calculation of the Dyson orbital, for example via configuration interaction (CI) or Green function methods. Such calculations are computationally demanding and, as such, have been limited to only the smallest molecules. The target Hartree-Fock approximation (THFA), in which the Dyson orbital is assumed proportional to a canonical Hartree-Fock orbital, has proven to be a popular alternative, but the need to use extended basis sets for accurate MDs is still a limitation for larger molecules. Kohn-Sham (KS) density functional theory (DFT) provides a more efficient alternative to conventional ab initio methods such as Hartree-Fock and CI, and the quality of DFT results is typically comparable to or better than HF for the calculation of many properties. Thus DFT may also be a useful tool for the electron momentum spectroscopist interested in analyzing results for molecules beyond the reach of the THFA. It has been shown that, although KS orbitals are not Dyson orbitals, they approximate Dyson orbitals in a well-defined variational sense. Thus there is a sound theoretical basis for using the KS orbitals to calculate MDs. We compare these KS MDs with those obtained from HF, CI, and experiment. The results show that KS and HF orbitals are of comparable quality for approximating Dyson orbitals, although the errors in the approximations are often in opposite directions. The effect of varying the functional is also discussed with particular emphasis on differences between the treatment of correlation in DFT and by conventional ab initio methods. Transition orbitals and a Kohn-Sham analogue of Koopmans' orbitals are also considered.

A Quantum Mechanical Study of the Friedel-Crafts Mechanism for the Alkylation of Arylamines

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The alkylation of arylamines in the presence of AlCl3 is an important reaction in many large scale industrial processes. Three possible mechanisms will be evaluated using semiempirical methods, density functional theory, and HF at the MBPT(2) level. Successive levels of refinement in search algorithm and electronic structure calculations will be used to examine the potential surface to locate the transition state. A mechanism involving a cyclic transition state containing both the aluminum and nitrogen atoms will be shown to be the most probable.

Quantum Effects on the Dynamical Behaviour of SF_6-(Rare Gas)$_n$ Clusters

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Abstract

A model developed by Eichenauer and Le Roy predicts the shift of the ν_3 band of SF_6 perturbed by neighbouring atoms in a cluster, as a function of the number of perturbers and their relative positions.[1] When combined with Monte Carlo or molecular dynamics simulations of the cluster dynamics, this model has shown that the IR spectra of these species should provide an incisive means of identifying cluster isomers and their dynamical state (liquid-like *vs.* solid-like).[2] However, all applications published to date have been based on the use of classical mechanical simulations for the cluster dynamics. Among other things, those studies predict the co-existence of solvated and non-solvated isomers of a given cluster species, which have distinctly different melting behaviour and spectroscopic properties. Our current work is examining whether these conclusions are an artifact of classical mechanics. The work described here uses Path Integral Monte Carlo methods to determine whether the conclusions of these classical studies are generally valid, or whether some of them are artifacts of classical methodology. In particular, we wish to determine whether the higher-melting temperature, "minimally solvated" isomers remain as distinct species when the effects of zero-point energy are taken into account. Also, the further effect on the simulated spectra of including a triple-dipole dispersion term to the pair-wise additive potential energy surface will be examined.

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[2] M.A. Kmetic and R.J. Le Roy, J. Chem. Phys. 95, 6271 (1991).

Antioxidant Activities of Natural and Unnatural Thiol Amino Acids: Implementing Ab initio Calculations to Investigate Factors Affecting Antioxidant Activity.

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Phenolic compounds related to α-tocopherol (vitamin E) are recognized for their antioxidant properties. While the antioxidant activity of thiol amino acids, such as the L-cysteinyl residue of glutathione, is documented, the mechanism of action for which the antioxidant effects are observed remains controversial.

The antioxidant activity (K_{inh}) of a series of natural and unnatural thiol amino acids, including L-cysteine, DL-homocysteine, N-acetyl-L-cysteine and glutathione, has been assessed experimentally, and the stability of each towards air-oxidation has been determined. Disparities in both the antioxidant activity and the stabilities of these thiols implies differences in the accessability of the hydrogen atom available for H-abstraction in free radical reactions. *Ab initio* calculations at the 3-21G* level have been implemented to determine the factors influencing the antioxidant activity of these selected thiol amino acids.

The Cations, Radicals, and Radical Dimers of Ditelluradiazolyl [HCN_2Te_2].

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Abstract

Dithia- and diselena- diazolyl radicals and dimers have proven to be important building blocks in the design of low dimensional molecular conductors. Research on the tellurium based analogues is much rarer. Thus, the molecular and electronic structures of the cations, radicals and radical dimers of ditelluradiazolyl were studied using *ab initio* theory including electron correlation by Moller-Plesset perturbation theory up to partial fourth order (MP4SDQ). A face to face C_{2v} dimer is predicted to be bound with respect to two radicals by approximately 18 kcal/mol. The C_{2h} dimer also has been studied and is *ca.* 2 kcal/mol less stable than the C_{2v} conformer. Relaxing the symmetry constraints on the dimers led to lower total energies at the Hartree-Fock level but when electron correlation is included the C_{2v} and C_{2h} dimers are predicted to be more stable than the relaxed structures. Comparisons of the results for the Te compounds with our earlier work on the S and Se analogues indicate that the predictions for the geometries, vibrational frequencies and ionization potentials of the Te species are of sufficient accuracy to guide future experiments.

TWO-ELECTRON INTEGRALS FOR MULTIPLET SPLITTINGS IN DFT.

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Calculating *ab initio* the multiplet structure of transition metal complexes is a demanding problem. Ziegler, Rauk and Baerends showed the formalism for doing so in density functional theory in 1977 (*Theor. Chim. Acta,* **43**, 261), and C. Daul has recently automated the group theoretical calculations necessary in the general case. However, numerical results require arbitrary two-electron integrals of the form $\int a(1)b(1)c(2)d(2)/r_{12}\, d1d2$, where a, b, c, d are molecular orbitals. We have adapted the grid scheme of Becke & Dickson (*J. Chem. Phys.* **89**, 2993 (1988)) to the problem of evaluating these integrals quickly. The method is applied to the problem of assigning the electronic spectrum of the permanganate ion, MnO_4^-.

Intelligent Software: The OpenMol Program

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OpenMol is an integrated, open and flexible program for quantum chemical calculations, based on the rigorous use of expert systems and abstract data types. User guidance, the evaluation and interpretation of results and computer based learning are the three unique features of OpenMol that distinguish it from all other programs in the field. It is, through these functions, easy for a novice to use and, through the possibility of rapid- prototyping and symbolic manipulation, for an expert to exploit as an important working tool, but also available for consultation and teaching/ learning. The ideas behind OpenMol are, however, quite general and apply equally to many other scientific areas where experience and different numerical techniques have to be combined in a flexible way to produce useful results. OpenMol gives an open framework which encourages further evolutionary developments. The broad structure of OpenMol has been established and many numerical modules have been designed and implemented. Work is now in progress to design, implement and interface the necessary data and knowledge bases and the computer based learning system and to acquire data and knowledge. OpenMol is the answer to the growing complexity of large packages used in Computational Chemistry and other fields of Computational Sciences.

Ground State PoO_2. A Trend Breaker.

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The group VI dioxides (O_3, SO_2, SeO_2, and TeO_2) have fairly well characterized ground state potential energy surfaces. The most striking feature of all these surfaces is the presence of two minima which correspond to a ring structure (with O-X-O angles below 60 degrees) and a bent conformation (with O-X-O angles near 115 dgress). The low angle minimum, in all cases, is metastable relative to the large angle minimum. The last member of this series is PoO2 and virtually no information is available on this species. Preliminary calculations show that the ground state surface of this molecule has a double minimum like its analogs but that the ring conformation lies substantially lower in energy than the open form. Relativistic, basis set, and f-shell effects are being investigated as possible contributors to this behaviour.

Density Functional Theory Predictions of Molecular Properties and Applications of Computational Chemistry to Atmospheric Chemistry

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This talk will describe DFT studies of molecular properties including reaction energies, vibrational infrared intensities, nuclear magnetic resonance shifts, the prediction of photoelectric spectra and comparison of experimental and theoretical densities. The talk will also describe how computational chemistry can be used to address problems in atmospheric chemistry with specific applications to the degradation reactions of HFC-134a and to the prediction of the kinetics of reactions involving hydroxyl radicals.

Conformations of a Cyclohexapeptide Related to the Nerve Growth Factor : a Molecular Dynamics Analysis and NMR Spectroscopy.

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ABSTRACT

Nerve Growth Factor (NGF) is a protein composed of 118 amino acids which crystallizes as a dimer related by a two-fold axis [1]. Each protomer is formed by three extended segments of twisted anti-parallel β-sheet linked by turns which lead to a somewhat elongated molecule. At the "top" of the molecule, there are three β-hairpin loops (27-38, 90-100, and 40-50); the "bottom" is characterized by three consecutive reverse turns (58-68). NGF has attracted considerable attention since the discovery that it can lead to neuronal regeneration and may be useful for the treatment of Alzheimer's Disease (AD) [2]. Furthermore, neuronal activity has been attributed to the presence of these particular loops in the protein.

In this work, we have focused our attention on a particular loop composed of the 62-67 amino acids for which we have constructed a true cyclopeptide (cGly-Ser-Glu-Val-Pro-Arg).

To identify the best conformer adopted by this cyclohexapeptide, a Monte Carlo random search, with the BIOGRAF 3.0 program [3] operating on a IBM RS/6000 550 processor, has led to 10 preliminary conformers. The ten conformers have been submitted to molecular dynamics (MD) at both 1000 K and 310 K. Following these calculations, ten new low energy conformers were selected for further optimization with the AM1 Hamiltonian [4] included in the MOPAC 6.0 semi-empirical molecular orbital program [5]. Parallel to this study, a conformational analysis by NMR spectroscopy has been done.

Based upon these results, we will discuss the validity of the different theoretical approaches (MD at 310 K and semi-empirical AM1) to reproduce the experimental conformer obtained with the NMR spectroscopy.

Supported by Allelix Biopharmaceuticals and the Canadian Networks of Centres of Excellence Program in Neural Regeneration and Functional Recovery.

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Advances in Parallel Processing : Prospectives And Results.

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The extraordinary advances in computational chemistry in the 80's resulted from the synergy between the development of new methods (gradient techniques in QC, free energy in MD, ...), and new algorithms, and the advent of vector supercomputers. Further advances in the 90's are expected, which will take full advantage of high-performance workstations, clusters, and massively parallel machines. In this presentation we will review elements for successful parallel processing, and describe our current work dealing with correlated methods in quantum chemistry. These parallel algorithms are embodied in the HONDO 8.5 program.

An Intrinsic Reaction Coordinate Analysis of the Competitive Ethylene Insertion and Chain Termination Reactions of Ziegler-Natta Polymerization by Density Functional Theory

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Ziegler-Natta catalysis is considered to follow the Cossee mechanism: $RTiCl_2^+ + C_2H_4 \rightarrow \pi\text{-complex} \rightarrow \text{transition state} \rightarrow RC_2H_4TiCl_2^+$. The reaction was studied previously by semiempirical and ab initio methods with the simplification of $R=CH_3$. Presented here is a density functional theory study of the reaction mechanism with $R=C_2H_5$. The major difference between CH_3 and C_2H_5 is that the latter can form a stable β-agostic conformation. An incoming ethylene can approach the β-agostic $RTiCl_2^+$ in two different directions and lead to two different products. The geometries of the transition states of both reactions are fully optimized and identified by vibrational analysis. The intrinsic reaction coordinates are then traced to further verify the transition states. The reaction pathways thus obtained connect clearly the reactants, the transition states and the products. It is found that only one of the reactions leads to the ethylene insertion into the Ti-R bond, and the other represents a β-hydrogen transfer from the R group to ethylene, which in other words, is a β-hydrogen elimination reaction of the polymer chain from the titanium centre. The energy barriers of the insertion and the elimination are calculated to be 2.2 kcal/mol and 5.3 kcal/mol, respectively, according to local density approximation with gradient corrections. On the other hand, β-hydrogen transfer to an ethylene is much less endothermic than β-hydrogen elimination without the aid of an ethylene. Also discussed is the possibility that the unique approach of ethylene insertion may relate to the stereocontroling propylene polymerization.

A Density Functional Study of Ethylene Dimerization by Acetylacetonate Nickel Hydride

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Density functional calculations have been carried out on the thermochemical aspects of catalytic ethylene dimerization by the d^8 hydride (propanedial(-)Ni-H (I), where the propanedial anion served as a model for the chelate acac ligand, acetylacetonate(-). The hydride (I) was found to have a low-spin d^8 configuration with a square planar structure where one site is vacated cis to hydrogen. It was shown that ethylene inserts readily into the Ni-H bond of (I) with an exothermicity of 44.6 kcal/mol. The resulting ethyl complex (II) has a strong agostic interaction between nickel and a β-hydrogen. It is suggested that the ethyl complex is the actual catalyst in the dimerization cycle. The agostic interaction in (II) is estimated to have a strength of 10 kcal/mol. The next insertion of ethylene into the Ni-ethyl bond of (II) leads to a butyl complex (III). The insertion is exothermic by 25 kcal/mol. The reaction between (III) and ethylene leads finally to the release of 1-butene and the regeneration of the ethyl complex (III). This step is nearly thermoneutral with a reaction heat of 0.1 kcal/mol. It is suggested that the elimination of 1-butene takes place via a transition state in which both ethylene and 1-butene are π-complexed to (I). The internal barrier of activation for the final step is estimated to be modest. The substitution of hydrogen by CH_3 or CF_3 groups on the propanedial(-) ligand were also considered. It was found that such substitution only had a minor effect on the thermochemistry of the insertion processes in the dimerization cycle.

Molecular Scene Analysis: Application of a Topology-Based Procedure for the Automated Interpretation of Protein Electron Density Maps at Medium Resolution

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A topological method to assist the spatial and visual analysis of protein electron density maps was investigated, as part of a project in Molecular Scene Analysis [Fortier et al. (1993) Acta Cryst. D49, 168-179; Leherte *et al.* (1994), Acta Cryst. D50, 155-166]. The approach followed is that proposed by Johnson [Johnson (1977), ORCRIT, The Oak Ridge Critical Point Network Program. Chemistry Division, Oak Ridge National Laboratory, U.S.A.] which provides a global representation of the electron distribution through the location, identification and linkage of its critical points. The topological approach was applied to calculated maps of three proteins of small to medium size, in order to develop a methodology that could then be used for the analysis of experimental maps at medium resolution. The methodology was then applied to an experimental map of penicillopepsin at 3Å resolution. The study shows that critical point networks can provide a useful segmentation of the maps, tracing the protein main chain and capturing its conformation. From the analysis of the geometry of critical point segments - e.g. statistical distributions of distances, bond and torsion angles - rules for the recognition of secondary structure motifs were derived. The application of the rules involves the calculation of the degree of belief in the hypothesis of a given secondary structure identification. The procedure provides a basis for further automation of the pattern recognition process through the use of artificial intelligence techniques.

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Kohn-Sham Study of the Association and Insertion Complexes of Nickel with Water, Methanol and Ammonia

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The complexes formed by simple association of the nickel atom with water, methanol and ammonia, and those formed by insertion of nickel into O–H, N–H and O–C bonds, have been studied with the Linear Combination of Gaussian-Type Orbitals-Density Functional (LCGTO-DF) method. The $Ni(H_2O)$ and $Ni(CH_3OH)$ association complexes are bound by roughly 10 kcal/mol whereas the $Ni(NH_3)$ has a much larger binding energy, roughly 25 kcal/mol. The insertion complexes HNiOH, $HNiCH_3OH$, and $HNiNH_2$ all have similar binding energies, roughly 25 kcal/mol. Moreover, in all three cases, the singlet and triplet states of the insertion complexes have comparable energies. The calculated harmonic frequencies, infrared intensities, and isotopic shifts are compared to infrared spectra of the matrix isolated insertion complexes HNiOH and $HNiCH_3OH$. On the basis of that comparison, it is suggested that the observed infrared spectra are due to the insertion complexes in their triplet states.

EHMO Investigation of Haptotropic Shifts in Metal (Fe, Cr, or Mn) Complexes of 4H-Cyclopenta-[def]-Phenanthrene: Are Naphthalene-Like Transition States Involved?

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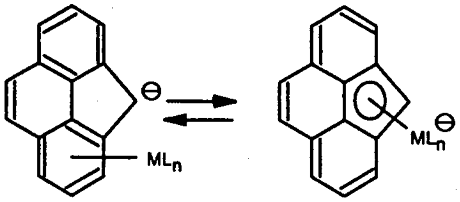
Haptotropic rearrangements of transition metal complexes of cpp (cpp = 4H-cyclopenta-[def]-phenanthrene) have been found to be facile in comparison with metal migrations in the analogous fluorene and dihydro-cpp systems. Differences in the rearrangement behavior of CPP, fluorene and dihydro-cpp will be rationalized in terms of valence bond and EHMO theory.



Density Functional Theory Calculations of the Nuclear Quadrupole Coupling Constants of deuterium and other nuclei.

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The Nuclear Quadrupole Coupling Constant (NQCC) is a one-electron property which is accessible theoretically through the calculation of the Electric Field Gradient (EFG) and the knowledge of the Nuclear Quadrupole Moment (NQM). Experimentally the EFG at the nucleus can couple with the NQM to give rise to hyperfine splittings in micro-wave transitions. Despite its usefulness, the NQCC has not been extensively called upon when characterising molecular systems. This might be due to several reasons, one being that, although the expression for the EFG is straightforward to implement, the calculation requires an orbital basis set with a proper description of the core region. We have undertaken a Density Functional Theory (DFT) study of the NQCC of several nuclei for elements from the three first rows with deMon, the DFT code developed at the Université de Montréal. The goal of our study is to acquire an idea of the accuracy of the EFG (or NQCC) calculated with DFT. The results will be discussed in terms of several parameters: the exchange-correlation functionals, the orbital basis sets, the number of grid points, the geometry and the uncertainties in the experimental values of the NQM and of the NQCC. There have been many reports of ab initio Hartree-Fock EFG and NQCC calculations. These studies involve mainly deuterium. There are also a few correlated and semi-empirical calculations. We have compared our results with these theories and with the experimental results available. On average, the agreement with experiment is better than 5 % for deuterium and within 10% for the other nuclei.

Applications of Computational Quantum Chemistry: Ab Initio Theoretical Studies of Group 16 Compounds.

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The results of a survey of a large number of organosulfur, organoselenium and organotellurium molecules will be summarized. Emphasis will be placed on the prediction of geometries, vibrational frequencies and dipole moments by several approaches including conventional all-electron Hartree-Fock, effective core potential Hartree-Fock, and local density functional methods. A new valence basis set for tellurium to be used in conjunction with core potentials will be presented. The various theoretical methods will be applied to some main group inorganic heterocycles, the dithia- and diselena-diazolyl cations and radicals, and to some organic heterocyles modelling tiazofurin and its selenium analogue.

POTENTIAL ENERGY SURFACES AND THE UV SPECTRUM OF H_2CS

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MRD–CI studies have been performed on ground and excited states of H_2CS.[1,2] In C_{2v} symmetry, C–S potentials were calculated for the 5 lowest $^1A_1$, $^1B_1$, $^1B_2$ and $^1A_2$ states. Furthermore, out-of-plane potentials were obtained at several values of CS. Full geometry optimizations were performed on the $^1(\pi,\pi^*)$ and $^1(n^2,\pi^{*2})$ states. The $^1(\pi,\pi^*)$ diabatic potential is shown to cross all bound states, including the n^2 ground state.

Resulting spectroscopic constants, including Franck–Condon factors and oscillator strengths, were used to explain many features of the observed spectrum. Several reassignments were suggested. Mechanisms for vibronic coupling and predissociation are proposed.

Similar studies have also been carried out for triplet excited states of H_2CS.

References

1. M. Hachey, F. Grein and R.P. Steer, Chem. Phys. Lett. **183**, 204 (1991).
2. M. Hachey and F. Grein, submitted for publication.

A CASE WHERE A BETTER GRID WAS NEEDED: GEOMETRY OPTIMIZATION OF Na_4 WITH THE LCAO-GAUSSIAN DFT PROGRAM deMon

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A grid is used in the density functional theory program for the calculation of exchange-correlation functionals. Alkali metal clusters, which are some of the "softest" clusters in the sense of having relatively flat potential energy surfaces, can require a very high quality grid for geometry optimizations. As part of a study of the polarizabilities of sodium clusters using the linear-combination-of-Gaussian-type-orbitals density functional program deMon, geometry optimizations were performed on the clusters Na_n, $n \leq 6$. Unusually unsymmetric geometries were encountered for the tetramer which was eventually traced to the use of the grid in the exchange-correlation part of this program. This problem was solved by improving the grid. This work is presented as a warning which is applicable to a variety of electronic structure programs where the Becke grid is used. Although grid methods have been optimized to work well in most cases, care must be taken when dealing with exotic molecules where small energy differences are important.

Performance of Density Functional Theory on Medium Sized Organic molecules

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To examin the performances of density functional theory on medium sized and conjugated organic molecules, density functional calculations with nonlocal gradient corrections (Becke-Perdew) have been performed for equilibrium structures of 14 cyclic compounds using TZP basis set. These are imidazole, imidazolium, pyrrole, pyrazole, oxazole, 1,3,4-oxadiazole, thiophene, thiazole, 1,3,4-thiadiazole, benzene, pyridine, pyridazine, pyrazine, triazine. For the C-C, C-N and N-N bonds, the mean absolute deviation in bond length from experiment is less than half of that from the Hartree-Fock (HF) calculations and the accuracy of the DFT method is comparable to available MP2 results. A relatively large deviation is found for the S-C bonds, but the error can be significantly reduced by using different functionals and basis set. Harmonic frequencies are also determined for most of the systems. For the in-plane vibrations, the deviations from the experimentally observed frequencies are much smaller than those from the HF calculations and are comparable to available correlated *ab initio* calculations. Relatively large deviations are found for the out-of-plane vibrations, probably, due to differential basis set superposition errors. For benzene, where the experimentally estimated harmonic frequencies are available, the mean absolute deviation of the Becke-Perdew/TZP frequencies from experiment is 1.5% for the in-plane vibrations and 2.7% for the out-of-plane vibrations.

Ab Initio Vibrational Levels for HO_2 and Vibrational Splittings for Hydrogen Atom Transfer

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N2L 3C5

We calculate vibrational levels and wavefunctions for HO_2 using the recently reported *ab initio* potential energy points of Walch and Duchovic [J. Chem. Phys. 94, 7068 (1991)] as fit by Dateo[unpublished]. There is intramolecular hydrogen atom transfer when the hydrogen atom tunnels through a T-shaped saddle point separating the two equivalent equilibrium geometries, and correspondingly, the vibrational levels are split. We focus on vibrational levels and wavefunctions with significant splitting. The first three vibrational levels with splitting greater than 2 cm^{-1} are (1,5,0), (0,7,1) and (0,8,0) where v_2 is the O-O-H bend quantum number. We discuss the dynamics of hydrogen atom transfer; in particular, the O-O distances at which hydrogen atom transfer is most probable for these vibrational levels.

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Measures of Distance for Position and Momentum Densities for Atomic and Molecular Systems.

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Atomic Charge- and Momentum Densities of 91 atoms (He–U) are classified in terms of their L_1, L_2 and entropic measures of distance from the densities of the preceding atoms. Also, measures of distance for a series of diatomics, as well as the hydrogen peroxide, ethane and difluoroethane molecules are discussed.

The Exact One-Electron Model of Molecular Structure: the Molecular Envelope - a Well-Founded Basis for Molecular Graphics

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The Exact One-Electron Model of molecular structure (G.Hunter, Int.J.Quantum Chem.,Vol.29,p.197,1986) is an application of the general theory of Conditional Probability Amplitudes in Wave Mechanics (G.Hunter, Int.J.Quantum Chem.,Vol.9,p.237,1975). In the model, the square-root of the electron density is the wave-function for the motion of one (any one) electron in the many-electron molecule. This wave-function is the ground-state solution of a one-electron, electronic (Born-Oppenheimer) Schrödinger equation in which the potential energy represents the effective field within which the one electron moves under the averaged Coulomb interactions with the nuclei and all the other electrons. Unlike the Hartree-Fock equations, the one-electron Schrödinger equation is, in principle exact. However (unlike Hartree-Fock theory) it is an interpretative model rather than an *ab initio* computational method; computation of the exact one-electron effective potential is from the electron density, which in turn is derived from the full many-electron wavefunction for the molecule in a particular electronic state. In this respect it is like (and in fact is closely related to) Bader's interpretative studies of the electron density in molecules (R.F.W.Bader, *Atoms in Molecules*, Clarendon Press, Oxford, 1990).

The local kinetic energy (i.e. the difference between the total and potential energies) in the one-electron Schrödinger equation is positive in classically allowed regions of space, and negative in classically forbidden regions. Each nucleus is surrounded by a (roughly spherical) allowed region that corresponds to the 1S shell of the simple aufbau model of atomic structure, and each higher $(n > 1)$ occupied shell is similarly represented in the model by a (roughly spherical) shell of finite thickness; in between the occupied (allowed) shells are forbidden (negative kinetic energy) regions. Thus the Exact One-Electron Model confirms the shells predicted by the simple aufbau model of atomic structure (confirmed in calculations by computational theorists at Queens University and in Germany).

Every covalently bonded molecule has an outermost allowed region that encompasses all of the nuclei; this is the union of the valence shells of all the covalently bonded atoms. The outermost surface of this valence region of space is the locus of the outer turning points of an electron in the valence shell; classically (i.e. no quantum mechanical tunneling) all of the electronic charge would be contained within this surface. Hence (apart from tunneling) it defines the size and shape of the electronic charge cloud that surrounds the nuclei. This outermost surface (beyond which the local kinetic energy is negative out to infinity) has been named (appropriately) "The Molecular Envelope" by Richard Bader. It is a natural adjunct to his *ab initio* definition of atoms and bonds within molecules, based (like the Molecular Envelope) upon the topology of the electron density and its derivatives.

The Molecular Envelope is the only *ab initio*, in principle exact (i.e. as accurate as the many-electron wavefunction from which it is calculated) definition of the size and shape of a molecule. Hence it is the most natural, well-founded (well-defined) basis for Molecular Graphics. Unlike space-filling graphics based upon intersecting spheres, the molecular envelope surface smoothly connects the (roughly spherical) surfaces around adjacent atoms. Furthermore (unlike fixed-size intersecting spheres graphics) the size of each atomic region varies depending upon the atom that it is bonded to; the H-atom in HF is less than half the diameter of an H-atom in H_2, which in turn is much smaller than the H^- ion in LiH. While H_2 and O_2 are about the same size, the shape of the former is a lozenge, while the latter is dumbbell-shaped - having a distinct constriction between the two roughly spherical O atoms.

The computed Molecular Envelope surfaces will be displayed for some simple diatomic molecules. The adoption of this well-founded way of displaying the size and shape of electronic charge clouds will be advocated, not only for stable molecules at their equilibrium nuclear configurations, but also for following the course of bond formation and breaking in chemical reactions. No development of this fundamental basis for molecular graphics (since its discovery in 1985) has occurred because of the repressive (*contra* originality and innovation) policies of the Canadian Natural Sciences and Engineering Research Council. Funding and collaboration is hereby invited for the development and application of this potentially very important interpretative tool; non-Canadian offers will be especially welcome.

GROUND STATE STRUCTURES OF Fe_n, Co_n AND Ni_n ($n \leq 5$) CLUSTERS.

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Density-functional calculations using local and gradient-corrected functionals and the linear-combination-of-gaussian-type orbitals program *deMon* are reported for small clusters of iron, cobalt and nickel. For each cluster, geometry optimizations and vibrational analyses were performed for several spin multiplicities beginning from a variety of initial geometries in order to determine the ground state structures. The calculated properties (bond lengths, binding energies, ionization potentials, magnetic moments and vibrational frequencies) are in good agreement with the experimental results and compare well with other theoretical calculations.

KOHN-SHAM RESPONSE THEORY: FORMULATION AND IMPLEMENTATION FOR AN AUXILIARY FUNCTION-BASED NUMERICAL METHOD.

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Response theory is a very general analytic method for calculating the response of a molecule to an arbitrary dynamic perturbation. As such it can be used to calculate a wide variety of properties including, but certainly not limited to, static and dynamic polarizabilities and electronic excitation spectra. The former play an important rôle in the theory of intermolecular forces and in the theory of nonresonant optical phenomena such as refraction and depolarization of scattered light. Excitation spectra can be obtained by an examination of the pole structure of the dynamic polarizability tensor. Although response theory is well-established in the molecular ab initio electronic structure literature in the form of the coupled Hartree-Fock and time-dependent Hartree-Fock methods, density-functional response theory is still in its infancy. In the case of time-dependent phenomena and excitation spectra, many formal questions remain unanswered but applications to atoms and solids have met with encouraging results. In contrast, relatively few formal questions arise in the case of time-independent density-functional response theory, but the development of methodology suitable for molecular calculations is only just beginning. The goal of the present study is the formulation and implementation of density-functional response theory in the auxiliary function-based density-functional program deMon (densité de Montréal). The formulation presented here is designed to give the same results (within numerical error bars) in the case of static fields as the finite field procedure already programmed in deMon. One consequence is that four center integrals are never used in our procedure. The method is currently being programmed and partial results will be presented. Computatonal bottlenecks will also be discussed.

Approaching the Ground State with the Lower Bound Method of Reduced Density Matrix Theory

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We are implementing the lower bound method of reduced density matrix theory for some interesting fermion systems with up to two body interactions. By this method, we obtain a lower bound to the ground state energy of the system, as well as an approximate reduced density matrix. Preliminary numerical results show fast convergence and a tight lower bound. Programming of this method for a two dimensional square lattice with nearest neighbouring interaction is under way.

Crystallographic Orbifold Atlas

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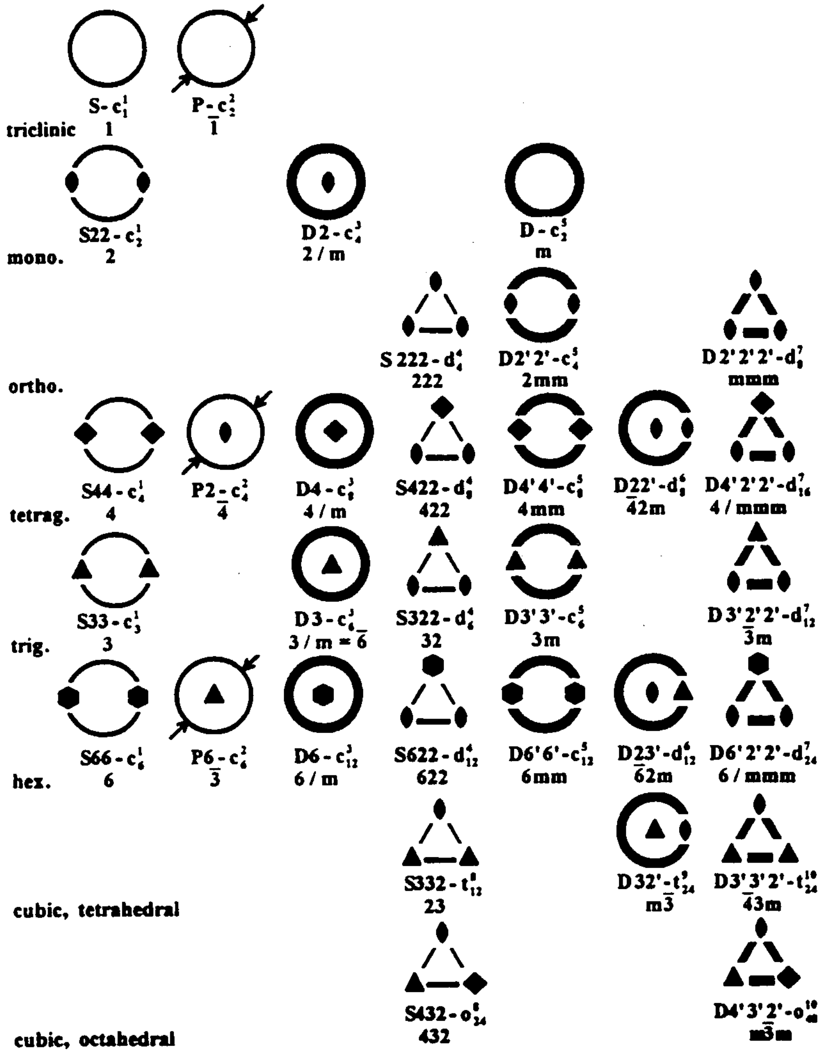
Topological analysis of mathematical problems often lead to new insights. The symmetry of crystals can be viewed topologically by overlaying all equivalent points within a crystal to form wrapped-up (closed) topological spaces called Euclidean 3-orbifolds. Manifolds can be considered orbifolds without singularities. The classical 13 Euclidean 3-manifolds are wrapped-up fundamental domains (asymmetric units) of space groups which lack special positions. The remaining 217 space groups have special symmetry positions which show up as singular sets of closed curves and surfaces in and on Euclidean 3-orbifolds. 3-Orbifold singular sets for polar space groups include topological knots, links, tangles and trivalent graphs. We are currently preparing an atlas of orbifold and singular set drawings, and other topological results, for the 230 space groups to aid in future topological interpretations of crystallographic mathematics and results.

Elliptic 2-Orbifolds for the Crystallographic Point Groups



Representation and classification for the elliptic 2-orbifolds corresponding to the point groups are shown in the figure. In row 6 column 6, the notation D23' signifies a disk (D) with one 2-axis cone point (2) and one 3-axis dihedral corner (3') The suffix -d_{12}^6 denotes derivation from a dihedral point group (d) of order 12 which belongs to topology class 6 of 10. Other symbols are S (sphere), P (projective plane), c (cyclic), t (tetrahedral), and o (octahedral). Note the graphical simplification compared with symmetry drawings of point groups in the International Tables for Crystallography. The notation and classification are adapted from F. Bonahon and L. Siebenmann, *Seifert 3-Orbifolds and Their Role as Natural Crystalline Parts of Arbitrary Compact Irreducible 3-Orbifolds, Appendix Y,* 1983 unpublished.

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A Conformational Analysis of Serotonin Uptake Inhibitors

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A series of conformational searches and molecular similarity calculations were carried out on R and S enantiomers of Fluoxetine, Nisoxetine and Tomoxetine and on their ortho substituted analogues. The objective was to gain an understanding of the enantioselectivity in the activities of the R isomers over the S isomers for Nisoxetine and Tomoxetine. It was found that the S isomers of Nisoxetine and Tomoxetine do not fit on the pharmacophor described by the overlay of the R isomers of each compound, but that the S isomer of Fluoxetine did fit reasonably well. This is concluded to be the explanation for the enantiomeric selectivity of both Nisoxetine and Tomoxetine and the lack of chiral selectivity for Fluoxetine. Conformational searching followed by similarity calculations on the ortho iodinated analogues indicated a conformational variation from the low energy conformer seen for the Fluoxetine-R, Tomoxetine-R and Nisoxetine-R compounds. This seems to come from the interaction between the iodine atom and the nitrogen hydrogen. This result is consistent with the observed activities of the R and S isomers of these compounds which do not follow the selectivity trends of Nisoxetine and Tomoxetine but rather show approximately the same activity for both enantiomers. The conclusion of this study is that it is possible to explain the enantioselectivity of serotonin uptake inhibitors based upon similarity and conformational search calculations.

Systematic Sequences of Well-Balanced Gaussian Basis Sets

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Systematic sequences of Gaussian basis sets with controlled energy errors for the studies of convergence of the basis set effects on the computed results of molecular calculations were optimized in atomic calculations. The basis sets were prepared for atoms H - Ne and Al - Ar and may be used in systematic ab initio ad limitem studies of molecular structure and properties.

Ab Initio Dynamics Studies of Li_7 and K_7 Microclusters

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The Car-Parrinello method for ab initio molecular dynamics has been used to investigate the structure and atomic dynamics of Li_7 and K_7 microclusters. An analysis of the structural properties as a function of time and temperature shows that the low energy form of these clusters is a pentagonal bipyramid. The K_7 cluster undergoes pseudorotation where an atom in the tip of the bipyramid exchanges with and atom in the pentagonal plane. In comparison, the Li_7 cluster remains rigid. The contrasting properties are in agreement with recent ESR observations.

The application of molecular dynamics and free energy perturbation calculations to organic and biochemical systems

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We will present recent results and perspectives on molecular dynamics and free energy calculations to model systems(solvation of small solutes in water), ionophore-ion recognition, protein-ligand interactions and nucleic acid-ligand interactions. The ability of the simulations to reproduce experimental free energies, give insights and make predictions will be critically assessed.

Re-examination of the Hyperfine Structure of $^{14}NH_2$

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The hyperfine structure of $^{14}NH_2$ is studied using the MRCI method. With a given basis set, the number of configurations is systematically increased by increasing the reference space and lowering the threshold for the selection of configurations. The final converged theoretical results provide a good estimate of the full-CI limit. Expansion of the basis set is also investigated, from (11s7p2d/7s2p) to (13s8p2d/8s2p). The basis sets are uncontracted to avoid any possible errors due to basis set contraction. The best theoretically predicted hyperfine coupling constants of $^{14}NH_2$ are virtually the same as the experimental values, much improved from previous studies.

Approximation of Molecular Electrostatic Potentials in Density Functional Theory

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The generalization of the asymptotic density model (JCP, 99, 1224, 1993) to density functional theory (DFT) is presented. The asymptotic density model (ADM) is designed to fit the asymptotic values of the exact molecular electrostatic potential at the nuclei and at large distances where it approaches the multipole expansion. In contrast to the common multipole expansion the correct topography of the molecular electrostatic potential surface can be obtained with the ADM. The computational effort is of the same magnitude as for a multipole expansion. Applications and comparisions of DFT and Hartree Fock results are shown.

Energy and Angular Momentum Dependent Transition Probabilities in Unimolecular Kinetics

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The calculation of unimolecular rate coefficients as a function of pressure for various diluent gases is a fundamental problem in gas phase kinetics. The study is facilitated by the use of a stochastic master equation. The latter is usually represented, in the steady state approximation, by an integral equation whose kernel contains probabilities for transitions between internal states and is a function of two variables, energy and total angular momentum of the reactant. Analytic solutions to the rate coefficient and collisional energy transfer efficiency for different diluent gases can be obtained in cases when the kernel can be approximated as separable in the variables and when simple functional forms for corresponding energy transfer probabilities can be assumed.

In the present work, kernels obtained by other research groups using extensive semiclassical trajectory calculations on a simulated H_2 dissociation in the presence of Argon at high temperatures will be analyzed. Our objective is to arrive at functional forms for the kernel based on trajectory results which would simplify the solution of the two dimensional master equation. In addition, the usefulness of a discrete form for the master equation presented earlier by one of us [N. Snider, J. Chem. Phys., **65**, 1800 (1976)] will be illustrated with a few examples for two dimensional transition probability kernels.

Structure in Molecular Liquids and Its Dynamical Implications

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The radial distribution function, g(r), has traditionally served as the principal source of structural information for atomic as well as molecular fluids. However, we will demonstrate that the full spatial distribution function can provide a much more complete picture of the local structure in molecular liquids. Liquid water and methanol as well as dipolar soft-sphere fluids will be examined. The dynamics within these systems will then be discussed and we will consider its relationship to the observed local structures.

Electronic structure analysis in Density Functional Theory

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The molecular electrostatic potential (MESP) has emerged as a powerful tool for studying both the structure and reactivity of simple as well as complex molecules. The topography of this physical observable is by far richer than that of the electronic density or the bare nuclear potential, for example. We present studies of the topography of the MESP for small organic and metallic systems, in the framework of Density Functional Theory (DFT). Critical points of the MESP are determined and correlated to particular aspects of the electronic structure (lone pairs, π systems, etc.). Electric field and field gradient is also studied. Comparison with Hartree-Fock calculations is provided.

Implementation of State-Specific Spin-Adapted Open-Shell Coupled-Cluster Methods

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An exploitation of the unitary group approach in a spin-adapted coupled cluster (CC) method, employing a single but multiconfigurational reference, which is applicable to open-shell systems, is described. The focus is on the three simple while important cases: simple open-shell doublet and open-shell singlet and triplet states arising through a monoexcitation from a closed-shell state. The derivation of the requisite CC equations, even for the simple cases just mentioned, required extensive algebraic manipulations. To facilitate the implementation of this approach, general programs were developed, which first generate the required explicit algebraic expressions and subsequently encode them in a FORTRAN program enabling the exploitation of this method at the *ab initio* level. Illustrative results for both ground and excited states, and for singlet-triplet separations and potential energy surfaces of several molecules will be presented. An extension of this methodology to spin-adapted open-shell Hilbert space multi-reference CC method and to spin-adaptation of triply and quadruply excited clusters will also be briefly discussed.

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Ab Initio Studies of the Reactions of OH with Fluorinated Ethanes

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The reactions of hydroxyl radicals (OH) with hydrofluorinated ethanes (HFEs) are potentially of great significance in atmospheric chemistry, since such reactions are proposed as the initial tropospheric degradation reactions for many of the compounds being developed as chlorofluorocarbon (CFC) replacements. We have been studying the reactions of OH with the full series of HFEs, $C_2H_nF_{6-n}$, n = 0 - 6. Fully optimized geometries, harmonic vibrational frequencies, and zero-point energies (ZPEs) for the reactants, transition state (TS) and products were calculated at unrestricted Hartee-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2). Energies were calculated using MP2 and MP4 theory and a modified Gaussian-2 (G2) theory. Trends in the transition state geometries, and the activation and reaction enthalpies, will be discussed.

Electronic Structure, Effective Spin Hamiltonian Expressions, and Experimental Evidence for the Parallel Paramagnetic Resonances of the Matrix-Isolated $(\eta^6-C_6F_6)V$ and $(\eta^6-C_6F_6)_2V$ Half- and Full-Sandwich Complexes

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Hexafluorobenzene is reacted with vanadium atoms and matrix-isolated in Ar at 12 K. The resulting $(\eta^6-C_6F_6)V$ and $(\eta^6-C_6F_6)_2V$ compounds are investigated by electron paramagnetic resonance (EPR) spectroscopy. Spectral features of $(\eta^6-C_6F_6)V$ and $(\eta^6-C_6F_6)_2V$, such as the resonance field positions and intensities, are analyzed and accounted for by computer simulation. The effective spin Hamiltonian tensor components and resonance field positions are derived in terms of their molecular orbital coefficients. The magnetic properties, such as the g, hyperfine and superhyperfine tensor components are compared with those computed using the local-density-functional (LDF) approximation. Both the experimental spectra and electronic structure computations confirm that the $(\eta^6-C_6F_6)V$ and $(\eta^6-C_6F_6)_2V$ complexes have $^2E_2$ and $^2A_{1g}$ ground states respectively.

Interpretation of the Electronic and Vibrational Spectra of the Neutral 4,5-Bis(Trifluoromethyl)-1,3,2-Diazolyl Radical

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The electronic and vibrational spectra of the neutral 4,5-bis(trifluoromethyl)-1,3,2-diazolyl radical are generated by the semiempirical PM3 method. Semi-empirical and ab-initio techniques, at the self consistent field level, are sufficient to adequately explain the electronic spectrum. Post-SCF configuration-interaction (CI) must be performed to generate the weak transitions in the red region of the spectrum that are responsible for the blue color of this compound. In addition, substitution of hydrogen centers instead of the trifluoromethyl functional groups, in order to simplify the computations, does generate the proper electronic spectrum when CI computations are performed. A vibrational analysis of this compound is also performed where all its vibrational normal modes are studied and interpreted. The computational results are compared with the existing infrared spectra in the literature.

Molecular Structure Analysis of Tricyclic Psychomimetic Drugs

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Tricyclic psychomimetic drugs possess remarkable structural similarity, yet they exhibit great stereochemical specificity. This specificity is exemplified in their large and quite progressive arrangement of pharmacological activities ranging from the antipsychotic drug chlorpromazine, to the antidepressant drug imipramine, to finally the anticonvulsant drug carbamazepine. This gradual transition of activity is further illustrated through tricyclic drugs with overlapping specificities.

Despite the fact that antidepressants, tranquilizers and anticonvulsants all operate through different biological molecular mechanisms, stereoelectronic effects have also been deemed to be key factors in their mode of action.[1] Previous investigations with tranquilizers and antidepressants have revealed that the ring topology of the common tricyclic moiety may influence their activity.[1]

Presently, a more in depth investigation of this phenomenon which extends to incorporate tricyclic anticonvulsant drugs has been undertaken. Several representative structures from each family of tricyclic drugs were chosen for analysis. Starting structures were generated through molecular mechanics and from x-ray crystallographic data. Their conformational space was analyzed by quenched high temperature molecular dynamics and subsequently optimized at the semiempirical level with the AM1 program. The bioactive conformation was chosen through a comparison of several optimized and distinct conformers from each individual starting structure. The topological features of the tricyclic moiety of these structures were then analyzed and related with their different psychomimetic activities.

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Stability of the BN bond, from BN^{2-} to BN^{3+}.

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Boron Nitride $(BN)_n$ is as technologically important as graphite and diamond $(C_2)_n$. Surprisingly, little is currently known about the properties of diatomic BN^q species with $q = 0, \pm 1, \pm 2$. For instance, whether $^3\Pi$ or $^1\Sigma^+$ constitutes the ground state of BN is yet unknown experimentally. To remedy this, MRD-CI calculations on BN^q ($q=0, \pm 1$) have been carried out in this laboratory.[1] These earlier results have been improved lately by using extended basis sets and CI expansions; the highly charged ions BN^{2+} and BN^{3+} are reported here for the first time. As expected, we found that BN^{2-} autodetaches into $BN^- + e^-$.

Since the forbidden transition $^3\Pi$-$^1\Sigma^+$ of BN cannot be studied directly via optical spectroscopy, the photoionization $BN \rightarrow BN^+ + e^-$ and the photodetachment $BN^- \rightarrow BN + e^-$ spectrum[2] are proposed as alternative techniques to solve this problem. Highly accurate calculations agree in that BN has a $X^3\Pi$ ground state, with $a^1\Sigma^+$ only 1 kcal/mol higher.[2,3] The ionization potential IP(BN) lies at 11.18 eV (experimentally unknown). On the other hand, the electron affinity EA(BN) of 2.84 eV agrees well with a measured value of 2.9 ± 0.3 eV.[4] Dipole moments, oscillator strenghts and radiative lifetimes are also reported for $BN^{0,\pm 1}$.

About a dozen states of BN^{2+} are metastable. While $X^3\Sigma^-$ is weakly bound (≈ 0.3 eV), experimental detection will probably involve the more strongly bound $1^5\Sigma^-$ (≈ 2.25 eV). In the case of BN^{3+}, a $^4\Sigma^-$ state is predicted to be metastable. Tunneling lifetimes for both doubly and triply ionized species are given.

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A 6-dimensional calculation for the vibrational bands of the HF dimer

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The vibrational levels of the (J=0) HF dimer are calculated with the *LANCZOS* method. The hamiltonian is written in Jacobi coordinates and the basis set used is a direct product of angular and radial functions. The angular functions are spherical harmonics and the radial part is a direct product of DVR (Discrete Variable Representiation) functions associated with three Morse-like oscillator functions. Matrix elements of the potential with spherical harmonic basis functions are computed with quadrature.

High-Resolution Shape Analysis of Macromolecules

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Macromolecular shape can be analyzed on various levels of resolution. For global shape characterization and for the evaluation of large scale variations of shapes such as protein folding, low resolution methods are appropriate. For detailed characterization of local shape features, such as local shape variations of active sites in enzymes, high resolution modeling techniques are needed. Some of the latest modeling approaches will be reviewed, with emphasis on local shape similarity and shape complementarity measures, as applied to detailed, ab initio electron densities of macromolecules.

Critical Evaluation of Molecular Mechanics Nonbonded Interactions for Saturated Alkanes

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Nonbonded interactions constitute the most problematic part of a force field. A rigorous test of their validity is to reproduce experimental properties in all phases. Based on a number of well-known intermolecular potential funtions, several thermodynamical and structural properties have been computed for simple saturated alkane molecules. Wherever possible, new parameters have been proposed to improve on the agreement between calculated and experimental values.

Time-Resolved Laser Control of Vibrational Excitations in Molecules

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Time-resolved control of vibrational motions in multimode molecules by detailed laser-pulse shaping is illustrated using a Wei-Norman type of factorization of the time-evolution operator for the laser-driven vibrational system, and discus sed in terms of the adiabatic transport of eigenstates of an approximate Lewis invariant.

COMPUTATIONAL STUDIES ON THE ACTIVE SITE OF PAPAIN

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The catalytically active site of the proteolytic enzyme papain is known to contain an ion - pair in the resting state. A study at the molecular level will help in understanding the effect of certain residues on the stability of the ion - pair and hence the catalytic mechanism itself. Models of increasing complexity for the active site of papain, based on experimental geometry, were constructed. Semiempirical Quantum Chemical calculations which explicitly include water molecules in the active site and the effect of the protein environment were performed on each model. The calculated relative stabilities of the zwitterionic and neutral forms of the active site were compared with experimental results. The importance of specific amino acid residues in stabilising the ion-pair was calculated and compared with mutation studies done in this laboratory. Results on explicit electronic effects on the local environment of the active site, the role of rotation of the His159 about the H bond between itself and Asn175 in the neutral and zwitterionic forms were modeled. These results and postulates of the mechanism of activity at the ion-pair are presented.

Use of Molecular Modeling in the Design of N-Methyl-D-Aspartate Antagonists

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Glutamate is a major excitatory neurotransmitter, and its interactions with membrane receptors control many neurologic functions. The N-Methyl-D-Aspartate (NMDA) receptor complex is one of the more well characterized, owing in part to the availability of specific ligands. As part of an effort to discover new therapies useful in the treatment of stroke, small-molecule molecular modeling techniques have been used to derive pharmacophore models of several NMDA antagonist receptor sites. The steps involved in the formation of the models, their use in the design of novel antagonists, and the fit of recently reported antagonists in the models will be described. Practical considerations in the development and use of models based on small molecules will also be discussed.

A Conformational Study of Four Membered Ring and Nine Membered Ring Compounds

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Squaric acid and its dilithium salt and 1,4,7 trithiacyclononane have been studied by ab initio SCF calculation employing a split-valence 6-31G basis set. The geometries of three different rotamers for squaric acid, two different rotamers for the dilithium salt and three different rotamers for 1,4,7 trithiacyclononane have been optimized by the force method. Raman and IR spectra of polycrystalline $C_4O_4H_2$, $C_4O_4Li_2$, and $S_3C_6H_{12}$ have been recorded at various temperatures.

Ion Solvation Dynamics

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Theoretical and computer simulation results for the dynamics of ion solvation in dipolar fluids and electrolyte solutions will be discussed. The theory takes account of inertial effects which are of critical importance for the fast initial phase of the relaxation of the ion-solvent energy. Diffusional effects important at long times are also included. It is shown that for ionic solutions there is an extremely slow long-time decay associated with the formation of an equilibrium "ion atmosphere" about the charged particle.

Automatic numerical integration techniques for polyatomic molecules. Backward trimming

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We have recently published [J. M. Pérez-Jordá, A. D. Becke and E. San-Fabián, J. Chem. Phys. **100**, xxxx (1994)] an algorithm for 3D numerical integration of multicenter molecular integrals. Given a *generating function* $F(\mathbf{r})$, the algorithm approximates $\int F(\mathbf{r})\,d\mathbf{r}$ as $\int F(\mathbf{r})\,d\mathbf{r} \approx \sum_i \omega_i F(\mathbf{r}_i)$. The set of abscissas $\mathbf{r}_i$ and weights ω_i constitutes a *3D grid* that can be used to approximate integrals of functions other than the generating function $F(\mathbf{r})$. We have used *promolecule densities* as generating functions. This algorithm works in the following way. First, we use the nuclear weight functions method of Becke [A. D. Becke, J. Chem. Phys. **88**, 2547 (1988)] to decompose a multicenter integral $\int F(\mathbf{r})\,d\mathbf{r}$ into a sum of atomic-like single-center integrals. Then, the 3D atomic-like integrals are arranged as three successive monodimensional integrals, each of which is computed according to a recently proposed monodimensional *automatic* numerical integration scheme which is able to determine how many points are needed to achieve a given accuracy. In a simplified way, this monodimensional automatic integrator generates a sequence of quadrature formulas I_1, I_2, I_3, I_5, I_7, I_{11}, I_{15}, I_{23}, $\ldots I_{l_0}$, I_l, where I_l is the l-point Gauss-Chebyshev quadrature formula of the second kind (this is for the radial coordinate, slightly different schemes are used for the θ and ϕ coordinates). When this sequence converges (that is, when $|I_{l_0} - I_l|$ is smaller than a target accuracy or *tolerance* ϵ), the last formula of the sequence, I_l, is added to the 3D grid. We will refer to this scheme as the *standard procedure*.

Here we present a simple but useful improvement over this standard procedure: the *backward trimming procedure*. Its essence is easy to understand: we run the previous sequence I_1, I_2, I_3, I_5, I_7, I_{11}, $\ldots I_{n_0}$, I_n, $\ldots I_l$ *backward*, removing (*trimming*) a quadrature I_n from the sequence if $|I_l - I_{n_0}|$ is smaller than the tolerance ϵ (I_{n_0} and I_n are any consecutive pair of quadratures). Then, the last formula of this trimmed sequence is the one that is added to the grid. Tests with 21 molecules, ranging in size from 3 to 60 atoms, indicate that the backward trimming procedure gives errors similar to those obtained with the standard procedure, but with a fivefold reduction in the number of grid points. It seems that the backward trimming procedure achieves a given accuracy with fewer points than other recently proposed methods.

Orthogonally Spin-Adapted Hilbert-Space Coupled-Cluster Formalism. Importance of the High-Order Coupling Terms

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Complete orthogonally spin-adapted Hilbert-space coupled-cluster (CC) theory involving singly and doubly excited clusters for a model space spanned by two closed-shell configurations is considered. Explicit expressions for the previously neglected cubic and quartic coupling terms are derived using diagrammatic methods of many-body perturbation theory and graphical methods of spin algebras. The resulting formalism has been implemented and the general purpose *ab initio* program has been written using newly developed procedure for improving the convergence of the reduced linear equation method. Results of the pilot calculations for the two lowest singlet states of the minimum basis and double zeta plus polarization (DZP) basis H4 models as well as for the CH_2 molecule at equilibrium and displaced geometries are presented and compared with the available single-reference CC and configuration interaction data. They indicate negligible role of the cubic and quartic coupling terms even for geometries far from equilibrium, which justifies the validity of approximations considered so far.

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OSIPE [a]

A tool for scientific programming in Fortran

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FORTRAN tools have been designed to support well-structured, modular, route-independent and easily interfaceable programming. The set of tools, which are referred to as OSIPE (Open Structured Interfaceable Programming Environment) creates a type of low-level Object-Oriented programming environment.

The OSIPE Object-management, File-management and Debugging tools will be described. Some illustrative examples from MUNGAUSS, written in the OSIPE environment, will be briefly described. The importance of OSIPE to High Performance Computing will also be discussed.

[a] Computer Physics Communications, in press, 1993

VIBRATIONAL BAND INTENSITIES OF POLYATOMIC MOLECULES WITHOUT WAVEFUNCTIONS VIA THE LANCZOS ALGORITHM

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We use an iterative algorithm (the recursive residue generation method — RRGM) to perform a variational calculation of the vibrational energy levels (J=0) and band intensities for 3- and 4-atom molecules using an exact kinetic energy operator. A direct product basis set (of size N) is employed with an 1-D potential optimised discrete variable representation (DVR) for each degree of freedom. This allows us to have a diagonal matrix representation of the coordinate operators, evaluated at grid points. By taking advantage of the DVR, we tridiagonalize the very large Hamiltonian matrix efficiently using the Lanczos recursion and keeping only 3 vectors of length N in memory. The eigenvalues and transition moment integrals are calculated simultaneously without constructing the eigenvectors, the dipole moment operator being used to define the first function of the recursion basis. A complete treatment of symmetry is applied to generate simulated experimental spectra for water.

Nonlocal Correlation Functional Involving the Laplacian of the Density

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The correlation functional derived in a previous work [Phys.Rev.B **49** (1994)] is extended to a nonlocal scheme beyond the gradient-corrected ones. The nonlocal corrections involve the Laplacian of the electron density, as well as the self-consistently determined Kohn-Sham kinetic energy density. With the aid of one additional parameter, the correlation contribution to the binding energy can be governed in a way to compensate as much as possible the error in the corresponding exchange contribution. Thus, the correlation functional can be adjusted to any exchange counterpart separately, achieving optimal results for the total energy differences. When combined in this manner with the the nonlocal exchange functional of Becke, the new scheme gives improved results for the binding energies and equilibrium geometries of a set of test molecules, even when the nonlocal corrections to the correlation are included in a perturbative manner (after the last SCF cycle).

π-Facial Diastereoselectivity in the Diels-Alder Reaction of the Plane-nonsymmetric Dienes

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The Diels-Alder reaction is a versatile reaction in organic synthesis. The endo-exo selectivity and regiochemistry of asymmetric dienes and dienophiles have been explored extensively. However, the π-facial selectivity with plane-nonsymmetric dienes, such as 5-monosubstituted cyclopentadienes and cis-5,6-disubstituted 1,3-cyclohexadienes, has been examined only recently.

The dienes and the syn and anti transition states of a large number of 5-substituted cyclopentadienes have been investigated using *ab initio* techniques. The results compare favorably with experiment, where experimental values are known.

Conformational Study of Substituted Poly(thionylphosphazenes) Molecular Models Using Density Functional Theory

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The structures and energies of the various conformations of the model compounds of substituted poly(thionylphosphazenes) are obtained using the density functional theory method. The substituents studied include: hydrogen, fluorine, chlorine atoms and methyl groups. The objective of this work is to investigate the flexibility of the chain backbone for the corresponding poly(thionylphosphazenes). It has been found that for all model compounds the non–planar trans–cis conformations have the lowest total energies. The conformational energy differences computed relative to these non–planar trans–cis conformations are of the order of few (1–5) kcal/mole. Using the spherically averaged total electron densities it is shown that the charge along the backbones of the model compounds is partially delocalized and accumulates primarily on the nitrogen atoms.

A time-energy resolution iterative method for the direct calculation of high-lying bound energies and wavefunctions

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Knowledge of high-lying bound states is useful in many instances such as the determination of unimolecular reaction rates, the interpretation of high-resolution spectroscopy and as a mean of probing the quality of potential surfaces near dissociation. For multidimensional systems, the variational calculation of such states is nearly impossible using explicit diagonalisation techniques due to the size of the matrices involved. A popular method to circumvent this problem is the Lanczos recursion algorithm. This method requires however a large number of iterations in order to converge high bound state eigenvalues and its convergence is sensitive to the gap structure of the Hamiltonian. An alternative method was proposed by Neuhauser (*J. Chem. Phys.* **93** 2611, (1990)) in which a few energy-localized basis functions are obtained using a time-energy Fourier resolution via a wave-packet propagation. An extension of this method is proposed here and different issues such as the orthogonalisation of the basis, the propagation procedure and the choice of the convergence function of the Fourier transform are investigated. The time-energy resolution idea is further used to explore the possibility of guiding the convergence of iterative methods including the Lanczos recursion. Comparison of traditional Lanczos, propagation guided Lanczos and the Fourier-resolved methods are made. The main advantage of time-energy resolution methods is their ability to converge energies and wave functions in an energy range of choice.

Structure-activity relationships in a family of anticonvulsant arylsemicarbazones. Between 2D and 3D QSAR studies.

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Continuing with our interest in semicarbazones as anticonvulsant agents [1], a new set of these compounds were tested displaying different levels of activity. These activity data have been used to correlate with different structural features of the molecules. In this work, a Quantitative Structure-Activity Relationship analysis over this family of compounds has been carried out by introducing new parameters.

The classical QSAR analysis is usually considered as two dimensional. The tools used in those analyses are basic molecular descriptors (topological indices) and many of them are related with the 2D structure of the molecules (Randic, Kier-Hall) [2]. In recent years, different 3D QSAR methodologies have been developed [3], since it has been agreed that the most relevant numerical property values should be shape-dependent. The one that has become most popular is the CoMFA analysis [3c]. This methodology considers that a suitable sampling of the steric and electrostatic fields surrounding a set of ligand molecules might provide all the information necessary for understanding their observed biological properties. Usually, these studies are carried out as implemented in the SIBYL package.

We propose the combined use of classical 2D QSAR parameters (those obtained from graph theory) and some new parameters that combine steric, electronic and lipophilic information. The use of these parameters add a certain third dimension to the QSAR analysis because they depend on the shape of the molecular surfaces (van der Waals [4]) and/or on the interrelation between these surfaces and other molecular properties as Molecular Electrostatic or Molecular Lipophilic Potentials [5].

Thus, the parameters used in this QSAR study are: geometric (bond lengths, angles, dihedrals, interatomic distances and Sterimol parameters), electronic (atomic charge densities, dipole moments, and maxima and minima of MEP on VDWS), topological (Randic, Kier-Hall, Zagreb and Platt), and physicochemical (theoretical logP, and maxima and minima of MLP on VDWS).

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Intercalation of Halogen Molecules in Alkali-Fluorides Lattices: A Theoretical Study

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Among the variety of intercalation compounds known[1], those formed by inclusion of halogen molecules in a lattice of CsF[2] are unique in that the guest molecules are neither placed in the van der Waals gap of a two-dimensional lattice, as in graphite or in metal chalcogenide derivatives, nor occupying cages or channels in three-dimensional structures, as zeolites intercalates. Instead, the halogen molecules transform the ionically bound layer of CsF into a layered structure and intercalate between the ionically bound layers of CsF.

Firstly, we analyze qualitatively the interaction energy in $CsF{\cdot}Br_2$ and $CsF{\cdot}I_2$ from the orbital point of view, with the help of extended Hückel tight-binding (EHTB) band calculations and COD curves. This analysis allows us to conclude that the π and σ^* MO's of Br_2 interact with the fluoride ions, whereas the π^* MO's interact with cesium cations. This results are confirmed and put in a quantitative basis by more precise periodic Hartree-Fock (p-HF) calculations and by molecular calculations on a cluster model, including electron correlation (MP2). The p-HF calculated formation energies for the Br_2 and I_2 intercalates are roughly the same (*ca.* 2 kcal/mol). The p-HF calculated structural parameters for CsF and $CsF{\cdot}Br_2$ are in excellent agreement with the experimental values. The p-HF calculations seem to correctly predict the trends in the vibrational variations from host···guest interactions, with a calculated frequencies slightly larger than the experimental ones. This result might be attributed to the exclusion of electron correlation in HF calculations, as would seem to be confirmed by the closer agreement between the experimental frequencies and those from the MP2 cluster calculations. A comparative study of the interactions in the MF·XY family (M:Li,K,Cs; X,Y:Cl,Br,I) shows that the CsF·ICl has the stronger host···guest interactions.

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Using Density Functional Theory and Other Tools to Model Complex Systems and Processes

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The recent advent of nonlocal gradient-corrected density functionals has allowed enormous progress towards the incorporation of DFT into quantitative and qualitative molecular and biomolecular modeling. I will give an overview of some of the following:

- Hydrogen bonds and model peptide conformations
- Water clusters, ion-water interactions, proton transfer barriers
- Preliminary results from a combined DFT/MD treatment of a hydrated water molecule and the proton transfer between two water molecules.
- NMR chemical shift tensors and the effects of hydrogen- bonding on them; preliminary results for C-H and C-C coupling constants
- Structure and bonding in transition-metal clusters

Forcefields and Massively Parallel Computers

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Calculation based on empirical forcefields – molecular mechanics and dynamics – are often limited in both their accuracy and applicability both by the empirical forcefields available as well as by the available computing resource. Massively parallel processors (MPP) offer the promise of providing much more available, cost effective computing. This will directly affect the mechanics and dynamics calculations of the type that are now being undertaken by making them faster. A less obvious affect, however, will come from the use of this computational power to reduce the approximations invoked in forcefield methods, and also to improve the parametrizations of the forcefields.

Results of the efforts underway at Biosym in the development of parallel computational chemistry codes and in developing forcefields will be presented. In many areas these efforts complement each other, but there are certainly implications and conflicts that arise where the goals in the development of forcefields are contrary to those of high performance parallel codes. These synergies and conflicts, and their implications on the commercial use of MPP machines, will be explored.

Local speed distributions based on electronic Husimi functions

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The Heisenberg uncertainty principle does not allow to assign momentum distributions of a chemical system to given points in position space. As a result, it is impossible to predict which "speed" electrons have at given sites in a molecule. However, if the uncertainty principle is built into the description of the chemical system, an approximate assignment becomes possible again. This may be realized with the so-called Husimi phase-space function. A "fuzzy" picture of the average speed of electrons in molecular systems can be obtained by computing local momentum space expectation values based on this function. Applications to some molecular systems are given and discussed.

Density Functional and Hartree-Fock Theories Applied to Large Systems: The Mechanisms of Fullerene Annealing, Fragmentation, and Window Opening

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When fullerenes are fragmented by laser irradiation, they lose C_2 units and retain a closed carbon cage. Survival of the cage implies that annealing (rearrangement of the bonding) must play an important role. Based on *ab initio* quantum chemical calculations, we recently reported [1] a series of novel processes demonstrating that fullerene annealing is more facile than fragmentation, and that both are intimately related. Our findings imply that the assumptions commonly made about fullerenes --- that they are composed of five- and six-membered rings of sp^2 carbons--- are not valid under high-energy conditions. In particular, the appearance of sp^3 carbons and seven-membered rings is central for both annealing and fragmentation. Our results may aid in the design of experimental processes for controlling the nature of fullerene cages (for example doping, opening and re-closing them).

We also present theoretical evidence of a "window" mechanism operable on the surface of C_{60} and other fullerenes [2]. Through this mechanism, large holes may be formed in fullerenes excited to their triplet state, openings through which atoms and small molecules may pass. This work provides a theoretical foundation for experiments which have prepared endohedral noble gas compounds of C_{60} under thermal excitation. Based on our calculations, we propose a new method which could dramatically increase the efficiency of the process of noble gas insertion into C_{60} and provide a more general means to create endohedral fullerene compounds.

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Theoretical Studies of Nitric Acid Monohydrate and its High-Energy Isomers

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Ab initio calculations were carried out for $HONO_2{\cdot}H_2O$, $HOONO{\cdot}H_2O$, and $HONOO{\cdot}H_2O$, $NO_3^-{\cdot}H_2O$, and $ONOO^-{\cdot}H_2O$. Completely optimized equilibrium geometries, binding energies, acid dissociation constants, proton transfer potentials, vibrational spectra, thermochemical parameters, and stable site labilities have been computed at the RHF/6-311++G** and MP2/6-311++G** levels of theory. Possible implications for atmospheric chemistry and free radical biology are discussed.

Gaussian Density Functional Calculations on Systems of Biochemical Interest

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We will present results obtained with the gaussian density functional program, DeFT, developed at the University of California, San Francisco and the University of Ottawa[1]. Benchmark calculations[2] on the molecules used to parameterize the Merck Molecular Force Field[3] compare local and nonlocal density functional geometries, conformational energies, and dipole moments with their HF, MP2, and MP4 counterparts. A perturbative approach to incorporating nonlocal corrections is shown to give results that generally equal MP2, with a computational expense less that that of HF and fractionally more than that of the significantly less accurate local density functional approach.

Time permitting, we would like to present some of DeFT's newer features:

- a coupling of the finite difference Poisson-Boltzmann method with density functional theory so as to incorporate solvent effects into our quantum mechanical calculations
- an implementation of Yang's "divide-and-conquer" scheme[4] within a gaussian density functional approach
- a combined quantum/molecular mechanical approach which combines the aforementioned "divide-and-conquer" method with the AMBER force field.

These new features should allow us to treat both simple reactions in solution, as well as complex enzyme-catalyzed reactions.

[1] DeFT is available upon request from request@theory.chem.uottawa.ca

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A Study of the H—X···π Hydrogen–Bonded Complexes Using the Theory of Atoms in Molecules

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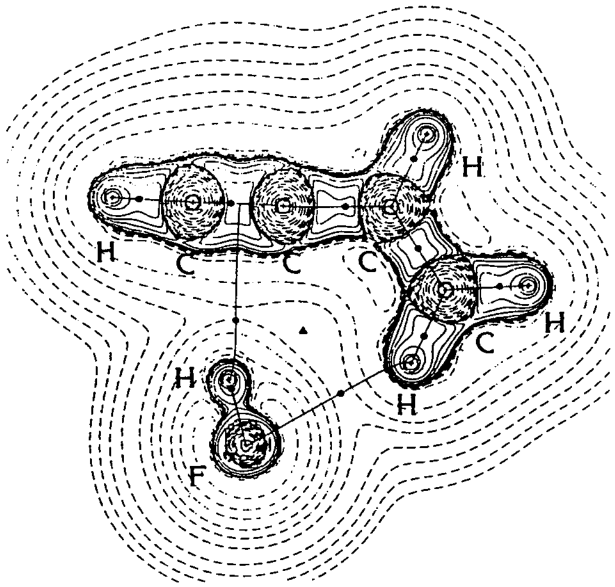
The π-type hydrogen-bonded complexes consisting of hydrogen halide HX (X = Cl, F) and the carbon-carbon triple or double bond of vinylacetylene (1-buten-3-yne, C4H4) have been studied. The vinylacetylene molecule contains two alternative π bonding sites (C ≡ C and C = C), it offers three possible structures of C4H4···HX which comprise two T-type bonds to C≡C (*endo* and *exo* approaches) and a T-type bond to C=C. From the results of optimized geometries and the hydrogen-bond stabilization energies, based on MP2/6-311++G**//6-31G** calculations, the π-type hydrogen bond to a C ≡ C bons leads to a more stable complex than for an analogous bond to C = C. The calculated global minima for the complexes with HF and HCl correspond to the H–X moiety lying along a bisector of the C ≡C bond in *endo* approach, predictions that are in good agreement with the reported FTMS results.

The topological properties of the electron density distributions of these two systems have been analyzed in terms of the theory of atoms in molecules. It is found, for HF complexes that both the *endo* and *exo* approaches lead to complexes that are nearly planar, with the proton of HF directed towards the triple carbon-carbon bond in vinylacetylene, forming a π-type hydrogen bond. Furthermore, a second hydrogen bond is formed between H of a C-H bond and F of HF and a ring structure is found. No second hydrogen bond is found in HCl complexes.



The nature of π-type hydrogen bonds has also been discussed using the Laplacian of the charge density ($\nabla^2\rho$).

Semi-topological NMR Spin Clusters: Establishment of the Mapping associated with $\lambda\vdash n$ partitions which map onto $\{[\lambda']\}(\mathcal{S}_n)$ in the *determinacy* of natural embeddings of $\mathcal{G}$ subgroups in $SU(m\leq n)\times\mathcal{S}_n$ nuclear spin algebras, characterising higher-n cluster NMR and aspects of related rovibrational spin statistics.

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Questions concerning the natural embedding associated with $SU(m\leq n,n/2)\times\mathcal{S}_n{\downarrow}\mathcal{G}$ for $\mathcal{G}\equiv\mathcal{I}\equiv\mathcal{A}_5$ and n=12,20 are examined in the context of the analogous properties for maximal SU(m=n) $\times\mathcal{S}_6{\downarrow}\mathcal{O}$ Casimir invariants[1] and the indeterminacy of similar NMR system invariants for $SU(m\leq 4)\times\mathcal{S}_8{\downarrow}\mathcal{O}$ natural embedding[2]. The question raised is important in understanding the NMR cluster structure and rovibrational spin statistics of $[A]_n$, in $[^{11}BH]^{2-}_{12}$, $[^{13}C^2D]_{20}$ -see [3,4]-, and ultimately the exo-cluster aspects of ^3He endohedral- and other $[^{13}C]_{60}$ fullerenes[5]. These aspects are derived in part from the nature of $\lambda\vdash n$ mapping[6] over $\mathcal{S}_n$-irreps yielding specific integer Kostka coefficients,$\Lambda_{[\lambda']}$:

$$\{\lambda \text{-->} \{\Lambda'_{[\lambda']}[\lambda']\}\,|\ \lambda,\text{permutational module, } \lambda\vdash n;\ \Lambda_{[\lambda']},\text{ a Kostka integer}\}, \qquad (1)$$

which in principle may enumerated by graphical combinatorial counting of the number of acceptable semi-normal contents which fit within a specific graph form[7].In the λ_{SA} (a self-associated form) $\rhd$ λ sector, the "Λ"s for all $\lambda\vdash n$ become large (>>7), so that direct methods become tedious; hence an alternative optimal form of enumeration is sought. One utilising a minimal number of low-valued Λ evaluations to yield the $\varepsilon^{\lambda}_i(\mathcal{S}_n)$ permutational invariance is presented[6]. Naturally, for n>>12 there is a coincident need to evaluate the general $\chi^{[\lambda']}_{(Xi)}(\mathcal{S}_n)$ characters for the calculation,

$$\{\Lambda_{[\lambda']}\}(\text{Kostkas of }\lambda) = \{\chi^{[\lambda']}_{(1^n)}\ /\lambda/ + \Sigma_{i=2}\ g_i\ \chi^{[\lambda']}_i\varepsilon^{(\lambda)}_i\}/\ /\mathcal{S}_n/,\ (g_i\text{ cycle order}). \qquad (2)$$

Hence, the full set of Kostka integers for specific λ-modules are established.

These initial aspects allow one to explore the $SU(m\leq n,n/2)\times\mathcal{S}_n{\downarrow}\mathcal{G}$ projective subduced invariance algebra to ascertain the strength(s) of any degeneracies present. The SU(m) "depth" to which the natural embedding is determinable follows directly. Certain alternative induced symmetry aspects, for the λ_{SA}s under the step-wise $\mathcal{S}_n\supset\mathcal{S}_{n-1}\supset\ .\supset\mathcal{S}_3\supset\mathcal{S}_2$ Racah chain,furnish us with additional critera for determinacy of $SU(m)\times\mathcal{S}_n{\downarrow}\mathcal{G}$ algebras-from the retention of self-associativity over $\{[\lambda']\}$, for a specific choice of an initial λ_{SA}.

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Dissociation of Diatomic Molecules in Intense Laser Fields: Stormy Separation or Peaceful Parting?

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The interaction of a diatomic molecule with an intense laser pulse is studied using classical trajectories with a one-dimensional model given by $V(x) - d(x)Ef(t)\cos(\mu t + \phi)$, where $V(x)$ is the field-free potential. If the laser intensity is great enough, dissociation of the diatomic can be induced. Some theoretical investigations have suggested that this dissociation occurs via chaotic dynamics. Using a variety of techniques, the dynamics of both the non-dissociation and dissociating trajectories are characterized. It is found that dissociating trajectories can originate from chaotic and non-chaotic regions in phase space. Simple models are introduced to explain the qualitative features of the system, including the threshold field strength for dissociation, the field strength at which all trajectories dissociate, the maximum kinetic energy of the dissociating products, the lifetime of the predissociating states, as well as the fraction of trajectories which dissociate via the chaotic route.

Accurate calculation of the hyperpolarizability of Li

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The accurate calculation of the static hyperpolarizability of the lithium atom poses a challenge to contemporary electronic structure methods. An extensive investigation of the effects of electron correlation and one-particle basis set choice is carried out. The dipole hyperpolarizability of Li is predicted to be $2900 \pm 300 au$. Our best finite-field computation uses a (20s11p9d5f)/[13s10p9d5f] basis set of contracted Gaussians, and the CCSD(T) method, that is the coupled cluster method in the space of single and double substitutions corrected non-perturbatively for triple substitutions.

Facility for the Analysis of Chemical Thermodynamics

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Ecole Polytechnique de Montreal

F*A*C*T is a system intended to facilitate classical chemical thermodynamic operations. A friendly interface to 10 programs is coupled to large files of data on compounds and solutions. Among the most frequently used programs are those which minimize the Gibbs energy to provide the equilibrium products of complex reactions (14 elements, 400 species) or generate stability diagrams of various styles. The system has operated since 1980 on the McGill University mainframe. The present user group is composed of industrial organizations, national laboratories and universities located mainly in North America. Until recently, the system was accessible only via standard data linkages. Recently, however, a stand-alone version of F*A*C*T has been developed for use on PCs. This version will be demonstrated with examples drawn from chemical engineering and materials science.

MD Simulations of Protein Dynamics and Unfolding

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The use of molecular dynamics simulations to study the dynamics of proteins in aqueous solution under native and unfolding conditions is discussed in the context of recent applications. The computed structural models are compared to available experimental data, i.e. pulse labeling experiments and site-directed mutagenesis. In particular, the properties of the final structures obtained on unfolding are compared to those attributed to "molten globules". These simulations also give amazingly rich detail of the pathways of protein unfolding at the atomic level and suggest explanations for some experimental observations.

The Structure and Dynamics of Protonated Methane and Acetylene

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Ab initio Molecular Dynamics (AIMD) method based on Vanderbilt ultrasoft pseudopotentials and a plane wave expansion for the electronic orbitals was used in the study of the dynamical properties of protonated methane (CH_5^+) and acetylene ($C_2H_3^+$). At finit temperatures, both molecules do not have well-defined structures. The hydrogen atoms were to be mobile and executed large amplitude vibrations. The stablilization of CH_5^+ by a hydrogen molecule does not alter the basic fluxional dynamics but only slow down the motions. The theoretical results will be discussed in light of the recent spectroscopic data.

Nucleic Acid MOdeling Tool (NAMOT): An interactive graphic tool for modeling nucleic acid structures

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The helical structure of the molecule (almost all of DNA and a significant portion of RNA) makes the modeling of nucleic acid a unique task. Unlike other biopolymeres (e.g. proteins, lipids, etc.), the integrity of the structures of a nucleic acid molecule depends strongly on the maintenance of the base pairing within the molecule. Structural alterations (i.e. bending, stretching, compressing, etc.), in general, should not disturb the base pairings. A custom-made molecular modeling tool is developed taking into consideration this specific property of the molecule. Instead of Cartesian coordinates, the modeling is carried out on a set of reduced coordinates developed here in our laboratory. One of the advantages of using this set of reduced coordinates is the readiness of maintaining the base-pairings while altering the structure. An algorithm (also developed at LANL) for modeling sugar-phosphate structures was used to ensure the backbone connectivity while changing the base geometry. A graphic routine is incorporated into the package to display the image of the molecule while the modeling work is being executed. The program is written in C using XView tool kit with Xlib routines to ensure portability to different workstations. This program is available through an anonymous FTP site.

The Mechanism of Conformational Interconversion of Calix[4]arenes: a theoretical study using the *Conjugate Peak Refinement*[1]

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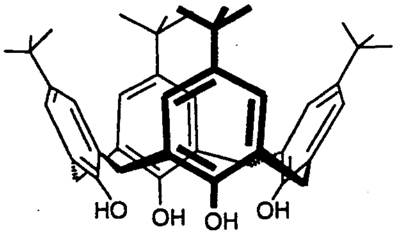
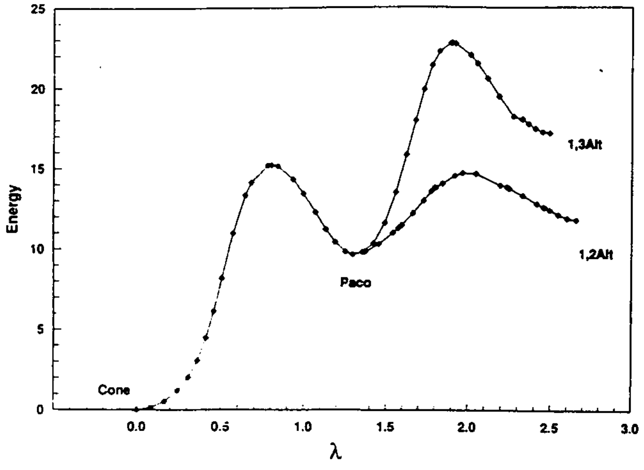
Calixarenes are popular building blocks in supramolecular chemistry.[2] They are cyclic condensation products of a phenol and formaldehyde. In particular calix[4]arenes (see figure) are used as molecular platforms, because they are easy to synthesize and chemical modification is well documented. Calix[4]arenes can occur in four extreme conformations: the cone, the partial cone, the 1,2-alternate, and the 1,3-alternate. The cone structure has four hydroxyl groups at the same side; the partial cone has one phenolic moiety rotated through the ring; the 1,2-alternate has two adjacent phenolic moieties rotated through the ring; and the 1,3-alternate has two opposite phenolic moieties rotated through the ring. Calix[4]arenes with hydroxyl groups or one to four methoxy groups are mobile and substituents should be as least as large as n-propyl to block the interconversions.

Up to now the mechanism of interconverion of calix[4]arenes with OH or OMe groups has not been clarified, although a number of (NMR) studies have appeared. For the tetrahydroxy-calix[4]arene both a stepwise and a concerted pathway have been proposed. We have used the *Conjugate Peak Refinement*,[1] implemented as the Travel module in CHARMm, to obtain more insight in the mechanism of interconversion.

Results will be shown for the tetrahydroxy-calix[4]arene, that predict a stepwise pathway as mode of operation, with the conversion from the cone to the partial cone as the rate limiting step (see figure). Agreement with experimental data is excellent.





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Molecular Mechanics and Molecular Dynamics in solution of well-shielded Eu(3+)-complexes: a critical note to observed life-times.

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On the basis of life-time measurements of Eu(3+)-complexes in D_2O and H_2O or CD_3OD and CH_3OH it is in principal possible to determine the number of OH-oscillators in the first coordination sphere by using the method of Horrocks. We have synthesized Eu(3+)-complexes of a hemispherand and determined the life-times in CD_3OD and CH_3OH and found that they are the same. Initially we concluded that the shielding is perfect, which was supported by MM calculations that showed a complete surrounding of the Eu(3+) by the ligand. However, an MD in a periodic methanol box showed that one methanol enters the firstcoordination sphere. Currently we are testing the hypothesis that the CH groups in the hemispherand are efficient quenchers of the excited Eu(3+). Our initial experiments show that the life-time increases by substituting CH for CD. I believe that this work shows that computational chemistry can give a very critical test of "accepted" methods.

Permanent Electric Moments in Density Functional Theory.

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The permanent electric moments (PEM) of a system are relevant for the description of the electronic distribution within a molecule and in the characterization of long range intermolecular interactions. The accurate calculation of the PEM at the SCF level has shown to be quite sensitive to the quality of the basis set and to the geometry of the molecule. The role of correlation has also been addressed as a very important factor in the calculation of these properties. There are several works concerning the quality of the multipole electric moments of small and medium size molecules calculated by conventional wave-function methods (HF, MPn, CI, CC, etc.). However, this aspect has not been thoroughly explored within the realm of density functional theory. Thus, in this work we present detailed calculations of the PEM of small and medium size molecules, analyzing the effect of the basis set, nature of the exchange-correlation functional (local and non-local) and geometry (standard vs. optimized geometry). The calculations have been done with the LCGTO realization of the Kohn-Sham equations as is done in code *deMon*. The calculation of the multipole moments, as well as other molecular properties, is done post-SCF with a newly developed code particularly efficient in the calculation and handling of molecular integrals. We show that with a proper basis set the calculated PEM are in excellent agreement with very well characterized experimental values.

The Hyperfine Structures of Al_3 and Ga_3 by Density Functional Theory

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Density functional theory (DFT) has been employed to predict the hyperfine structures of Al_3 and Ga_3. Several low-lying electronic states have been investigated. The geometries calculated have been compared with previous theoretical results. The predicted hyperfine structures have been used to explain the new ESR experiment.

The Effects of Flexible Charges in Molecular Dynamics Simulations

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In molecular dynamics simulations of biological molecules, one usually allows the geometry of molecules to be flexible in order to "model" the system more realistically. But the atomic charges, which are used to describe intermolecular interactions in molecular dynamics simulations, are fixed. In this poster a flexible charge model based on quantum chemistry calculations is proposed. The effects of flexible charges on radial distribution functions, time correlation functions, and interactions between solute and solvent molecules are investigated in terms of molecular dynamics simulations.

Discrete variable representations of complicated kinetic energy operators

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Abstract

Probably the most important advantage of the discrete variable representation (DVR) is its simplicity. The DVR potential energy matrix is constructed *directly* from the potential function without evaluating integrals. For simple kinetic energy operators the DVR kinetic energy matrix is determined from transformation matrices and exact matrix representations of one-dimensional kinetic energy operators in the original delocalized polynomial basis set. For complicated kinetic energy operators, for which matrix elements of terms or factors with derivatives must be calculated numerically, defining a DVR is harder. A DVR may be defined from a finite basis representation (FBR) where matrix elements of terms or factors in the kinetic energy operator are computed by quadrature but implicating quadrature undermines the simplicity and convenience of the DVR. One may bypass quadrature by replacing the matrix representation of each kinetic energy operator term with a product of matrix representations. This product approximation may spoil the hermiticity of the Hamiltonian matrix. In this paper we discuss the use of the product approximation to obtain DVRs of complicated, general kinetic energy operators and devise a product scheme which always yields an hermitian DVR matrix. We test our ideas on several one-dimensional model Hamiltonians and apply them to the Pekeris coordinate Hamiltonian to compute vibrational energy levels of H_3^+. The Pekeris coordinate Hamiltonian seems to be efficient for H_3^+. We use Jacobi polynomial basis sets and derive exact matrix elements for $\frac{d}{dx}G(x)\frac{d}{dx}$, $r(x)\frac{d}{dx}$, $r(x)$ and $(1-x)^\lambda e^{-xt}$ with $G(x)$ and $r(x)$ rational functions. We discuss the utility of several Jacobi DVRs and introduce an improved FBR for general kinetic energy operators with more quadrature points than basis functions. We also calculate Euclidean norms of matrices to evaluate the accuracy of DVRs and FBRs.

Correlation In Molecules

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Molecular correlation energy is approached from Quantum Field Theory, and Density Functional Theory is developed. Field-Theoretical Many-Body methods are considered to describe correlation and their advantages and merits relative to the usual approaches discussed. It is shown that methods developed in nuclear physics can be successfully carried over into chemical physics problems.

Large-Scale Parallel SCF

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Several alternative approaches were examined that avoid the diagonalization bottleneck in parallel self-consistent field (SCF) implementations. These algorithms demonstrate between linear and quadratic convergence using various approximations to the orbital Hessian. The optimal approach was found to be a conjugate-gradient method preconditioned with a level-shifted approximation to the orbital Hessian. Test cases performed demonstrate the scalability of this approach.

Rydberg Dimer Cations: $(H_2)_2^+$ and $(H_3)_2^+$

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ABSTRACT

It was shown by Boldyrev and Simons (J. Phys. Chem. 96, 8840 (1992)) that Rydberg molecules such as NH_4 can dimerize to form a "Rydberg dimer", with a weak chemical bond on the order of 10-20 kcal/mol. Although these dimers are thermodynamically unstable, they are local minima with all bound vibrational modes. The cation of this dimer, $(NH_4)_2^+$ was bound even more strongly. We found evidence recently for the analogous Rydberg dimer of H_3, although the dimer state in that case was the fifth excited electronic state. The molecule $(H_3)_2$ contains two H_3^+ "cores" and a pair of electrons in the bonding molecular orbital formed by the (weak) overlap between 2s Rydberg electrons on each core. The present paper is a study of the dimer cations of both H_3 and also H_2, which represent the simplest possible cases of this new type of chemical bonding. The results for the two dimer cations are very similar: Both show a pronounced potential minimum in the first electronic excited state, at an extended geometry. For $(H_2)_2^+$ this occurs at 8.0 bohr, where the well depth is 30 kcal/mol. For $(H_3)_2^+$, the minimum also occurs near 8.0 bohr, and the well depth is 29 kcal/mol. These values resemble those for the Li_2^+ dimer (bond distance 6 bohr, well depth 30 kcal/mol). The stability and possibilities for observation of spectra of these Rydberg dimer cations will be discussed.

Quantum Dynamics of Energy Flow in Molecules

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The quantum mechanical study of energy flow in multistate systems is becoming possible. Strategies for dealing with the huge number of vibrational basis functions will be reviewed. These approaches construct a relatively small active space from the very large primitive basis set. Accurate dynamical calculations can then performed in the active space with the RRGM or Chebychev propagation algorithms. Results will be reported for overtone dynamics in benzene. Computed spectra and survival probabilities will be compared with experimental results. Then, more detailed calculations will follow the flow of energy through the various local stretch and bend modes. These results will answer the questions: Where does the energy go, and how long does it take to get there?

A Divide-and-Conquer Method and Its Applications to Large Molecules

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We will present the recent progress in a divide-and-conquer density-functional approach for the quantum-mechanical description of molecular electronic structure. The method uses electron density as the basic computational variable and divides a large system into subsystems. The molecular electron density and energy are determined as the sums of contributions from subsystems. The computational effort of the method in principle scales linearly with the number of electrons. We have applied the method to predict the shape and energetics of large single and multi-shell fullerenes up to the size of 1000 atoms.

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Application of the Finite Element Method to Time-Dependent Quantum Mechanics : II-H_2^+ in a Laser Field

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The ionization rates, nonlinear optical polarizabilities and harmonic generation spectra of H_2^+ in Cartesian coordinates in 3 dimensions have been calculated nonperturbatively using FE methods for field directions parallel and perpendicular to the hydrogen molecule ion axis. We present for the first time nonperturbative ionization rates for excitations perpendicular to the molecular axis. The results obtained here, including those previously calculated for H and He atoms show that FE basis sets which are local in nature, are ideally suited to treat nonperturbative time dependent problems which lead to high excitations into Rydberg and continuum states. Our numerical calculations of low order hyperpolarizabilities agree well with previous perturbative calculations and offer the possibility of calculating high order ones since our basis sets, which allow for calculation of ionization rates,therefore implicitly contain continuum state contributions.

Calculation of Spectra by Method of Self - Similar Approximations

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A new method is presented for calculating the spectra of Hamiltonians in quantum mechanics. This method permits to treat perturbation theory from the point of view of dynamical theory. In this method a sequence of perturbative approximations is put into one - to - one correspondence with a trajectory of a dynamical system with discrete time, called the approximation cascade. Approximate fixed points of the latter define the self - similar approximations for an effective limit of a perturbative sequence. The stability of the method is controlled by calculating the mapping multipliers and Lyapunov exponents. As an illustration, the self - similar approximations for the spectra of several Hamiltonians are constructed.

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APPROXIMATE DENSITY FUNCTIONAL THEORY AS A PRACTICAL TOOL IN MOLECULAR ENERGETICS AND DYNAMICS:

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Approximate Density Functional Theory (DFT) has over the past decade emerged as a tangible and versatile computational method. It has been employed successfully to obtain thermochemical data; molecular structures; force fields and frequencies; assignments of NMR-, photoelectron-, E.S.R- , and UV- spectra; transition state structures as well as activation barriers; dipole moments and other one-electron properties. Thus , approximate DFT is now applied to many problems previously covered exclusively by ab initio Hartree-Fock (HF) and post-HF methods. The recently acquired popularity of approximate DFT stems in large measure from its computational expedience which makes it amenable to large size or real life molecules. More importantly, perhaps, is the fact that expectation values derived from approximate DFT in most cases are better in line with experiment than results obtained from post-HF calculations . This is in particular the case for systems involving transition metals. It is the primary objective of this talk to demonstrate the great potential of DFT in studies on organometallic energetics and kinetics.

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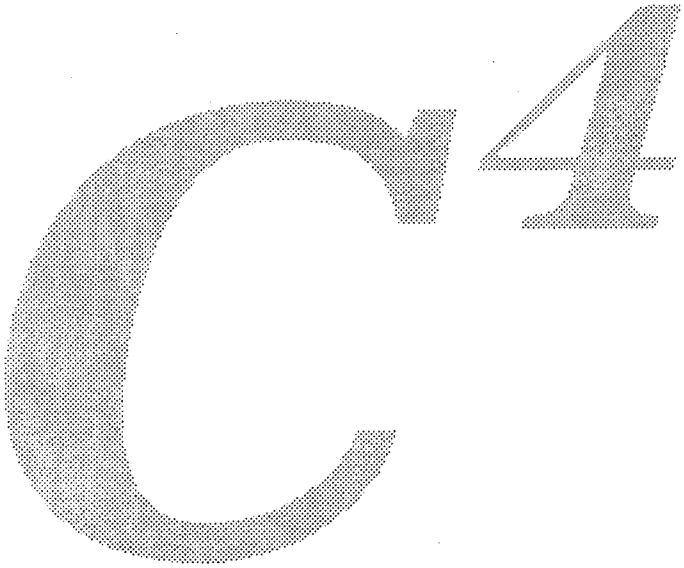

Updates will be made available later.

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Updates and Omissions

Program Omissions

Sunday afternoon refreshment break sponsored by the
High Performance Computing Center.
Monday afternoon refreshment break sponsored by
IBM Canada.

Revised Schedule

Wednesday, May 25, 1994

Morning		Current and Future Trends Chair: M. Klobukowski Lecture Theatre D, Stirling Hall
8:30AM	M. Dupuis	Advances in Parallel Processing: Prospectives and Results
9:20AM	C. Johnson	Crystallographic Orbifold Atlas
9:50AM	Refreshment Break, Lower Common Room, Victoria Hall	
10:20AM	A. Wong	Large-Scale Parallel SCF
10:50AM	G. Diercksen	Intelligent Software: The OpenMol Project
11:40AM	Lunch and END, Lower Common Room, Victoria Hall	

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Poster Session Schedule

Session abreviations: S - Sunday
M - Monday
The number indicates the board number.

Sunday, 5:00-7:00PM

S1	M. T. Banh	
S2	C. I. Bayly	
S3	A. Berces	I
S4	F. Bohr	
S5	P. Bruna	
S6	P. Calaminici	
S7	K. A. Dakin	
S8	R. M. Dickson	
S9	M. Dory	
S10	L. Fan	I
S11	L. Girard	
S12	J. Guan	
S13	I. P. Hamilton	
S14	C. Jamorski	I
S15	M. Kaupp	
S16	R. A. Kirby	
S17	M. Klobukowski	
S18	J. Kong	
S19	M. S. Krishnan	
S20	X. Li	
S21	S. M. Mattar	I
S22	R. C. Mawhinney	
S23	A. McNichols	
S24	S. H. Nilar	
S25	Y. S. Park	
S26	M. M. Poulin	
S27	C. C. Pye	
S28	P.-N. Roy	
S29	I. Rozas	
S30	H. Schmider	
S31	T.-H. Tang	
S32	M. Thachuk	
S33	W. T. Thompson	
S34	F.C.J.M. van Veggel	
S35	Jiahu Wang	
S36	H. Wei	
S37	M. A. Whiteside	
S38	H. Yu	

Monday, 5:00-7:00PM

M1	E. E. Aubanel	
M2	A. Barkley	
M3	A. Berces	II
M4	P. Bündgen	
M5	M. E. Casida	
M6	D. Chartrand	
M7	W. M. Davis	
M8	G. DiLabio	
M9	L. Fan	II
M10	R. Fournier	
M11	N. Godbout	
M12	F. Grein	
M13	H. Guo	
M14	G. Hunter	
M15	C. Jamorski	II
M16	B. Jin	
M17	S. T. Kim	
M18	D. D. Klug	
M19	A. M. Köster	
M20	M. Leboeuf	
M21	J. M. Martell	
M22	S. Mattar	II
M23	S. Marone	
M24	J. Nagy	
M25	T. T. Nguyen-Dang	
M26	J. M. Pérez-Jordá	
M27	E. I. Proynov	
M28	A. V. Raja	
M29	E. Ruiz	
M30	F. Senese	
M31	F. P. Temme	
M32	A. J. Thakkar	
M33	C.-S. Tung	
M34	A. Vela	
M35	Jian Wang	
M36	J. S. Wright	
M37	V. I. Yukalov	
M38	M. Hô	