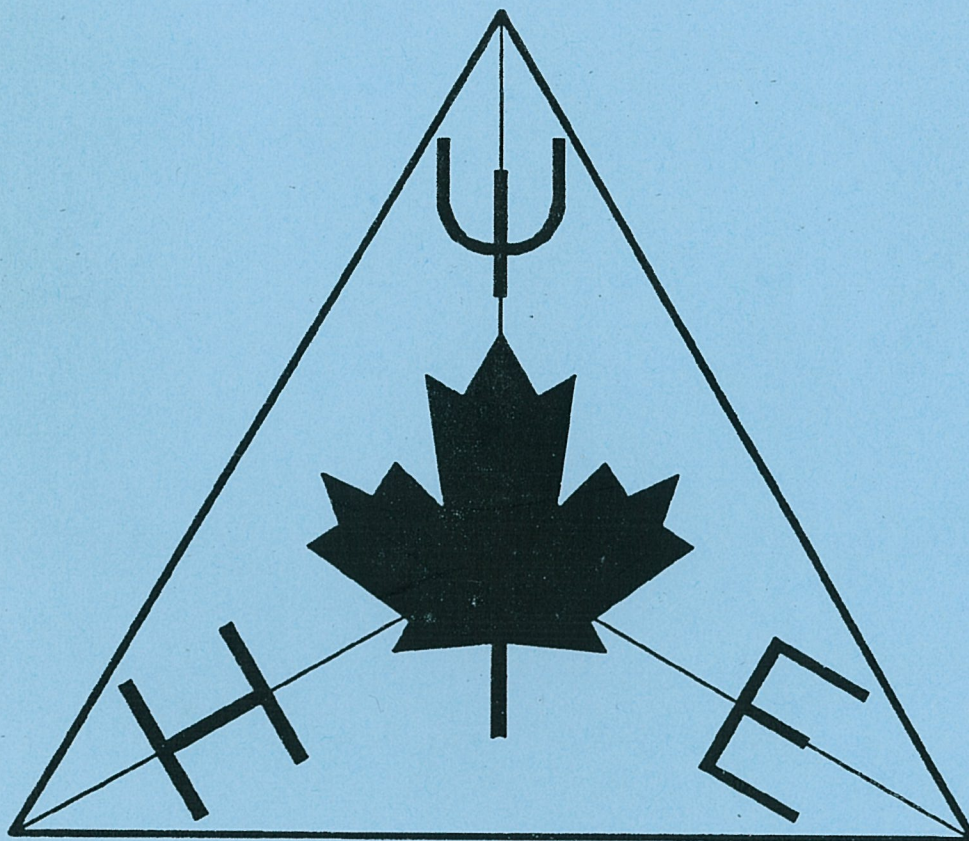


PROGRAM and ABSTRACTS  
PROGRAMME et RÉSUMÉS

**12th Canadian Symposium on Theoretical Chemistry**  
**12ième Symposium Canadien sur la Chimie Théorique**

August 6-11, 1995  
Fredericton, Canada



Sponsored by the  
**Canadian Association of Theoretical Chemists**



12th Canadian Symposium on Theoretical Chemistry  
12ième Symposium Canadien sur la Chimie Théorique

Fredericton, 6-11 August/Août 1995  
Cochairs: William J. Meath and Ajit J. Thakkar

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**Welcome to Fredericton!**

This book was sent to press on the morning of July 24, 1995. Therefore abstracts and registrations received after that time do not appear in this book.

We are pleased to acknowledge with gratitude the material assistance of

- Department of Chemistry, University of New Brunswick
- Department of Chemistry, University of Western Ontario
- Faculty of Science, University of New Brunswick
- Faculty of Science, University of Western Ontario
- IBM Canada Ltd.
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- Bank of Montreal
- Silicon Graphics
- Bank of Nova Scotia
- VWR CanLab
- Royal Bank

We are delighted to acknowledge the indispensable assistance of

- Krista Coy, Conference Secretary
- Christine Lodge, Secretary
- Diana Timmermans, Secretary
- Robert J. Doerksen, Conference Gofer

This symposium would not have been possible without the support mentioned above.

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**12th Canadian Symposium on Theoretical Chemistry  
12ième Symposium Canadien sur la Chimie Théorique**

	Monday, August 7	Tuesday, August 8	Wednesday, August 9	Thursday, August 10	Friday, August 11
8:30 am	Posters up for Poster Session A	Posters up for Poster Session B		Posters up for Poster Session C	
8:45	S1: M.C. Zerner	S5: S.M. Rothstein	S9: J.S. Wright	S11: B.C. Sanctuary	9:30 S15: G.N. Patey
8:45	H.A. Scheraga	D. Ceperley	E.R. Davidson	M.A. Ratner	9:30 S.A. Rice
9:25	A. Rauk	R.E. Kapral	J. Simons	H.J. Kreuzer	10:20 W. Meyer
10:05	B R E A K				11:00 B R E A K
10:25	S2: R.A. Poirier	S6: T.T. Nguyen-Dang	S10: R.J. Boyd	S12: T. Ziegler	11:15 S16: V.H. Smith
10:25	W.L. Jorgensen	H.A. Rabitz	R.J. Bartlett	D.M. Bishop	
11:05	P.G. Mezey	A.D. Bandrauk	S.D. Peyerimhoff	J. Oddershede	11:15 J.N. Murrell
11:45	J.T. Hynes	K.C. Showalter	P. Botschwina	P. Pyykkö	
12:25 pm	LUNCH	LUNCH		CATC Meeting LUNCH	12:05 pm Symposium ends
2:15	S3: S.G. Whittington	S7: J. Paldus	KING ' S		
2:15	J.M. Andre	D.J. Moore		C.E. Dykstra	
2:55	D.W. Sumners	W. Yang		B. Jeziorski	
3:35	B R E A K				
3:55	S4: R.S. Dumont	S8: W.G. Laidlaw	LANDING		
3:55	W.H. Miller	D.R. Salahub		S14: I.P. Hamilton	
4:35	D.M. Wardlaw	K.B. Whaley	TRIP		
5:15	Poster Discussions - A	Poster Discussions - B		Poster Discussions - C	
7:30				BBQ AND JAZZ	

All lectures, poster presentations, and vendor displays will be in the Wu Conference Centre

**12th Canadian Symposium on Theoretical Chemistry  
12ième Symposium Canadien sur la Chimie Théorique**

<i>Monday, August 7</i>	<i>Tuesday, August 8</i>	<i>Wednesday, August 9</i>	<i>Thursday, August 10</i>	<i>Friday, August 11</i>
<p>Poster discussions A 5:15 - 7:15</p> <p>G.A. Arteca K.F. Ranvard P. Barbat D. Berard J. Berges R.J. Boyd A. Brown P.J. Bruña R. Cammi N.M. Cann T. Carrington, Jr. R. Cimraglia J. Cizek B.J. Clark A. Conjusteau S. Constat P. Csavinszky J. Cullen K.V. Darvesh G. de Brouckere G.A. DiLabio C. Dion R.J. Doerksen R.S. Dumont N. El-Bakali Kassimi B. Engels M. Ernzerhof A. Ferreira F. Grein J.R. Gunn M.R.J. Hachev I.P. Hamilton</p>	<p>Poster discussions B 5:15 - 7:15</p> <p>M. Hô C.-H. Hu S.P. Karnã S.M. Kast B. Kendrick M. Klobukowski M. Kolbuszewski J. Kong S. Koseki M.S. Krishnan H.A. Kurtz M. Lam T.-S. Lee G. Lushington S.M. Mattar R.C. Mawhinney E.A. McCullough, Jr. S.A.C. McDowell V. Murashov S.V. Pai J. Paldus P. Piecuch R.A. Poirier C. Pouchan N.M. Poulin M. Ramek S.H. Robertson I. Røeggen A.E. Koitberg S.M. Rothstein P.-N. Roy A. Salam</p>		<p>Poster discussions C 5:15 - 6:45</p> <p>S.D. Schwartz I. Shamovsky A. Skancke P.N. Skancke J. Stohner H. Subramanian I.M. Svishchev F.P. Temme D.R. Truax D.F. Tuan C. Ursebach S. Wildman H.L. Williams P.I. Winn K. Worsnop T.H. Wu D.M. York T. Ziegler</p> <p align="center">7:30</p> <p align="center"><b>BBQ AND JAZZ</b></p>	

32  
All lectures, poster presentations, and vendor displays will be in the Wu Conference Centre 18





**12th Canadian Symposium on Theoretical Chemistry**  
**12ième Symposium Canadien sur la Chimie Théorique**

Fredericton, 6-11 August/Août 1995

Co-chairmen: **William J. Meath** and **Ajit J. Thakkar**

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All lectures, poster presentations and vendor displays will be in the Wu Conference Centre.

**MONDAY, August 7**

**8:30 a.m. - 7:15 p.m.**      **Poster Session A.** Posters displayed all day. Authors at posters during evening poster discussion session.

**8:45 a.m. - 10:05 a.m.**      **Session 1**

---

**M.C. Zerner**  
University of Florida

Chair

**H.A. Scheraga**  
Cornell University

Theoretical Studies of Protein Folding

**A. Rauk**  
University of Calgary

Oxidative Damage to Peptides: Breaking the Ground

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**10:05 a.m. - 10:25 a.m.**      **Refreshment Break**

**10:25 a.m. - 12:25 p.m.**      **Session 2**

---

**R.A. Poirier**  
Memorial University

Chair

**W.L. Jorgensen**  
Yale University

Molecular Recognition in Organic and Biochemical Systems

**P.G. Mezey**  
University of Saskatchewan

Molecular Shape Analysis from Diatomics to Proteins:  
*Ab Initio* Quality Local and Global Electron Density  
Representations by the Medla Methods

**J.T. Hynes**  
University of Colorado

Acid Ionization in Solution

---

**12:25 p.m.**

**Lunch**



## POSTER DISCUSSIONS A, Monday, August 7, 5:15 - 7:15 p.m.

<b>Presenter</b>	<b>Title</b>
A1. <b>G.A. Arteca</b>	Molecular shape transitions between "open" and "closed" protein conformations
A2. <b>K.E. Banyard</b>	Momentum Space: Coulomb Correlation in $2p^2\ 3P$ States of He-like Ions
A3. <b>P. Barbarat</b>	Optical properties of cubic semiconductors predicted by density functional theory (DFT).
A4. <b>D. Berard</b>	Computer Simulations of Quantum Water in Aqueous Solution
A5. <b>J. Bergès</b>	Theoretical approach of self-association of Amphotericin in water using a continuum model and Molecular Dynamics.
A6. <b>R.J. Boyd</b>	Density functional theory and the electron density of molecules.
A7. <b>A. Brown</b>	The harmonic two-colour rotating wave approximation; its validity and an application to the effects of permanent dipoles and laser phase in molecular excitations.
A8. <b>P.J. Bruna</b>	Electron-spin magnetic moments of simple radicals containing H, Li and Be.
A9. <b>R. Cammi</b>	<i>Ab Initio</i> Calculation of the Dynamical Polarizability and Hyperpolarizabilities of Molecular Solutes
A10. <b>N.M. Cann</b>	An integral equation approach to surface excess thermodynamics
A11. <b>T. Carrington, Jr.</b>	A time dependent multi-surface calculation of the orientation and alignment of photofragments
A12. <b>R. Cimiraglia</b>	Many-body multireference Møller-Plesset and Epstein-Nesbet perturbation theory: fast evaluation of second order energy contributions
A13. <b>J. Čížek</b>	Study of spin Hamiltonians for regular polygons
A14. <b>B.J. Clark</b>	Information Entropies and Relative Entropies of the Two Particle Density Function
A15. <b>A. Conjusteau</b>	High intensity photodissociation of $HCl^+$ : Electronic and permanent dipole effects



## POSTER DISCUSSIONS A, Monday, August 7, 5:15 - 7:15 p.m.

Presenter	Title
A16. S. Conostas	Proton transfer in mesoscopic, molecular clusters.
A17. P. Csavinszky	Gram determinantal inequalities with elements $\langle r^m \rangle$ obtained from Hylleraas wave functions for the $^2S$ states of the three-electron systems $Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}$ and $Ne^{7+}$
A18. J. Cullen	Optimized Orbital Solutions to Multireference Problems within the Coupled Cluster Ansatz
A19. K.V. Darvesh	<i>Ab Initio</i> Studies of Small 1,3-Dipolar Systems
A20. G. de Brouckère	Configuration interaction (CI) calculations of spectroscopic properties of $P_2 X^1\Sigma^+$ ground state and $a^3\Sigma_u^+, b^3\Pi_g, A^1\Pi_g$ low lying excited states
A21. G.A. DiLabio	Group 14 carbene analogs: The first stable plumblyene?
A22. C. Dion	Numerical simulation of HCN in an intense laser field.
A23. R.J. Doerksen	<i>Ab initio</i> computations and additive models for the polarizabilities of aromatic five-membered rings: azoles
A24. R.S. Dumont	Statistical properties of chaotic energy eigenvalues & eigenfunctions
A25. N. El-Bakali Kassimi	Oxazoles: <i>Ab initio</i> structures, polarizabilities, and additive models
A26. B. Engels	<i>Ab initio</i> calculation of ESR parameters of distorted electronic states
A27. M. Ernzerhof	Long-range Asymptotic Behavior of Ground-state Wave Functions, One-matrices, and Pair Densities
A28. A. Ferreira	Solvent Effects in TDHF Calculations
A29. F. Grein	Oscillator strengths for VUV transitions of $C_2$
A30. J.R. Gunn	Improved Size-scaling in Simulations of Reduced-model Proteins using a Hierarchical Potential Evaluation
A31. M.R.J. Hachey	Rydberg-valence mixing in formaldehyde. A multireference CI study
A32. I.P. Hamilton	High-lying Vibrational Levels for $HO_2$ and $HO_2^-$

**TUESDAY, August 8**

**8:30 a.m. - 7:15 p.m.      Poster Session B.** Posters displayed all day. Authors at posters during evening poster discussion session.

**8:45 a.m. – 10:05 a.m.      Session 5**

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**S.M. Rothstein**  
Brock University

Chair

**D. Ceperley**  
University of Illinois  
at Urbana-Champaign

Quantum Monte Carlo Methods for Electronic Structure

**R.E. Kapral**  
University of Toronto

Reaction Dynamics in Mesoscopic Molecular Clusters

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**10:05 a.m. - 10:25 a.m.      Refreshment Break**

**10:25 a.m. – 12:25 p.m.      Session 6**

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**T.T. Nguyen-Dang**  
Laval University

Chair

**H.A. Rabitz**  
Princeton University

Intervention and Interrogation of Molecular Dynamics

**A.D. Bandrauk**  
Université de Sherbrooke

Molecules in Intense Laser Fields: Dissociation,  
Ionization, Coulomb Explosions and Stabilization

**K.C. Showalter**  
West Virginia University

Stabilizing and Tracking Stationary States and Periodic  
Orbits in Chaotic Systems

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**12:25 p.m.                  Lunch**

## TUESDAY, August 8 (continued)

### **2:15 p.m. - 3:35 p.m.      Session 7**

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**J. Paldus**  
University of Waterloo

Chair

**D.J. Moore**  
Université de Geneve

Berry Phases: Theory and Applications

**W. Yang**  
Duke University

Linear Scaling Methods for Electronic Structure  
Calculations: The Divide-and-Conquer Strategy

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### **3:35 p.m. - 3:55 p.m.      Refreshment Break**

### **3:55 p.m. - 5:15 p.m.      Session 8**

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**W.G. Laidlaw**  
University of Calgary

Chair

**D.R. Salahub**  
Université de Montréal

Structure, Properties, and Reactivity of Clusters  
and Surfaces from Density Functional Theory

**K.B. Whaley**  
University of California,  
Berkeley

Clusters - interpolations and surprises in  
the science between molecules and bulk phases

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### **5:15 p.m. - 7:15 p.m.      Poster discussions, Session B**



**POSTER DISCUSSIONS B, Tuesday, August 8, 5:15 - 7:15 p.m.**

<b>Presenter</b>	<b>Title</b>
B1. <b>M. Hô</b>	An Investigation of the Dependence of Shannon Information Entropies on Molecular Geometry and Chemical Reaction Paths
B2. <b>C.-H. Hu</b>	Potential energy surface for interactions between N <sub>2</sub> and He: <i>ab initio</i> calculations, analytic fits, and second virial coefficients
B3. <b>S.P. Karna</b>	Spin-unrestricted time-dependent Hartree-Fock theory of frequency-dependent linear and nonlinear optical properties
B4. <b>S.M. Kast</b>	Constant Temperature Molecular Dynamics Simulations by Means of a Stochastic Collision Model
B5. <b>B. Kendrick</b>	Geometric Phase Effects in H + O <sub>2</sub> Scattering
B6. <b>M. Klobukowski</b>	Electron affinity of SF <sub>6</sub>
B7. <b>M. Kolbuszewski</b>	Adiabatic and Strictly Diabatic Potential Curves of He <sub>2</sub> <sup>2+</sup>
B8. <b>J. Kong</b>	On the isomerization of HMO/MOH, M = Be, Mg and Ca
B9. <b>S. Koseki</b>	Main Group Effective Nuclear Charges for Spin-orbit Calculations
B10. <b>M.S. Krishnan</b>	Collisional Energy Transfer Models for H <sub>2</sub> Dissociation in the Presence of Argon
B11. <b>H.A. Kurtz</b>	Intermolecular interaction effects on molecular NLO properties
B12. <b>M. Lam</b>	Mechanism of C <sub>2</sub> H <sub>4</sub> Dehydrogenation to C <sub>2</sub> H <sub>2</sub> on the Ni(111) Surface
B13. <b>T.-S. Lee</b>	Applying the divide-and-conquer method to quantum calculations of large systems
B14. <b>G. Lushington</b>	Complete to Second-Order Calculations of Molecular g-Tensors
B15. <b>S.M. Mattar</b>	MRSD-CI Studies of the BN Hyperfine Tensor: The Lowest <sup>3</sup> Π State
B16. <b>R.C. Mawhinney</b>	(CN <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> , (CNSNS) <sub>2</sub> , and (CNSSS <sup>+</sup> ) <sub>2</sub> ; a comparative study
B17. <b>E.A. McCullough, Jr.</b>	Theoretical calculations on the conformation of cyclopentadienyl coordination in ru nitrosyl and thionitrosyl complexes.

## POSTER DISCUSSIONS B, Tuesday, August 8, 5:15 - 7:15 p.m.

Presenter	Title
B18. S.A.C. McDowell	An exact computational expression for the anisotropic dispersion energy for interactions involving linear molecules with examples for Ne-Ne-O <sub>2</sub> and Ne-O <sub>2</sub> -O <sub>2</sub>
B19. V. Murashov	Thermal Conductivity of Soft-sphere Solids
B20. S.V. Pai	A Comparative Study of Nonlocal Density Functional Theory and <i>ab initio</i> Methods: The Potential Energy Surface of s-Triazine Reactions
B21. J. Paldus	Unitary Group Based Open-shell Coupled-cluster Theory
B22. P. Piecuch	Calculation of Property Functions Using the Single- and Multi-reference Coupled-cluster Approaches
B23. R.A. Poirier	Programming using the Open Structured Interfaceable Programming Environment (OSIPE)
B24. C. Pouchan	Calculation of Dynamic Polarizabilities and van der Waals Coefficients of Atoms in Their Excited States
B25. N.M. Poulin	Exact Vibrational (J=0) Simulation of I-R Spectra Using the RRGm: Application to Formaldehyde
B26. M. Ramek	<i>Ab Initio</i> RHF Conformational Analysis of the Auxin Phytohormones Indol-3-yl-acetic Acid and 4-Chloro-indol-3-yl-acetic Acid
B27. S.H. Robertson	The Analysis and Fitting of Kinetic Rate Data
B28. I. Røeggen	The interatomic potential for the X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> state of Be <sub>2</sub>
B29. A.E. Roitberg	Anharmonic Wavefunctions in Proteins From Multiple Minima
B30. S.M. Rothstein	Correlated sampling of the valence energy: CuH dissociation energy
B31. P.-N. Roy	Direct calculation of selected eigenvalues in quantum molecular dynamics: Application to vibrations and reaction rates
B32. A. Salam	Competitive Atomic Two-Colour, Two-Photon Absorption in the Presence of a Static Electric Field

**WEDNESDAY, August 9**

**8:45 a.m. - 10:05 a.m. Session 9**

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**J.S. Wright**  
Carleton University

Chair

**E.R. Davidson**  
Indiana University

Unconventional Applications of Conventional *Ab Initio*  
Methods

**J. Simons**  
University of Utah

Chemically Incorrect Molecular Structures

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**10:05 a.m. - 10:25 a.m. Refreshment Break**

**10:25 a.m. - 12:25 p.m. Session 10**

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**R.J. Boyd**  
Dalhousie University

Chair

**R.J. Bartlett**  
University of Florida

Excited States Using the Equation-of-Motion Coupled  
Cluster Method

**S.D. Peyerimhoff**  
Universität Bonn

Multi-Reference CI Calculations of Molecular Spectra:  
From small to large molecules

**P. Botschwina**  
Universität Göttingen

Interaction Between Theory and Experiments in the  
Molecular Spectroscopy of Reactive Species

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**12:25 p.m. King's Landing Trip.**  
**Buses leave from outside the Wu Centre.**







POSTER SESSION C, Thursday, August 10, 5:15 - 6:45 p.m.

Presenter	Title
C1. S.D. Schwartz	The Interaction Representation and Non-Adiabatic Corrections to Adiabatic Evolution Operators
C2. I. Shamovsky	The Stereochemical Fit of Carcinogenic PAH Triol Carbocations to B-DNA
C3. A. Skancke	On the conversion of cyclopropane radical cation to propene cation
C4. P.N. Skancke	Structural Aspects of a Possible Transannular Interaction in Silatranes and Azasilatranes. An <i>Ab Initio</i> Study
C5. J. Stohner	Vibrational-rotational spectra of H <sub>2</sub> O in space-fixed coordinates using the Lanczos algorithm
C6. H. Subramanian	Investigation of the geometric and the electronic structure in novel organic polymers possessing very small intrinsic band gaps.
C7. I.M. Svishchev	First Computer Simulations of Crystallization in Molecular Systems: Water and Carbon Dioxide
C8. F.P. Temme	m-Branching Limit to Determinacy in (Cayleyan) SU(m) × ζ-10 ⊃ D-5 Spin Symmetry Embedding in Ro-Vibrational Statistics of (1,12)-Carborane Cage Isotopomers
C9. D.R. Truax	Algebraic methods in quantum mechanics
C10. D.F. Tuan	Studies of C <sub>28</sub> H <sub>4</sub> and Hf@C <sub>28</sub> H <sub>4</sub>
C11. C. Ursenbach	Effect of Solvent on Semiconductor Surface Electronic States: A First-Principles Study
C12. S. Wildman	A Re-investigation of Sixth-Row Relativistic Effective Potentials
C13. H.L. Williams	The Intermolecular Interaction Energy of the Helium Dimer Using a Monomer-Centered Plus Basis Set
C14. P.J. Winn	The effect of the methyl group in thymine on the stability of the thymine-adenine base pair compared with the uracil-adenine base pair
C15. K. Worsnop	Optimization of the Gradient-Corrected Exchange Term in DFT

**POSTER SESSION C, Thursday, August 10, 5:15 - 6:45 p.m.**

<b>Presenter</b>	<b>Title</b>
C16. <b>T.H. Wu</b>	Potential Energy Models for Closed Shell Atom or Ion - Closed Shell Atom or Molecule Interactions
C17. <b>D.M. York</b>	A Generalized Formulation of the Chemical Potential Equalization Principle from Density-Functional Theory
C18. <b>T. Ziegler</b>	Computational modelling at the University of Calgary. A density functional approach to transition metal chemistry.

**FRIDAY, August 11**

**9:30 a.m. - 11:00 a.m. Session 15**

---

**G.N. Patey**  
University of British Columbia

Chair

**S.A. Rice**  
University of Chicago

Properties of Langmuir Monolayers and Other  
Pseudo-Two-Dimensional Systems

**W. Meyer**  
Universität Kaiserslautern

Theoretical Investigation of the Autoionization Process  
in Molecular Collision Complexes

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**11:00 a.m. - 11:15 a.m. Refreshment Break**

**11:15 a.m. - 12:05 p.m. Session 16**

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**V.H. Smith, Jr.**  
Queen's University

Chair

**J.N. Murrell**  
University of Sussex

Potentials for Elemental Solids, Surfaces and Clusters:  
A Unified Scheme

---

**12:05 p.m. Symposium ends**



# **ABSTRACTS**

**Arranged in alphabetical  
order of presenter**

# Theoretical Aspects of the Calculation of Polarizabilities of Organic Polymers

**Jean-Marie Andre**

Facultés Universitaires Notre-Dame de la Paix  
Département de Chimie  
Rue de Bruxelles 61, B-5020 NAMUR Belgium

A quantum approach to the electronic structure of stereoregular polymers is presented. The emphasis is given on the relation between solid state physics and molecular orbital theory at the level of the topology of the orbitals. The computational methods developed for computing the energy band structure and the related properties of regular polymers are also detailed as well as the computational difficulties encountered.

The electronic structure of polyethylene is then analyzed and the shape of the valence electronic bands is interpreted in connection with XPS and with recent ARUPS data. The existence of s-conjugation in tetrahedrally bonded polymer chains (polyethylene and polysilane) is also discussed.

The question of the computation of static or frequency-dependent polarizabilities in extended systems is analyzed. Basic difficulties due to unbounded character of the position operator are reviewed. The differences between coupled and uncoupled Hartree-Fock schemes are pointed out. Methods for taking into account the influence of electron correlation and of nuclear vibrations are presented.

Applications are given on saturated chains (polyethylene and polysilanes) and conjugated chains (polyacetylenes and polydiacetylenes) in the framework of all-electron *ab initio* calculations.

## Molecular shape transitions between "open" and "closed" protein conformations

Gustavo A. Arteca

*Département de Chimie et Biochimie, Laurentian University - Université Laurentienne,  
Ramsey Lake Road, Sudbury (Ontario), Canada P3E 2C6.*

Induced-fit configurational transitions in proteins can range from small closures of a loop onto the substrate to large rearrangements which affect entire domains. The nature of these transitions is normally assessed by visual analysis or in terms of simple geometrical parameters. This approach is limited and rather nondiscriminating. In this communication, we improve on this situation by developing an analytical tool which recognizes the occurrence of certain folding features in a molecular chain. We use recent ideas from macromolecular shape analysis to characterize various "open $\rightleftharpoons$ closed" transitions in proteins. We study the interrelation between shape descriptors associated with two distinct properties: *molecular size and self-entanglements*. The method is applied to a series of proteins exhibiting pairs of structurally different conformations (adenylate kinase, hexokinase, citrate synthase, alcohol dehydrogenase, triosephosphate isomerase, thioredoxin, and aspartate aminotransferase). We classify these pairs according to an order parameter which takes into account changes in shape features. The results indicate whether the structural changes are local or global. The technique provides also an insight into folding features which may remain invariant during the configurational transitions.



# **Molecules in Intense Laser Fields: Dissociation, Ionization, Coulomb Explosions and Stabilization**

**A.D. Bandrauk, T. Zuo, S. Chelkowski**

Labo de Chimie Theorique

Université de Sherbrooke

Sherbrooke, QC J1K 2R1, Canada

The dressed state picture of photon molecule interaction predicts the creation of new laser induced molecular states by the mechanism of laser-induced avoided crossings (see chaps 2&3 in "Molecules in Laser Fields", ed. A.D. Bandrauk, M. Dekker Pub.1993). At intensities of  $10^{14}$  W/cm<sup>2</sup> ionization begins to occur according to tunnelling models. A full 3-D numerical calculation of H<sub>2</sub><sup>+</sup> in an intense laser field, including both electronic and nuclear dynamics will be presented to show the competition between photodissociation, ionization and coulomb explosion of the nuclei.

A new phenomenon, CREI (Charge Resonance Enhanced Ionization) was discovered from the numerical simulations, i.e., odd-charged ions have a propensity for large ionization rates at large internuclear distances, exceeding that of the atomic fragments. This will be shown to explain the experimentally observed nuclear kinetic energy distributions. Time dependent density functional methods (TDDF) are being examined in order to treat multielectron systems. Finally at superintense conditions,  $I > 10^{18}$  W/cm<sup>2</sup> "superdressed" molecules will be shown to exist in principle.

# Momentum Space: Coulomb Correlation in $2p^2\ 3P$ States of He-like Ions

K E Banyard and D R T Keeble

Department of Physics and Astronomy  
University of Leicester  
University Road  
Leicester  
LE1 7RH

## Abstract

Highly-correlated wavefunctions for He( $2p^2\ 3P$ )-like ions, when  $1 \leq Z \leq 4$ , are expressed as natural expansions and converted into momentum space by applying a Dirac-Fourier transform. Coulomb shifts for inter-particle momentum distributions are examined for each Z. The separate angular and radial components of electron correlation are also studied. Expectation values and statistical correlation coefficients are reported. Responses of these momentum properties to the level of correlation is investigated via selected truncations for each natural expansion.

The uniqueness of the negative-ion is clearly demonstrated, as is its poor representation at the Hartree-Fock level. Unlike position (real) space for the He( $2p^2\ 3P$ )-like ions, the angular and radial correlation effects in momentum space are found to work in opposition. Comparisons can be made with the ground and single-excited states.

# **Optical Properties of Cubic Semiconductors Predicted by Density Functional Theory (DFT)**

**Philippe Barbarat and Jean-Pierre Dognon**

Commissariat à l'Energie Atomique  
Centres d'Etudes du Ripault  
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Using a first-principles quantum mechanics method based on the local spin density (LSD) and the atomic sphere approximation (ASA), the electronic structures and the optical properties of 15 cubic semiconductors (Si, Ge, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb, ZnS, ZnTe, CdS, CdTe) are investigated. Bandstructures and band gaps are reported and compared with experimental data. It is shown that the method used here underestimates the fundamental band gaps by about 40%. The center of the gap, however, is predicted exactly. The dielectric functions (real and imaginary parts) are also presented for photon energies up to 14 eV. Calculated dielectric constants in the static limit,  $\epsilon(0)$ , are seen to be 25% larger than the experimental values. Finally, predicted curves for  $n$  and  $k$  as a function of the photon energy (near-IR, VIS, UV) are discussed and compared with experiment.

# Excited States Using the Equation-of-Motion Coupled Cluster Method

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Excited states of molecules offer a wealth of fascinating studies. Yet, unlike the development of *ab initio* methods for the ground state, where a wealth of accurate and widely applicable approaches are now available, and routinely applied, no such systematically improvable, dependable tools have been available for excited electronic states, particularly those of the same symmetry as lower states. The equation-of-motion coupled cluster method offers several tools that can efficiently address such problems. I will survey the variety of approaches that can be used, illustrating them by interesting and informative examples.

# COMPUTER SIMULATIONS OF QUANTUM WATER IN AQUEOUS SOLUTION

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*Ab initio* density functional theory is combined with classical Monte Carlo and molecular dynamics simulations to study quantum water in a classical aqueous solution. Different models of the quantum/classical boundaries are considered. Molecular properties such as the dipole moment, potential energy and molecular structure are also examined.

# Theoretical approach of self-association of Amphotericin in water using a continuum model and Molecular Dynamics

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Amphotericin B, a polyene macrolide, has a particular cyclic structure: one hydrophobic side containing seven conjugated double bonds and one hydrophilic side with some hydroxyl substituents. This amphiphilic molecule may form small or large aggregates in water.

Two levels of organization have been proposed as an interpretation of experimental spectroscopic changes: the first step of aggregation could be characterized by small units associated with the absorption maxima hypsochromic shift, while the intense CD couplet could result of further interactions between small units inside big aggregates.

As a preliminary step, we have studied the interaction energy of all possible dimers, in vacuo and in water. Interaction energy calculations have been performed in the framework of Molecular Mechanics methods (SIBFA and INTER) based upon *ab-initio* calculations. Two types of possible isoenergetic dimer configurations, Head-to-Head and Head-to-Tail, were obtained and their stability depends on the polar head conformations.

The solvent effect has been taken into account within a continuum model and an environment simulated by a box of water molecules with periodic boundary conditions. The results indicate a very good stability of the dimeric units and also reveal the importance of the water molecules and of the intermolecular interactions in the stabilization of the polar heads.

# Linear and Nonlinear Optical Properties: the Magnetic Story

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In recent years much attention has been given to the calculation of the effect of electric fields on optical properties. This nonlinear optics "bandwagon" has, to a degree, obscured the equally interesting phenomena which are induced by magnetic fields acting on optical properties, e.g., magnetic optical rotation and magnetic birefringence. These "counterpart" properties will be discussed and some recent calculations reported. It will be seen that the theoretician has as much to offer as the experimentalist; perhaps more, since the experiments are both costly and difficult.

# Interaction between theory and experiment in the molecular spectroscopy of reactive species

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Despite much progress over the past few decades, the spectroscopic investigation of reactive species like radicals or molecular ions remains difficult and is often restricted to special wavelength regions. Accurate quantum-chemical calculations may be of considerable help in assignment and interpretation problems and can provide valuable complementary information. Quite often, experiment and theory may be combined in a fruitful way. E.g., accurate equilibrium geometries may be determined by combination of experimental ground-state rotational constants ( $B_0$ ) with theoretical values for the differences  $B_e - B_0$ , where  $B_e$  is an equilibrium rotational constant. In this way, the equilibrium structure of  $C_5O$  could be established with an accuracy of better than  $0.001 \text{ \AA}$ . Other examples to be presented concern infrared spectra of the radicals  $H_2C_3H$ , of great interest to combustion processes, and  $CH_2CN$ , electronic spectra of  $C_6^-$  and  $C_8^-$  and the vibrational structure of photoelectron spectra of  $CF_3$ ,  $HO_2^-$ ,  $SiH_3^-$ ,  $CH_2N^-$ ,  $C_6^-$  and  $C_7^-$ .



**DENSITY FUNCTIONAL THEORY AND  
THE ELECTRON DENSITY OF MOLECULES**

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Electron densities calculated for a variety of systems by means of density functional theory (DFT) will be compared with the results given by several conventional *ab initio* methods, including Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2) and quadratic configuration interaction including single and double excitations (QCISD). The latter is used as a reference by which the accuracy of the DFT electron densities is measured. By specific examples from our recent research interests, it will be shown that accurate electron densities and related properties can be obtained by means of density functional theory. Among the properties discussed, particular attention will be paid to certain topological properties, the Laplacian of the electron density and DFT spin densities.

**The Harmonic Two-Colour Rotating Wave Approximation;  
Its Validity and an Application to the Effects of  
Permanent Dipoles and Laser Phase in Molecular Excitations**

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The harmonic two-colour excitation of a two-level molecule, where the frequencies of the two continuous wave lasers are multiples of a certain frequency, is studied in the rotating wave approximation (RWA) and by using exact methods. Included are the effects of a non-zero difference  $d$  between the permanent dipole moments of the two states involved in the transition. For two independent frequencies, the two-colour RWA yields analytical results only when one two-colour resonance dominates the transition, while for the harmonic analogue, analytic solutions, exhibiting the effects of both laser and molecular parameters, are available for problems involving competing two-colour resonances. Analytical solutions for both the time-dependent populations of the excited state, and for the associated resonance profiles, are derived, applied to a model two-level molecule, and tested by comparison with exact results obtained using Floquet techniques. The results are used to discuss the phase control of molecular excitation through the interplay of competing resonances involving the effects of a non-zero  $d$ ; the competition vanishes if  $d=0$ . Both fixed molecule-laser configurations, and the effects of orientational averaging, are considered.

## Electron-Spin Magnetic Moments of Simple Radicals Containing H, Li and Be.

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Molecular electric properties such as dipole moments, polarizabilities and hyperpolarizabilities have been studied extensively by *ab initio* methods. In comparison, little has been done on their magnetic analogues, except for the magnetizability (or induced magnetic moment) of closed-shell molecules. In open-shell paramagnetic radicals, however, there also exists a permanent magnetic moment due to the unpaired electrons, with a magnitude proportional to the total (spin plus orbital) angular momentum.

Permanent magnetic moments are typically expressed in terms of *g*-tensors, these parameters being proportional to the energetic splitting of different  $m_s$  levels in an external magnetic field. Deviations from the free electron *g*-value arise from the presence of orbital magnetism that adds to, or subtracts from, the electron-spin magnetism. Thus, the *g*-tensor provides information about both the magnetically-coupled excited states and the spin-density.

Computer programs have been written by one of us [1] to calculate electronic *g*-tensors from Hartree-Fock wavefunctions. The MRD-CI package has also been used to derive correlated data. The dependence of the  $g_{\parallel}$  and  $g_{\perp}$  components on geometry has been examined for the doublet states of small diatomic radicals. The species studied include  $\text{Li}_2^+$  and  $\text{Be}_2^-$ , as well as the isoelectronic series  $\text{LiH}^+/\text{BeH}^{++}$ ,  $\text{LiH}^-/\text{BeH}$  and  $\text{Li}_2^-/\text{LiBe}/\text{Be}_2^+$ .

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[1] G.H.L., PhD Thesis, in progress. See also poster by G.H.L and F.G.

# Ab Initio Calculation of the Dynamical Polarizability and Hyperpolarizabilities of Molecular Solutes

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The theory for the *ab-initio* calculation of the dynamical linear and nonlinear polarizabilities of molecular solutes within the framework of the solvent Polarizable Continuum Model (1), is here presented. The molecular solute is described at SCF level in a cavity of an infinite linear and homogeneous dielectric medium, characterized by an appropriate value of the dielectric constant. The molecular cavity is defined in terms of the solvent accessible surface(2). The various linear and nonlinear electrical properties are determined via time-dependent Hartree-Fock theory for molecular solutes (3). Numerical examples showing the dependence of the results on the basis set and on the characteristics of the solvent, are also presented and commented.

- (1) S. Miertus, E. Scrocco, and J. Tomasi, *Chem. Phys.*, 55, 117, (1981).
- (2) J.L. Pascual-Ahuir, E. Silla, J. Tomasi, and R. Bonaccorsi, *J. Comp. Chem.*, 8, 778(1987).
- (3) R. Cammi and J. Tomasi, *Int. J. Quantum Chem.*, submitted.

# **An integral equation approach to surface excess thermodynamics**

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In recent years, the reference hypernetted-chain (RHNC) integral equation theory has been applied to a variety of liquid systems. In particular, model aqueous electrolyte systems and the interactions of various solvents with a metallic wall have been successfully examined. The changes in free energy, energy, and entropy of solvation, due to particle insertion in liquid systems are investigated via a coupled set of integral equations which describe the perturbation on the liquid system due to particle insertion. The poster will outline the theory and present preliminary results for the insertion of inert hard-sphere particles in inert hard-sphere solvents, dipolar hard-sphere solvents, and water-like models.

# A time dependent multi-surface calculation of the orientation and alignment of photofragments

Hua Wei and Tucker Carrington Jr.

Département de chimie

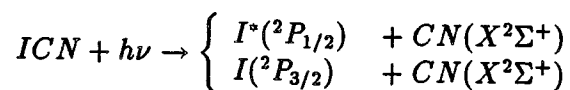
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## Abstract

Many groups have used time dependent quantum mechanical methods to calculate total and partial photodissociation cross sections for triatomic molecules which dissociate on a single excited electronic potential surface. The time dependent Schroedinger equation is usually solved for the  $J = 0$  Hamiltonian of the upper surface taking as the initial wave packet a  $J = 0$  (vibrational) solution of the ground electronic state Hamiltonian multiplied by the appropriate transition dipole function. This procedure ignores the role of rotation and the fact that if the state being excited is a  $J = 0$  state the state which is excited cannot also be a  $J = 0$  state. Several groups have used similar methods for molecules which dissociate on several (coupled) electronic surfaces. Time dependent methods have been used to solve the  $J \neq 0$  Schroedinger equation for an upper electronic state but they have not been used for both  $J \neq 0$  and multiple (coupled) excited electronic states. In this poster we present a time-dependent method to calculate partial cross sections, alignment and orientation (for which one requires a  $J \neq 0$  calculation) for dissociation on coupled electronic surfaces. The method is applied to the photodissociation of ICN:



# Quantum Monte Carlo Methods for Electronic Structure

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We report on progress in the application of Monte Carlo methods to calculate properties of atoms, molecules, clusters as well as extended systems. Recently diffusion Monte Carlo has been extended to treat atoms with pseudopotentials enabling much more ambitious calculations with heavier atoms. We will discuss the two methods, the pseudo-Hamiltonian and model locality. We describe results for various systems including transition metal atoms, carbon and silicon clusters.

The second development is in path integral methods for many electron systems. Path integrals have the advantage that no trial wavefunction is needed, only the Hamiltonian is used, though for fermions, a restriction is placed on the allowed paths. The path integral calculations are at a positive temperature. Recently we have simulated 32 hydrogen atoms (32 electrons and 32 protons) at several thousand degrees with the RPIMC method, seeing directly the transition from atomic to molecular hydrogen.

**Many-body multireference Moeller-Plesset and Epstein-Nesbet  
perturbation theory: fast evaluation of second  
order energy contributions**

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Multireference perturbation theory (MRPT) is examined in connection with the two partitions referred to as "Moeller-Plesset baricentric" and "Epstein-Nesbet": the former is based on a definition of the zero-order Hamiltonian in terms of a quasi one-electron operator, coinciding with the Fock operator in the one-determinant case, whereas the latter utilizes the total electronic Hamiltonian in the definition of the zero-order energies. The respective advantages of both partitions will be discussed. An efficient technique, based on the diagrammatic evaluation of the second order energy contributions, will be shown and a recent implementation, allowing for large variational determinant spaces, will be described. The possibilities of this form of MRPT will be shown with the help of a few example calculations involving the cis-trans thermal conversion of diazene and the metal-metal bond in the molecule of  $\text{Cr}_2$ .



# **STUDY OF SPIN HAMILTONIAN FOR REGULAR POLYGONS**

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It has been shown that Bethe equations for Spin Hamiltonian can be transformed into a system of nonlinear algebraic equations. The secular polynomial, which gives ALL energies for the given symmetry can be extracted from the above mentioned system by finite number of steps. Bethe equations were formulated in 1931. Until today there were used only for the LOWEST state of given symmetry, where iterative technique works well.

The relevance of Spin Hamiltonian to Quantum Chemistry will be discussed.

# Information Entropies and Relative Entropies of the Two Particle Density Function

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June 20, 1995

## Abstract

We introduce a method to quantify the uncertainty of an electron pair distribution. To accomplish this, we apply the Shannon Entropy function, introduced within the context of information theory, to the two particle probability function.

In addition, we study a relative entropy function which quantifies the uncertainty of a second particle when the probability function of the first particle is known.

# High Intensity Photodissociation of $\text{HCl}^+$ Electronic and Permanent Dipole Effects

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Numerical solutions of coupled time-dependent Schrödinger equation for multiphoton dissociation of  $\text{HCl}^+$  molecular ion are used to demonstrate the importance of both diagonal (nuclear) and non-diagonal (electronic) dipole moments. For three-channel simulations (X  $\Pi$ , 2  $\Pi$  and 3  $\Pi$  states) at four wavelengths (1.064  $\mu\text{m}$ , 5.15  $\mu\text{m}$ , 10.3  $\mu\text{m}$  and 20.6  $\mu\text{m}$ ), we demonstrate that the dissociation threshold (minimum laser intensity for 100% total dissociation) *and* branching ratios between different  $\Pi$  states of  $\text{HCl}^+$  show high dependence on the wavelength of radiation. Also, selectively neglecting a dipolar contribution in the potential matrix shows a large dependence upon the nature of the neglected dipole. Elucidation of the photodissociation dynamics was done by studying the proton kinetic energy distribution of the dissociated fragments and correlation with classical chaotic models was examined.

# Proton Transfer in Mesoscopic, Molecular Clusters

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Proton transfer reaction within a proton-ion complex embedded in a liquid cluster composed of dipolar molecules is studied. The clusters under investigation are large with dimensions in the nanometer regime and contain tens of solvent molecules. Such mesoscopic clusters possess properties that differ from those of either bulk liquids or small clusters containing a few solvent molecules. The free energy along the reaction coordinate for a quantum proton in a classical cluster solvent is computed using path integral techniques. The mechanism of proton transfer as reflected in the solvent structure for given values of the reaction coordinate is examined. The solvent structure that exists in the cluster as a result of the surface forces and finite size gives rise to a coupling between the solvent and the proton-ion complex that differs from that in the bulk. This leads to a mechanism of the transfer process that involves gross solvent density shifts and orientational changes distinct from those seen in bulk polar liquids. Furthermore, the adiabatic and non-adiabatic dynamics of proton transfer is studied. We are examining if a first-order phenomenological rate law holds and the dependence of the rate on the size of the cluster.

Gram determinantal inequalities with elements  $\langle r^m \rangle$  obtained from Hylleraas wave functions for the  $^2S$  states of the three-electron systems

Li, Be<sup>+</sup>, B<sup>2+</sup>, C<sup>3+</sup>, N<sup>4+</sup>, O<sup>5+</sup>, F<sup>6+</sup>, and Ne<sup>7+</sup>.

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The present work considers  $2 \times 2$ ,  $3 \times 3$ ,  $4 \times 4$ ,  $5 \times 5$ , and  $6 \times 6$  Gram determinants whose elements are expectation values of powers of  $r$ , where  $r$  is the distance from the nucleus of a three-electron system. The  $\langle r^m \rangle$  values are those of King and Dressel [1], who calculated them using Hylleraas wave functions with a large ( $> 100$ ) number of variational parameters. In the present work it is assumed, for purposes of illustration, that  $\langle r^{-1} \rangle$  is unknown. It is found that lower bounds to  $\langle r^{-1} \rangle$ , calculated from the  $2 \times 2$ ,  $3 \times 3$ ,  $4 \times 4$ ,  $5 \times 5$ , and  $6 \times 6$  Gram inequalities converge to the quantum mechanical value obtained in King and Dressel [1].

[1] F.W. King and P. R. Dressel, J. Chem. Phys. 90, 6449 (1989).

# Optimized Orbital Solutions to Multireference Problems within the Coupled Cluster Ansatz

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Recently we have shown that the coupled cluster ansatz can be used in place of the Rayleigh-Ritz principle in the GVB-PP method to generate optimized orbitals. This is somewhat surprising since the coupled cluster method is not really a variational method. In this paper we use the coupled cluster singles, doubles (CCSD) method to numerically examine whether one can optimize orbitals within this coupled cluster ansatz for a variety of MCSCF methods, as for example GVB-RCI and CASSCF. Results are compared to literature benchmark full CI calculations. Other possible approaches such as Brueckner orbitals and iterative natural orbitals are also examined.

## ***Ab Initio* Studies of Small 1,3-Dipolar Systems**

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Small 1,3-dipolar systems are potential building blocks for cycloaddition reactions. For example, the cycloaddition chemistry of RCNS, the nitrile sulphides has been explored experimentally by one of us (MS). *Ab initio* calculations at the HF and MP2 level have been carried out with the aim of assessing the suitability of the nitrile sulphides and other systems. Geometries, energies and orbitals of such species as HCPS, SNS<sup>+</sup> and HCNS will be presented, in continuation of the work presented last year at the Atlantic CIC Chemistry Conference.

## Unconventional applications of conventional ab initio methods

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The application of conventional bound state CI methods to the calculation of the location and intensity of the satellite region of photoelectron spectra and electron momentum spectra will be discussed and illustrated by examples. This requires calculating Dyson orbitals for a large number of Rydberg excited states of radical cations.

The binding of CO to a NaCl surface is computed using an embedded cluster with effective core potential for the salt surface and the Lee-Yang-Parr correlation potential evaluated with the valence electron density to calculate the dispersion energy.



Configuration interaction (CI) calculations of spectroscopic properties of  $P_2$   $X^1\Sigma_g^+$  ground state and  $a^3\Sigma_u^+$ ,  $b^3\Pi_g$ ,  $A^1\Pi_g$  low lying excited states

G. de Brouckère and David Feller

Extended basis set, multireference configuration interaction (CI) calculations, using the MELDF suite of programs, have been performed on the ground state and a few excited states of  $P_2$ . To the best of our knowledge, no excited state CI calculations on  $P_2$  have been reported in the theoretical literature. A broad ensemble of spectroscopic properties such as  $R_e$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ,  $\alpha_e$ ,  $T_e$ ; vibrational transition energies for the  $a^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ ,  $b^3\Pi_g \rightarrow a^3\Sigma_u^+$ ,  $A^1\Pi_g \rightarrow X^1\Sigma_g^+$  bands and related Franck-Condon factors, pure rotational excitations for the ground and excited states, selected first order one-electron properties, have been calculated and compared with the available experimental data in order to judge of the qualities of the respective wavefunctions. Certain ground state property results are also compared with those issued from other CI treatments.

## Group 14 Carbene Analogs: The First Stable Plumbylene?

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Methylene,  $\text{CH}_2$ , has been the subject of numerous controversial studies. Both theoreticians and experimentalists have debated since the early 1930s the infamous "singlet-triplet splitting". The heavy group 14 analogs have been characterized theoretically. However, all of these are highly reactive and as a result are difficult to study using experimental methods.

Recently, several groups have synthesized carbene, silylene, and germylene structures that are isolable. These species are characterized by bulky, organic side groups bonded to the central divalent atom and are of interest owing to their unique chemistry.

Carbon dioxide has been shown to have a metastable, cyclic structure lying about 140 kcal/mol above the ground state, linear species. This ring molecule has a divalent carbon singly bound to two oxygen atoms and represents a carbene-type species. Preliminary *ab initio* studies by our group have determined that the cyclic structures for the heavier analogs become increasingly stable down the group. In the case of lead, the ring species is found to be more stable than the linear molecule.

We present here the result of preliminary *ab initio* studies of group 14 dioxides. The trends in the behaviour of these species and some thermodynamic properties of lead dioxide will be explored.

## Numerical simulation of HCN in an intense laser field

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We wish to study the behavior of a triatomic molecule in an intense laser field ( $\approx 10^{13}$  W/cm<sup>2</sup>), using HCN as a model molecule. By varying the frequency, duration, and shape of a laser pulse, it is possible to control selectively the excitation and dissociation of molecular bonds, therefore allowing control of chemical reactions. First, we look at the isomerization reaction  $\text{HCN} \rightleftharpoons \text{HNC}$ . This reaction is forced by the use of two laser beams, of different wavelength, perpendicular to each other, for alignment in a plane. The isomerization probability for different laser frequency combinations is compared. Second, we investigate the possibility of aligning the molecule along the laser field. This is studied for the dissociation of linear HCN. In this case, a singularity appears in the hamiltonian at an angle of  $\theta = 0$ . We show how one can get rid of this singularity using a scheme proposed by Dateo and Metiu.

## ***Ab initio* computations and additive models for the polarizabilities of aromatic five-membered rings: azoles**

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*Ab initio*, electron correlated calculations of dipole moments and static dipole polarizabilities are reported for ten heteroaromatic five-membered rings: pyrrole, pyrazole, imidazole, all four triazoles, both tetrazole tautomers, and the hypothetical pentazole. They are expected to be accurate to within 5%. Structural isomerism affects the dipole moments strongly but the dipole polarizabilities are rather insensitive to it. Uncoupled Hartree-Fock calculations indicate that only about half the polarizability comes from the  $\pi$ -electrons. Simple empirical formulas based upon atom and bond additive models correlate the calculated polarizabilities quite well. Aromaticity scales based on polarizabilities are discussed.

# Statistical properties of chaotic energy eigenvalues & eigenfunctions

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The energy eigenvalues and eigenfunctions of classically chaotic systems have been described as random variables characterized by certain statistical properties. For example, the eigenvalues are described in terms of the Gaussian orthogonal ensemble (GOE) of random matrices. Chaotic eigenfunctions are viewed as Gaussian random variables completely characterized by their spatial correlation function. These statistical properties are tested for T-shaped  $\text{Ar}_3$ , a chaotic two-degree-of-freedom system. We explore the prospect of exploiting such statistical properties in constructing a statistical quantum dynamics aimed at reproducing dynamical properties in terms of randomly generated eigenvalues and eigenfunctions. Numerical means of generating these random quantities are investigated.

# Ab Initio and Model Studies of Weakly Bound Trimers and Other Clusters

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Recent spectroscopic studies of weakly bound trimers are revealing a range of interesting behavior, much of it directly connected with the potential energy surface features of the trimers. Trimers are the simplest clusters that may display many-body intermolecular interactions, and so, an understanding of the potential surfaces of trimers is a crucial step in understanding large aggregations where many-body effects have significant manifestations. And, being able to compare with detailed spectroscopic information on trimers means there are meaningful tests for such understanding.

We have carried out a number of *ab initio* calculations on isolated monomers, weakly bound dimers, and weakly bound trimers that provide insight into what interaction elements are crucial for understanding the potential surfaces and properties of trimers along with other weakly bound clusters. A model interaction scheme has been applied to over one hundred trimers and several larger species in order to understand the energetics of the growth of mixed clusters. The model has been successful in predicting and then interpreting microwave data for a few trimers. Results of *ab initio* studies, model calculations, limited dynamical analysis of certain clusters, and comparison with spectroscopic data will be presented.

## **Oxazoles: *Ab initio* structures, polarizabilities, and additive models**

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*Ab initio*, electron correlated calculations of the equilibrium geometries, dipole moments and static dipole polarizabilities are reported for ten heteroaromatic five-membered rings: furan, oxazole, isoxazole, all four oxadiazoles, both oxatriazoles, and the hypothetical oxatetrazole. Our geometries and dipole moments agree well with available experimental microwave determinations. The polarizabilities are expected to be accurate to within 5%. Structural isomerism affects the dipole moments strongly but the dipole polarizabilities are rather insensitive to it. Uncoupled Hartree-Fock calculations indicate that as much as half the polarizability comes from the  $\sigma$ -electrons. Simple empirical formulas based upon atom and bond additive models correlate the calculated polarizabilities of twenty five-membered heteroaromatic rings (ten azoles and ten oxazoles) quite well. Aromaticity scales based on polarizabilities are discussed.

# ***Ab initio* calculation of ESR parameters of distorted electronic states**

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The magnetic hyperfine coupling constants (hfcc's) represent an interesting bridge between experimental and theoretical studies. In the present work we discuss *ab initio* calculations of the hfcc's of small molecules which are characterised by the interaction of two or more electronic states. An important example is the C<sub>2</sub>H molecule where the groundstate X<sup>2</sup>Σ is distorted by the first excited state X<sup>2</sup>Π. The hfcc's of such systems can only be understood if the nuclear motion is taken into account, e.g. if the hfcc's are calculated for single vibronic states. The calculations show that the effects can already be seen in the lowest vibronic state. As examples we discuss triatomic (e.g. C<sub>2</sub>H, BH<sub>2</sub>) and tetraatomic (e.g. H<sub>2</sub>B<sub>2</sub><sup>+</sup>) molecules.



# **Long-range asymptotic behavior of ground-state wave functions, one-matrices, and pair densities**

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The asymptotic behavior of the  $N$ -electron ground-state wave function is analyzed, as one electron wanders far from the system. Implications for the one-matrix and pair density are worked out. It is shown that the asymptotic behavior currently discussed in the literature, in which the remaining  $(N-1)$  electrons relax to their ground state, requires explication when the  $(N-1)$ -electron ground state is degenerate. Unexpected, infinitely long-ranged correlations are reported. Moreover, a standard limit for the one-matrix must be corrected. Our numerical and analytic studies of accurate wave functions for small spherical atoms support the asymptotic behavior derived here. Furthermore, we address the question of how large the separation of one electron must be before the limiting behavior is realized. We also discuss the implications of our conclusions for density functional theory. In particular, we critically examine the long-range and short-range behavior of several common approximations for the exchange-correlation hole density.

# **Solvent Effects in TDHF Calculations**

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A method for the inclusion of solvent effects in the calculation of NLO properties of materials is presented. The method is based on the TDHF formulation as developed by Karna and Dupuis and the SCRF theory as implemented by Zerner. The method allows for the inclusion of solvent effects in the time-dependent model currently used for the calculation of frequency dependent polarizabilities and first and second hyperpolarizabilities. Results will be shown for several systems.

## Oscillator Strengths for VUV Transitions of C<sub>2</sub>

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Only one experimental work on the high-lying states of C<sub>2</sub> (from 8.88 to 9.25 eV) has been reported [1]. The  $f^3\Sigma_g^-$  and  $g^3\Delta_g$  states were classified as  $\pi_u \rightarrow 3s$  excitations with respect to  $a^3\Pi_u(3\sigma_g 1\pi_u^3)$ , and the same for  $F^1\Pi_u$  relative to  $X^1\Sigma_g^+(1\pi_u^4)$ .  $E^1\Sigma_g^+$  was also assumed to be a Rydberg state. Theoretically,  $F^1\Pi_u$  has been assigned to  $\pi_u \rightarrow 3p_\sigma$  rather than  $\pi_u \rightarrow 3s$  [2], whereas  $E^1\Sigma_g^+$  was found to be a doubly-excited state  $2\sigma_u^2 \rightarrow 3\sigma_g^2$  [3]. The character of the  $f$  and  $g$  triplets remains an open question.

To estimate interstellar C<sub>2</sub> densities the oscillator strengths ( $f_{v,v'}$ ) are required. These have been measured for all valence but not for Rydberg transitions. In Ref. 2,  $f_{00}^{FX}$  was predicted to be 0.02. However, Lambert [4] recently analyzed the  $F \leftarrow X$  band using Hubble Space Telescope data, obtaining  $f_{00}^{FX}/f_{00}^{DX} = 1.83 \pm 0.18$ . Taking for the Mulliken system  $f_{00}^{DX} = 0.0545$ , thus  $f_{00}^{FX} = 0.10 \pm 0.01$ . There is certainly a need for a state of the art calculation of  $f_{00}^{FX}$ .

In this *ab initio* MRD-CI work, several Rydberg states of C<sub>2</sub> were studied in detail.  $F^1\Pi_u$  is confirmed to be  $\pi_u \rightarrow 3s$  [1], whereas  $f^3\Sigma_g^-$  shows a mixed character  $\sigma_u \rightarrow \pi_g/\pi_u \rightarrow 3s$ . Near equilibrium,  $g^3\Delta_g$  is not a Rydberg but rather a valence state  $\sigma_u \rightarrow \pi_g$ . The calculated  $f_{00}$  values are 0.095 for  $F^1\Pi_u$  (confirming the Hubble data), 0.027 for  $f^3\Sigma_g^-$  and 0.051 for  $g^3\Delta_g$ .

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[1] Herzberg et al., *Can.J.Phys.* **47** (1969) 2735. [2] Pouilly et al., *J.Phys.B.*

**16** (1983) 437. [3] Bruna and Wright, *J.Phys.Chem.* **96** (1992) 1630.

[4] Lambert et al., *Astrophys. J.* **438** (1995) 740.

# **Improved Size-Scaling in Simulations of Reduced-Model Proteins Using a Hierarchical Potential Evaluation**

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A simple model will be described which consists of alpha- and beta-carbon atoms with phi and psi degrees of freedom with a potential function having the general form of a multi-index lookup table based on the interatomic distances for each pair of residues. The calculation is dominated by the evaluation of the potential, but the total time required can be reduced dramatically by screening the trial moves, most of which are ultimately rejected in a close-packed structure. This is accomplished by using a systematic series of coarse-grained approximations to the potential with a reduced set of variables and using a reduced table with weighted-average entries. This results in a progressive filtering of trial structures thus eliminating most unnecessary evaluations. The number of levels can be increased with the size of the molecule leading to an improvement over N-squared scaling. Results will be presented for selected test cases.

# Rydberg-valence mixing in formaldehyde. A multireference CI study.

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The  $^1(\pi,\pi^*)$  state in formaldehyde lies at 9.65 eV vertically, lower than previously assumed. Along the C–O coordinate,  $^1(\pi,\pi^*)$  crosses the entire state manifold of  $\text{H}_2\text{CO}$ , including the ground state. In fact, near 3.0 bohr,  $\pi,\pi^*$  is the main contributor to the ground state. The  $^1(\sigma,\pi^*)$  potential, which runs close to  $^1(\pi,\pi^*)$  in the Franck-Condon region, also crosses all Rydberg states. The long-standing question about the apparent absence of the  $^1(\sigma,\pi^*)$  and  $^1(\pi,\pi^*)$  valence bands in the UV spectrum of formaldehyde can now be better understood. Mixing of the valence with the Rydberg states prevents  $^1(\sigma,\pi^*)$  and  $^1(\pi,\pi^*)$  from developing regular potentials. The observed Rydberg states show the effects of this mixing in their absorption intensities, quantum defects, and band profiles. We show that:

- 1) Both the anomalous intensity and band profile of the  $^1(n\rightarrow 3s)$  transition are due to interactions with  $\sigma,\pi^*$  and  $\pi,\pi^*$ . In fact, the  $S_2$  surface is very complex, with minima for  $n,3s$ ,  $\sigma,\pi^*$  and  $\pi,\pi^*$ .
- 2) The so-called "n,3d" band, first observed in 1935 by experimentalists, has little to do with the  $n \rightarrow 3d$  transition. Rather, it belongs to an excitation into an upper state having  $\pi,\pi^*/n,3p_y$  character.

Thus, the  $^1(\pi\rightarrow\pi^*)$  transition has been unknowingly observed all along, but it was not recognized until this study was carried out.

## High-lying Vibrational Levels for HO<sub>2</sub> and HO<sub>2</sub><sup>-</sup>

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We calculate vibrational levels and wavefunctions for HO<sub>2</sub> and HO<sub>2</sub><sup>-</sup>. 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 high-lying vibrational levels with significant splitting. 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.

# An Investigation of the Dependence of Shannon Information Entropies on Molecular Geometry and Chemical Reaction Paths

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June 20, 1995

## Abstract

The Shannon Information Entropies of several polyatomic molecules with varying geometrical parameters in both position and momentum space are calculated from UHF/6-31G\* wavefunctions. Also, Shannon information entropies were used to study a series of gas-phase  $S_N2$  reactions following the IRC paths. The results show that there are definite patterns between the information entropies, molecular geometrical changes, chemical changes and energies.

# Potential energy surface for interactions between N<sub>2</sub> and He: *ab initio* calculations, analytic fits, and second virial coefficients

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An *ab initio* potential energy surface (PES) for the interaction of rigid N<sub>2</sub> with He is calculated by supermolecular fourth-order Møller-Plesset perturbation theory. The 61 *ab initio* points on the PES are fitted to an algebraic form with an average absolute error of less than 0.4% and a maximum error less than 1.2%. The characteristics of the fitted PES are compared with those of previous surfaces. Unlike the older surfaces, our PES has the anisotropy thought to be required for a proper description of experimental data. Pressure second virial coefficients that measure deviations from ideal gas behaviour are calculated from our surface and compared with experimental values.



# Acid Ionization In Solution

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In this talk, we will describe our recent theoretical efforts to unravel the microscopic level mechanism of the ionization of acids in polar solvents. Illustrations will be drawn from our studies of HCl and HF in liquid water. Attention will be focused on the quantum character of, and the critical role of the solvent in, these elementary reactions. Possibilities for infrared-induced mode selective proton transfer will be considered.

This work was supported by grants from NIH, NSF and The Pittsburgh Supercomputer Center.

# Symmetry-adapted perturbation approach to intermolecular potential energy surfaces

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It has been assumed for a long time that the interaction energies of closed-shell atoms and molecules result from a delicate balance of electrostatic, induction, dispersion and exchange interactions. Very recently it has become possible to quantitatively verify this hypothesis in *ab initio* calculations. The symmetry-adapted perturbation approach, developed originally as a theory of exchange effects in simple one- and two-electron systems, was combined with powerful coupled cluster and many-body perturbation theory techniques to take account of intramonomer electronic correlation contributions to the basic interaction energy components. To include the short-range, penetration part of the electrostatic, induction and dispersion energies the complete non-expanded form of the interaction operator is used at all stages of the calculations. The accuracy of the proposed perturbation approach will be illustrated by the results of calculations of full, analytically expressed, interaction potentials for complexes involving rare gas atoms and small molecules of varying degree of polarity. The quality of these potentials will be assessed by comparing them with empirically derived potentials and by confronting the resulting infrared spectra, transport coefficients and scattering cross-sections with experiment.

## Molecular Recognition in Organic and Biochemical Systems

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Monte Carlo statistical mechanics and molecular dynamics simulations are being used to study chemistry in solution including the origin of solvent effects on reaction rates and the structures and binding affinities for host/guest complexes. Striking variations in solute-solvent hydrogen bonding have been found to contribute to pronounced rate changes for pericyclic reactions in protic solvents. Recent results for the Mislow-Evans rearrangement of allylic sulfoxides will be presented; the deceleration in alcohols is found to involve both diminished hydrogen bonding and longer-range electrostatic interactions. The conformational energetics for the initial and transition states have also been characterized.

In the host/guest area, a program, MCPRO, has been written to perform Metropolis - Monte Carlo simulations for protein-ligand complexes in solution. Using the AMBER/OPLS force field, free energy perturbation calculations are performed to evaluate relative free energies of binding for modifications of protein residues or the ligand. The utility of the Monte Carlo approach is demonstrated through calculations of relative binding affinities for complexes of ligands with trypsin, FKBP, and sulfate binding protein.

# Reaction Dynamics in Mesoscopic Molecular Clusters

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A description of solvent-influenced reactions in large molecular clusters with linear dimensions in the mesoscopic range will be given. Such clusters have properties that differ from those of few-molecule clusters and bulk liquids. The distinctive features of reaction dynamics in such molecular environments will be discussed. Results for two types of quantum reactions involving protons will be described.

Proton transfer in a proton-ion complex in liquid-state clusters composed of polar molecules show a number of features that differ from those for the same reaction carried out in bulk solvent.[1] The free energy barrier is higher and the reaction rate exhibits effects due to the strong fluctuations and shape changes that influence the reaction. The calculations of the activation free energy were carried out using Feynman's path integral method and the reaction rate calculations were performed for adiabatic proton transfer. The modification of the cluster geometry in the course of the proton transfer gives rise to the distinctive cluster reaction dynamics.

Acid ionization in mesoscopic clusters composed of aprotic, polar molecules will also be described.[2] In bulk there are strong solvent effects on the dissociation process; for example, dissociation constants can differ by orders of magnitude in solvents with comparable dipole moments. The free energy as a function of the ion pair separation was computed for liquid-state clusters composed of aprotic, polar solvent molecules and studied as a function of the cluster size. The tendency to form solvent-separated ion pairs in the cluster and other finite-size effects on the ionization process will be discussed.

[1] S. Consta and R. Kapral, *J. Chem. Phys.* **101**, 10908 (1994).

[2] D. Laria, R. Kapral and G. Ciccotti, *Acid Ionization in Aprotic, Polar Solvents: Cluster and Bulk Environments*, to be published.

# Spin-Unrestricted Time-Dependent Hartree-Fock Theory of Frequency-Dependent Linear and Nonlinear Optical Properties

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A spin-unrestricted time-dependent Hartree-Fock theory of linear and nonlinear optical (NLO) properties has been developed. Analytical expressions have been derived to calculate the elements of the frequency-dependent polarizability tensor,  $\alpha(-\omega_\sigma; \omega_a)$ , first-hyperpolarizability tensor,  $\beta(-\omega_\sigma; \omega_a, \omega_b)$ , and the second-hyperpolarizability tensor,  $\gamma(-\omega_\sigma; \omega_a, \omega_b, \omega_c)$ , from the self-consistent solution of the unrestricted time-dependent coupled perturbed Hartree-Fock equations. For the higher-order polarizability tensors,  $\beta(-\omega_\sigma; \omega_a, \omega_b)$ , and  $\gamma(-\omega_\sigma; \omega_a, \omega_b, \omega_c)$ , expressions have also been derived using the  $(2n+1)$  rule of the perturbation theory which obviates a large number of iterative calculations. The present theory represents the first analytical method for the self-consistent calculation of frequency-dependent linear and NLO properties of open-shell structure. A novel feature of this theory is that it permits to separate the contributions to the linear and NLO properties by the  $\sigma$  and  $\beta$ -spin electrons. This is particularly useful in studying the NLO properties of the defect centers in silica glass and one-dimensional conjugated chains, which have open-shell ground state and/or low-lying valence state structures with large spin polarization. Results of the implementation of the present theory and its application to selected atoms, molecules, free radicals and ions within the *ab initio* theory will be presented.

# Constant Temperature Molecular Dynamics Simulations by Means of a Stochastic Collision Model

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A new stochastic method for molecular dynamics (MD) simulations at constant temperature is presented. The technique is based on central impulsive collisions of system particles with imaginary heat bath particles of finite mass. The Verlet algorithm is reformulated to include the resulting velocity dependent forces, yielding a high-order system of stochastic difference equations representing a non-Markovian stochastic process. The difference equation is analytically solved for a system of free particles [1] and of harmonic oscillators [2] subject to the heat bath. The solutions are analysed in terms of stationarity, phase space distribution functions, and time correlation functions. It is demonstrated that the new stochastic technique generates the functional form of the canonical phase space density, wherein the resulting stationary temperature in the case of the harmonic oscillator depends on both the coupling parameter (mass ratio) between system and heat bath, and the resolution of the vibration period, i.e. the number of time steps per period. An efficient compensation method is described and numerical results are discussed.

1. S. M. Kast, K. Nicklas, H.-J. Baer, and J. Brickmann, *J. Chem. Phys.* 100, 566 (1994).
2. S. M. Kast and J. Brickmann, *J. Chem. Phys.*, submitted for publication.

# Geometric Phase Effects in H + O<sub>2</sub> Scattering

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The effects of the geometric phase in accurate 3D quantum scattering calculations for H+O<sub>2</sub> (J=0) are reported. Using Pack's hyperspherical coordinate system, the nuclear surface wavefunctions are obtained numerically by using both an FBR (Finite Basis Representation) and a DVR (Discrete Variable Representation). The surface Schrodinger equation contains the relevant vector potential necessary for including geometric phase effects due to the C<sub>2v</sub> conical intersection. The resulting real surface functions are not single-valued but change sign around the conical intersection. A given function exhibits both even and odd permutation symmetry which implies that in measuring and assigning the rovibrational spectra of HO<sub>2</sub>, spectroscopists will need to account for wavefunctions of both types of symmetry. The calculated energies and lifetimes of the resonances are significantly altered. The effects on equilibrium constants, rate coefficients and state-to-state transition probabilities are also reported.

# Electron Affinity of SF<sub>6</sub>

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Electron affinity of octahedral SF<sub>6</sub> was calculated using various density functionals. In the *sp* space, flexibly contracted well-balanced Gaussian basis sets were used: (19s, 13p) → [15.13] for sulphur and (16s, 10p) → [12.7] for fluorine. The basis sets were gradually augmented by adding up to three *d*-type and two *f*-type functions for sulfur and three *d*-type and one *f*-type function for fluorine. The exponents of the polarization functions were optimized in molecular SCF DFT calculations, separately for SF<sub>6</sub> and SF<sub>6</sub><sup>-</sup>, at their respective equilibrium geometries. Equilibrium structures were determined for the two species using three combinations of nonlocal functionals. The results for the largest basis set used in the optimization, [15.13.3.1/12.7.3.1], are given below:

Method	r <sub>e</sub> /Å		E <sub>A</sub> /eV
	SF <sub>6</sub>	SF <sub>6</sub> <sup>-</sup>	
HF	1.529	—	—
B/LYP	1.609	1.766	2.46
B/P86	1.597	1.750	2.20
B+HF/LYP	1.578	1.730	1.78

Harmonic vibrational analysis, performed for the octahedral SF<sub>6</sub><sup>-</sup> ion using the B/LYP functional, shows that the stationary point is a minimum and not a transition state.



# Adiabatic and strictly diabatic potential curves of $\text{He}_2^{2+}$

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Adiabatic and strictly diabatic potential curves were calculated for the two lowest electronic states of  $\text{He}_2^{2+}$ . The diabatization procedure leads to a repulsive diabatic curve dissociating to  $\text{He}^+ + \text{He}^+$  and a bound curve dissociating to  $\text{He}^{2+} + \text{He}$ , crossing at the internuclear distance of 1.55 bohr. The diabatic bound state has dissociation energy of 3.15 eV. The existence of a metastable potential well in the (adiabatic)  $X^1\Sigma_g^+$  state of  $\text{He}_2^{2+}$ , usually rationalized using the Coulomb repulsion + covalent bond model, can be also explained in terms of strong interactions between diabatic states.

# On the isomerization of HMO/MOH, M = Be, Mg and Ca

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In the past, the focus of theoretical studies of alkaline earth hydroxides has been on their similarity to alkali hydroxides, as both are ionic compounds. In this theoretical study, it is shown that there exists a family of linear isomers, HMO, which suggests comparison with Group III elements. The spectroscopic parameters of the new isomers in their low-lying states will be reported, and paths for isomerization in various electronic states will be discussed. The calculations are done at the CASSCF and CISD levels with extensive basis sets.

**Main Group Effective Nuclear Charges  
for Spin-orbit Calculations**

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The effective nuclear charges ( $Z_{\text{eff}}$ ), which are empirical parameters in the approximate spin-orbit hamiltonian, are determined for main group elements in the second to fifth periods by using experimental results of the fine structure splittings (FSS) in the  $\Pi$  states of diatomic hydrides. All calculations use full valence multiconfiguration self-consistent-field (MCSCF) wavefunctions with the effective core potential (ECP) basis set proposed by Stevens *et al.*, augmented by one set of polarization functions. These effective nuclear charges are tested by predicting FSS in many diatomic molecules, and are then applied to evaluate the relativistic potential energy curves of  $\text{H}_2\text{Y}$  ( $\text{Y} = \text{O}, \text{S}, \text{Se}, \text{and Te}$ ),  $\text{AH}_2$  ( $\text{A} = \text{C}, \text{Si}, \text{Ge}, \text{and Sn}$ ), and  $\text{XHX}$  and  $\text{NaX}$  ( $\text{X} = \text{Br}$  and  $\text{I}$ ).

# Oscillating Hydrogen-Water Reactions on a Platinum Field Emitter

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The spatial and temporal behavior of surface reaction-diffusion fronts has been examined during oscillating hydrogen/water reactions on a platinum field emitter. Different reaction pathways leading to the formation of such ions as  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$  have been identified. Periodic outbursts of ions correlate with the passage of fast reaction fronts across the emitter surface. All these features can be modeled in a kinetic lattice gas. We will show the experimental data and matching theoretical results.

## COLLISIONAL ENERGY TRANSFER MODELS FOR H<sub>2</sub> DISSOCIATION IN THE PRESENCE OF ARGON

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The gas phase unimolecular decomposition of a diatomic or a polyatomic molecule may be visualized in terms of elementary processes involving collisional excitation of the reactants followed by intramolecular energy redistribution. The thermal unimolecular rate coefficient is often obtained by solving the appropriate master equation governing the change in relative populations of internal molecular states. Analytic solutions to the master equation which can be obtained by approximating collisional energy transfer probabilities to simple functional forms are useful in interpreting experimental data on collisional energy transfer and the dependence of rate coefficients on the energy transfer efficiency.

In this paper we investigate the usefulness of models on energy transfer probabilities, the possible simplification of the master equation by suitable choices of variables and the dependence if any of these variables on the initial states for the dissociation of Hydrogen in the presence of Argon. We use the extensive Monte Carlo trajectory results obtained by Haug, Blais and Truhlar [J. Chem. Phys., **86**, 2697 (1987)] for our study.

# **Intermolecular Interaction Effects on Molecular NLO Properties**

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Most calculations of NLO properties are done on isolated (gas phase) molecules and most experiments are done on condensed phase systems. As a beginning for understanding the changes in going from isolated to interacting systems, we have performed calculations on small interacting systems. Results will be presented for interactions of two, three, and four acetylene molecules as a function of orientation and distance. An analysis will be given on the ability to use simple two- or three-body interactions for larger collections of molecules.

## Mechanism of C<sub>2</sub>H<sub>4</sub> Dehydrogenation to C<sub>2</sub>H<sub>2</sub> on the Ni(111) Surface

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The thermal-induced decomposition of ethylene, C<sub>2</sub>H<sub>4</sub>, to acetylene, C<sub>2</sub>H<sub>2</sub>, on the Ni(111) surface has been treated theoretically within both a semiempirical, modified extended-Hückel framework, the atom-superposition and electron-delocalization molecular-orbital (ASED-MO) method, and a non-equilibrium, statistical mechanical, master-equation formalism. As a preliminary step, adsorbate geometries and binding energies were optimized for one and two molecules of each hydrocarbon species adsorbed in various sites on rigid cluster models of the Ni substrate: on the largest, four-layered, eighty-atom cluster, C<sub>2</sub>H<sub>4</sub> favours the di-σ bonding configuration, while C<sub>2</sub>H<sub>2</sub> prefers the di-σ/π, or triangular binding site. A fragmentation pathway, entailing the concerted tunnelling of interior intermolecular H's from a transient bimolecular complex comprised of two rotated C<sub>2</sub>H<sub>4</sub>'s, is proposed which rationalizes the observed second-order kinetics [L. Hammer and K. Müller, *Prog. Surf. Sci.* **35** (1991) 103-111].

# Applying the divide-and-conquer method to quantum calculations of large systems

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A divide-and-conquer approach based on density matrix formulation is proposed. The system is divided into subsystems in the density matrix space and the system density matrix and total energy can be obtained from subsystems contributions. This approach reduces the scaling of computational effort in quantum chemistry calculations from  $O(N^3)/O(N^4)$  to  $O(N)$ . Some results of large systems using density functional theory and semi-empirical calculations show this method can be expected to handle quantum calculations of large molecules beyond the reach of conventional approaches.



# Determining Accurate Potential Energy Surfaces for van der Waals Complexes

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The current status of the problem of determining accurate and easy-to-use multidimensional potential energy surfaces for van der Waals molecules is reviewed, and outstanding difficulties are delineated. In spite of remarkable recent successes, fully *ab initio* methods are not yet quantitatively reliable for most systems of interest. At the same time, accurate empirical potential surfaces have so far been obtained for only a very limited range of systems. In recent years, improved computational methods have made the determination of such surfaces from the detailed simulation and analysis of discrete spectra and other experimental data feasible for increasingly complex systems. However, the problems of developing realistic and reliable models for such surfaces and of devising compact and computationally efficient representations for them remains a challenge. One possible approach is presented here, and its successes (and drawbacks) illustrated by recent applications to (rare gas)-H<sub>2</sub> and (rare gas)-CO systems.

# Complete to Second-Order Calculations of Molecular g-Tensors

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Molecular g-tensors parametrize the electronic Zeeman splitting in EPR spectroscopy. Due to the complexity of their theoretical evaluation, there has been very little work done on ab initio g-tensor computation compared to other magnetic properties. Our work expands g-tensors as a Rayleigh-Schrödinger perturbation expansion *complete to second-order* in Breit-Pauli terms. This represents the most ambitious treatment to date.

Computing the expansion has meant considerable formulation and code development. The resulting library of FORTRAN programs, called GSTEPS, includes routines for commercial package interfaces, one- and two-electron density generation and expectation value evaluation. A notable addition to the suite is code for computing two-electron spin-Zeeman gauge correction integrals.

We have treated several test cases, including the  $\text{NO}_2$ ,  $\text{H}_2\text{O}^+$  and  $\text{CO}^+$  radicals. The theoretical results correctly reproduce trends in gas-phase experimental data.

## **MRSD-CI Studies of the BN Hyperfine Tensor: The lowest $^3\Pi$ State.**

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The electronic structure, spectroscopic parameters and hyperfine tensors for the  $^3\Pi$  state of the BN diatomic are investigated using *ab initio* multi-reference single and double excitation configuration interaction. The magnitudes of the hyperfine tensor components are investigated as a function of the number reference configurations and of the number of double excitations included in the CI wave function. The relationship between the hyperfine tensor components and the molecular structure and bonding are also discussed.

(CN<sub>2</sub>S<sub>2</sub>)<sub>2</sub>, (CNSNS)<sub>2</sub>, and (CNSSS<sup>+</sup>)<sub>2</sub>; a comparative study

Robert C. Mawhinney and John D. Goddard

The electronic nature (*i.e.* disjoint diradicals) of these molecules leads to the potential for exciting magnetic properties like ambient temperature conductivity. With this in mind, the nature of the ground state must be determined along with the singlet-triplet energy splitting and spin couplings. We have studied the title compounds using *ab initio* techniques and basis sets ranging from CEP-31G\* to 6-311G\*. The three lowest electronic states are of particular interest and will be examined here: the triplet, corresponding open shell singlet, and the closed shell singlet. The optimized geometries will be reported and compared with experimental findings. Also included will be both adiabatic and vertical transition energies, CC bond rotation, dipole moments and the infrared frequencies and corresponding intensities. Finally, the dimerization and binding energy for these molecules will be presented.

# Theoretical calculations on the conformation of cyclopentadienyl coordination in Ru nitrosyl and thionitrosyl complexes

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X-ray structural characterization of a series of Cp\*Ru(NE)LL' complexes (Cp\* = pentamethyl cyclopentadiene; L, L' = ligand; E = O, S) reveals systematic trends in the coordination conformation of the Cp\* ligand. The thionitrosyl complex (L, L' = Cl; E = S) exhibits a slipped [ $\eta$ -3, $\eta$ -2] Cp\* ring, with the central C(skeletal)-methyl bond of the more tightly bound  $\eta$ -3 portion eclipsing the Ru-N-S vector. With NO derivatives, ring "slippage" is less significant but ring orientation is variable depending upon the L and L' ligand set. Although the complexes exhibit specific ring orientations in the solid, low temperature NMR measurements show that the barriers to changes in ring conformation are very low in solution. For catalytic purposes, it would be desirable to be able to control the Cp\* geometry with respect to rotation by a suitable choice of ligands.

*Ab initio* SCF and DFT calculations have been performed on the simpler Cp complexes (Cp = cyclopentadiene) using the NWCHEM suite of computer codes, developed at Pacific Northwest Laboratories, to investigate how the choice of ligand affects the Cp orientation and the barrier to rotation of the Cp. Results of these calculations will be presented.

**An exact computational expression for the anisotropic dispersion energy for interactions involving linear molecules with examples for Ne-Ne-O<sub>2</sub> and Ne-O<sub>2</sub>-O<sub>2</sub>**

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An expression for the exact anisotropic triple-dipole dispersion energy (DDD) for interactions involving linear (sigma state) diatomic molecules has been developed. This expression uses pseudo-dipole oscillator strengths (DOSs) for the diatomic molecules as input. The anisotropy of the DDD energy for three-body molecular systems is investigated relative to that from a frequently used average energy expression for DDD using Ne-Ne-O<sub>2</sub> and Ne-O<sub>2</sub>-O<sub>2</sub> as models.

# Theoretical Investigation of the Autoionization Process in Molecular Collision Complexes

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*Ab initio* treatments of electronic structures and detailed studies of the collisional dynamics are applied to various collisional complexes involving  $\text{He}^*(2s^3S, ^1S)$ . The autoionizing resonance state is defined through Feshbach projection based on orbital occupancy, and the corresponding potential is determined from MR-CI calculations with an accuracy of about 10 meV. The energy dependent coupling with the continuum is derived from a compact ( $L^2$ ) "Penning MO" without any phase information being lost. This MO is projected onto the states of the continuum electron of proper energy, which are calculated within the static-exchange approximation for up to 30 coupled angular momentum channels. This provides the  $\ell$ -dependent complex coupling elements on which the scattering calculation is based. Weighting with experimental collision energy distributions gives angle-dependent as well as the angle-integrated electron and ion spectra for Penning and associative ionization processes. The close agreement of our theoretical spectra with the most recent high-resolution experimental Penning electron spectra demonstrates the adequacy of the local complex potential approach, as well as the importance of electron angular momentum transfer, so far neglected in theoretical treatments.

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# MOLECULAR SHAPE ANALYSIS FROM DIATOMICS TO PROTEINS: *AB INITIO* QUALITY LOCAL AND GLOBAL ELECTRON DENSITY REPRESENTATIONS BY THE MEDLA METHODS.

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Molecular shape[1], as defined by the shape of the fuzzy, three-dimensional electron density, is a fundamental molecular property, determining most other chemical properties, molecular interactions, and reactions. Both *global* and *local* shape properties are important. The shape variations of various *functional groups*, as influenced by the rest of the molecule, have dominant effects on chemical reactivity. The Density Domain approach to chemical bonding [2] provides a quantum-chemically sound description of functional groups [3], and a consistent framework for a detailed shape characterization [1,4].

The focus of this report is on shape analysis based on fuzzy density fragmentation methods, avoiding artificial fragment boundaries and providing *local molecular fragments fully analogous to complete molecules*. These methods allow the direct application of rigorous shape analysis methods, such as the Shape Group Methods [5], developed for complete molecules and suggested for molecular fragments [6]. Several schemes of local shape analysis will be reviewed, including the AJM truncation scheme of Arteca, Jammal, and Mezey [7], the PDW *pseudo-density scheme* of Walker (1992, see also ref. [8]), the PGM *additive fuzzy density fragment scheme* of Mezey (1992, see also refs. [9-11]), and various generalizations [12-14]. The PDW pseudo-density scheme has important diagnostic advantages in detecting local shape variations [8], whereas the additive PGM scheme is the basis of the Molecular Electron Density Lego Assembler (MEDLA) method for generating *ab initio* quality electron densities for macromolecules [9-11].

The MEDLA method, with virtually no size limitation on molecules, extends the scope of *ab initio* quality electron density calculations. For the first time it is possible to analyze macromolecular electron densities at a resolution far exceeding the resolution of current X-ray diffraction and other experimental and macromolecular computational techniques. Both global and local shape, similarity and complementarity, local shape conditions for intermolecular interactions, and approximate energy relations for macromolecular conformational problems can be studied from a new perspective.

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# Quantum Theory of Chemical Reaction Rates

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Theoretical approaches are described for determining the rate of a chemical reaction both *directly*, i.e., without having to solve the complete state-to-state reactive scattering problem, yet also *correctly*, i.e., without inherent approximation. This is possible for the canonical rate constant  $k(T)$ , where the reactants are characterized by a given temperature, and also for the microcanonical rate  $k(E)$ , where the reactants are characterized by a given total energy. Recent developments of the methodology and its applications will be presented.

# **Berry Phases: Theory and Applications**

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I will give a brief review of the theory and history of Berry phases before turning to a survey of recent developments and applications. There are several techniques available for the study of Berry phases using, for example, the tools of functional analysis, Lie groups or differential geometry. The use of each will be illustrated by a class of problem where it has proved particularly fruitful. Finally the impact of Berry phases on the adiabatic and Born-Oppenheimer approximations will be analysed in some detail.

## **Thermal conductivity of soft-sphere solids**

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Non-equilibrium NVT Molecular Dynamics (MD) simulation studies of soft-sphere solids will be described. Anisotropy of the response of the cubic fcc system on the applied homogeneous heat field was observed. The temperature dependence of the thermal conductivity coefficient was calculated for a set of softness parameter values. The dynamic structure factor was used to calculate phonon dispersion curves, which in turn allowed for a calculation of Debye temperatures. The effect of the inclusion of an attractive term into the potential model will be discussed.

# Potentials for Elemental Solids, Surfaces and Clusters: A Unified Scheme

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Potentials have been obtained as a sum of 2-body and 3-body terms for simple metals, transition metals and group 4 elements which reproduce the cohesive and vacancy energy of the solid, its lattice spacing, phonon frequencies and elastic constants, and also the average surface energy of the solid. These potentials give a good description of the relative energies of different solid phases and of the surface layer contractions, and should therefore be appropriate for medium and large clusters. The potentials are also being used to examine surface melting. The following elements have been treated or are under examination: Al, Cu, Ag, Au, C, Si, Ge, Ca, Sr, Fe, Mo, and the alkali metals.

# **Response Calculations of Dipole Oscillator Strength Sum Rules and Related Quantities**

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Initially a new and more efficient implementation of the Second Order Polarization Propagator Approximation (SOPPA) will be reviewed. Numerical examples will demonstrate that inclusion of dynamical correlation in an MP2-like approximation is a cost-efficient way of computing excitation spectra and oscillator strength sum rules for many molecules.

The applicability of polarization propagator or response methods to the description of energy deposition and frequency dependence of electric properties will be illustrated. More specifically, we will discuss anisotropy in Bethe Stopping for oriented targets, calculations of Generalized Oscillator Strengths, and the use of scaling and/or addition as means to predict the frequency dependence of dipole polarizabilities.

# A Comparative Study of Nonlocal Density Functional Theory and *ab initio* Methods: The Potential Energy Surface of s-Triazine Reactions.

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Stable points and transition states on the potential energy surface for s-triazine ( $C_3N_3H_3$ ) have been calculated using high-level *ab initio* and nonlocal density functional (NDFT) methods. The *ab initio* and NDFT results, including structures, relative energies, harmonic vibrational frequencies and corresponding eigenvectors, are compared. Additionally basis set size dependence is examined. *Ab initio* geometry optimizations were performed with Moller Plesset second order perturbation theory (MP2) followed by single point energy corrections at the quadratic configuration interaction single, double and triple excitations [QCISD(T)] level. The nonlocal density functionals used were the exchange functional of Becke and the correlation energy functional of Perdew (BP86); Becke's exchange and the correlation energy functional of Lee, Yang and Parr (BLYP); Becke's three parameter hybrid exchange functional with the LYP correlation energy functional (B3LYP) and the Becke exchange with Perdew and Wang's 1991 gradient corrected correlation functional (BPW91). Basis sets used were 6-31G\*\*, 6-311++G\*\* and cc-pVTZ. Decomposition mechanisms investigated are a stepwise addition and a concerted triple dissociation. The concerted triple dissociation is clearly the low energy path at all levels of theory and with all basis sets. Reaction endothermicity predicted by B3LYP and BPW91 are in closer agreement with experiment than the QCISD(T) and MP2 predictions using the largest basis set. MP2 and B3LYP frequencies agree most closely with experimental values for the stable points. Geometries predicted by all methods are in excellent agreement with experiment.

# Unitary Group Based Open-Shell Coupled-Cluster Theory

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The basic principles and merits of a fully spin-adapted, state-selective coupled-cluster (CC) method, based on the formalism of the unitary group approach (UGA), and employing a single but multiconfigurational spin-free reference state, will be discussed together with its implementation for systems involving the high-spin doublet and triplet states, as well as low-spin open-shell singlet states. The performance of this UGA based CC method at the first order interacting space or full single and double excitation space level will be illustrated by examining both the energetic other properties, including the ionization potentials, equilibrium geometries, harmonic vibrational frequencies, electronic excitation energies, and potential energy curves. The systems examined involve first row hydrides and diatomics, methylene, OH, CN and other radicals, as well as ozone and H<sub>4</sub> and H<sub>8</sub> models. A comparison with other methods of both CC and variational character will also be given.

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# **Multi-Reference CI Calculations of Molecular Spectra: From small to large molecules.**

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Recent progress in three areas will be discussed and exemplified by a number of molecules:

- fine structure details in small molecules due to vibronic coupling and spin-orbit effects
- spectra of large systems, including circular dichroism, by a combination of semiempirical computations with ab initio MRD-CI
- influence of solvent molecules, represented by effective potentials, on spectral properties.



# Calculation of Property Functions using the Single- and Multi-Reference Coupled-Cluster Approaches

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Several multipole moment and (hyper)polarizability surfaces have been obtained by employing the newly formulated and implemented orthogonally spin-adapted single-reference coupled-cluster (CC) linear response method enabling to calculate first- and higher-order static properties of closed-shell systems. Further, the recently developed orthogonally spin-adapted state-universal multi-reference CC theory using a two-dimensional model space has been applied to calculate multipole moment and polarizability surfaces of a few typical quasidegenerate systems using the finite-field method. Finally, the linear response CC property curves for the HF and nitrogen molecules in their ground electronic states in conjunction with various experimental and theoretical potential energy curves have been used to evaluate the rovibrational averages and transition quadrupole moments over a wide range of values of the vibrational and rotational quantum numbers. Various aspects as well as the reliability of the property calculations based on CC methods will be addressed.

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# **Programming using the Open Structured Interfaceable Programming Environment (OSIPE\*)**

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OSIPE a new "Object-Oriented" approach, designed for large complex scientific codes, is presented. OSIPE consists of Fortran tools designed to support well-structured, modular, route-independent and easily interfaceable programming. Some of the OSIPE tools are described along with the resulting subroutine structures. Advantages to the user, the programmer and to high performance computing are presented.

\*F. Colonna, L.-H. Jolly, R.A. Poirier, J.G. Angyan and G. Jansen, *Comput. Phys. Commun.*, 81, 293-317 (1994).

CALCULATION OF DYNAMIC POLARIZABILITIES  
AND VAN DER WAALS COEFFICIENTS  
OF ATOMS IN THEIR EXCITED STATES

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The time-dependent gauge-invariant method (TDGI) we have developed [1] enables the dynamic polarizabilities of systems in their ground state, as well as in their excited states, to be obtained, which requires a thorough description of wave functions.

Then the variations of dynamic polarizabilities as functions of imaginary frequencies  $\alpha(i\omega)$  leads to the determination of  $C_6$  van der Waals coefficients between atoms (or molecules). They may be obtained with the Casimir-Polder relationship for atoms in the ground state, or in the excited states whose energies are lower than those of all the states contributing to their perturbation by an electric field. In other cases, the calculation of the initial spectral lines ( $\Delta E_i, \mu_i$ ) for each atom can be used to propose a method for fitting these parameters with an iterative procedure using the corresponding calculated values of  $\alpha(i\omega)$ . We deduce:

$$C_6 = 6 \sum_{i,j} \frac{\mu_i^2 \mu_j^2}{\Delta E_i + \Delta E_j} \text{ for } \Delta E_i + \Delta E_j \neq 0.$$

This limited sum remains valid even if one or several transition energies is negative.

As an illustration, we present the results obtained with excited states: He ( $2^1P, 2^3P$ ) [2], Li ( $^4P$ ) [3] and Li ( $^2P$ ) [4].

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EXACT VIBRATIONAL (J=0) SIMULATION OF I-R SPECTRA USING THE RRGM :  
APPLICATION TO FORMALDEHYDE.

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We use the Recursive Residue Generation Method (RRGM) with an exact kinetic energy operator, to calculate excitation energies and vibrational band intensities for formaldehyde, treating all 6 degrees of freedom. The variational basis is a product of 1-D Potential Optimised functions in the Discrete Variable Representation (PO-DVR) for each coordinate. Our biggest basis set consists of  $N = 800\ 000$  functions, localised about grid points to have diagonal matrices of multiplicative operators. The reduced tridiagonal Lanczos representation of the Hamiltonian is generated iteratively (without constructing matrix elements explicitly) by sequential transformations that scale as  $N \log N$ . With the RRGM, we obtain simultaneously energy levels and the corresponding transition moment integrals from this reduced basis. One is able to compute intensities directly (without constructing eigenvectors in the PO-DVR), because one dipole moment component and the initial state are used to generate tridiagonal representations. Exploitation of symmetry in each recursion permitted us to refine current understanding of numerical instabilities related to the Lanczos algorithm. We present simulated (J=0) infra-red spectra of CH<sub>2</sub>O and CD<sub>2</sub>O, showing the importance of using Eckart body-fixed axes to define dipole moment components (particularly for anti-symmetric states).

# Relativistic Quantum Chemistry: Recent Results

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The recent original work in the author's group deals with:

1) The 'aurophilic' or 'metallophilic' [1c] Au(I) ... Au(I) attraction, identified as a correlation effect, strongly influenced by relativity [1]. Loosely, this is a dispersion effect between closed-shell metal cations, having a strength, comparable with the strongest hydrogen bonds. Similar mechanisms are shown to be responsible for X...X interactions between chalcogen and pnictogen atoms in dimers, like (H<sub>2</sub>Bi--BiH<sub>2</sub>)<sub>2</sub> [2] and to be important in the Tl--Pt bond of Tl<sub>2</sub>Pt(CN)<sub>4</sub> [3].

2) The coordination chemistry of uranyl, UO<sub>2</sub><sup>2+</sup> [4]. The large variation of the uranyl bond length as function of equatorial ligands is ascribed to a frozen soft mode of the innermost, UO<sub>6</sub><sup>6-</sup> system.

3) New isoelectronic species have been studied: the matrix species NUN (known since 1976) and the new uranium atom insertion product in carbon monoxide, CUO. The predicted NUO<sup>+</sup> [4] has now been synthesized in the gas phase in Berlin. The noble-metal -- noble-gas chemical bonds in the so far experimentally unknown species AuXe<sup>+</sup> and XeAuXe<sup>+</sup> are predicted to have a D<sub>e</sub> of nearly 1 eV per bond [5].

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# **Intervention and Interrogation of Molecular Dynamics**

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The active manipulation of molecular-scale dynamical events has been a long-standing challenge in the chemical community. Recent years have seen the establishment of the key principles of coherent manipulation of such events. The relevant concepts will be reviewed, leading to the presentation of a unified formulation for the control (intervention) and inversion (interrogation) of molecular dynamical events on ground and excited state potential surfaces. Particular emphasis will be given to the method of inverse control, where an objective quantum mechanical trajectory is posed and the goal is to find the controlling laser field to track the trajectory. Related research on interrogation of evolving molecular dynamical events for inversion aims to determine potential surface and optical coupling coefficient information. Similar logic to the case of intervention may be applied in this circumstance, except now, the track is measured in the laboratory and inverted for the sought-after Hamiltonian information.

Ab Initio RHF Conformational Analysis of the Auxin Phytohormones Indol-3-yl-acetic Acid and 4-Chloro-indol-3-yl-acetic Acid

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Indol-3-ylacetic acid (IAA) is an auxin plant growth hormone, which regulates physiological functions such as cell divisions and enlargement, developmental differentiation, and the syntheses of specific proteins. A large number of its conjugates and derivatives with various degrees of activity were analysed until today. 4-Chloro-IAA in particular is a naturally occurring derivative with higher biological activity than IAA.

As a first step into an exploration of the structure/activity relationship of auxins, detailed conformational analyses were performed for IAA and 4-chloro-IAA at the ab initio RHF level with the 6-311G\*\* basis set. The results of these analyses indicate considerable differences between the two potential energy surfaces, regarding not only the structures and the relative stability of the various conformers, but also the number of symmetry unique local minima (4 (IAA) vs. 3, including the mirror symmetrical global minima).

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## ABSTRACT

### ELECTRON TRANSFER IN MOLECULES AND MOLECULAR WIRES

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Transfer of electronic charge from one region of a molecule to another has striking similarities to scanning tunneling microscopy (STM) through molecular adlayers: in each case, electrons are transferred from an initial state through a bridging structure to a continuum of final states. This analogy permits increased understanding of the STM result through intramolecular electronic transfer measurement and computations.

We focus on three related aspects of the charge transfer problem. First, formal model construction for the STM experiment is discussed; the self energies due to the metallic electrodes result in rate type (rather than a slow oscillatory) behavior, and permit understanding of superexchange type mechanisms in STM. Second, the role of disorder in this system is emphasized, and conditions under which electron transfer in disordered systems is in fact more efficient than in ordered systems are discussed. Third, the role of electron repulsions, and possible single electron transfer (coulomb blockade) phenomena is included.



# **Oxidative Damage to Peptides: Breaking the Ground**

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Free radicals and radical cations in proteins and enzymes are believed to be associated with a variety of processes, from basic repair mechanisms to Alzheimer's and aging. The radicals may be generated by ionizing radiation, oxidants including oxygen itself, or reaction with other radicals. This talk will outline a direct research strategy for the characterization of the structures, electronic states, thermodynamics, and reactivity of the radicals associated with peptides and the constituent amino acids by high level theoretical investigations. The "ground" is well and truly broken in this field. Some of the results will be presented and discussed.

# **Properties of Langmuir Monolayers and Other Pseudo-Two-Dimensional Systems**

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Recent theoretical studies of phase transitions in Langmuir monolayers and recent tests of theoretical predictions of the asymptotic ( $t \rightarrow \infty$  and  $q \rightarrow 0$ ) properties of the transport coefficients in a two dimensional fluid will be discussed with emphasis on the information provided by such studies concerning the dimensionality appropriate for the description of the system.

# The Analysis and Fitting of Kinetic Rate Data

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Data analysis and representation is a central aspect of any experimental investigation of gas phase reaction kinetics. The advent of cheap computing power has made more realistic techniques accessible. We present two case studies for the reactions,



The basis of the analysis is the Inverse Laplace Transform/Master Equation method (ILT/ME). Recent work on Diffusion Equation approximations to Master Equations has greatly enhanced the speed of fall-off calculations. The application of Fast Fourier Transform techniques to the ILT method allow rapid calculation of microcanonical rate coefficients. The combination of these advances allows efficient calculation of canonical rate coefficient data for any temperature and pressure. This makes possible the calculation of the  $\chi^2$  function which allows estimates of adjustable parameters to be obtained, together with errors. Results will be presented for both of the above systems.

# The interatomic potential for the $X^1\Sigma_g^+$ state of $\text{Be}_2$

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An (extended geminal model) has been applied to determine the interatomic potential for the  $X^1\Sigma_g^+$  state of  $\text{Be}_2$ . By adopting a [11s,9p,6d,4f,2g] contracted Gaussian type basis, the following potential minimum parameters are obtained:  $R_e = 4.67$  au (4.63 au) and  $D_e = 3.70$  mH ( $3.82 \pm 0.05$  mH), experimental values in parentheses. A calculation with a nuclei-centered [9s,7p,4d,2f,1g] GTO basis plus two sets of bond type functions, each set comprising diffuse (2s,2p,2d,2f,1g) GTO's, yielded -3.79 mH as the value of the potential at  $R = 4.63$  au. On the basis of an error analysis the best theoretical estimate of the binding energy is determined to be  $3.83 \pm 0.08$  mH.

## **Anharmonic Wavefunctions in Proteins From Multiple Minima**

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In a previous publication [1] we presented a way to calculate anharmonic vibrational wavefunctions, and some properties derived from it, for a very large system, consisting of the protein BPTI surrounded by a water shell. In the present poster we will investigate the effect of the multiple minima problem. Each one of these minima was obtained by quenching a classical molecular dynamics run. A ground state (and first excited state) wavefunctions was obtained for each structure.

The density of states, as well as the predicted low frequency infrared spectrum was obtained for each minima. Average properties for the system as a whole were calculated. The difference between individual minimum and the averaged properties will be shown and analyzed. In the case of the IR spectra, one expects an inhomogeneous broadening to be present, due to the presence of these multiple minima.

[1] A.Roitberg, R.Benny Gerber, R.Elber and M.Ratner Science 268:1319 (1995)

# **Correlated Sampling of the Valence Energy: CuH Dissociation Energy**

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We perform all-electron variational Monte Carlo calculations with split-tau sampling on CuH and Cu, implementing a correlated sampling scheme. Both systems share the core electrons which move independently of the valence ones, followed by valence electron moves taken conditional upon the core electron locations. Sampling the valence energies in this manner, we obtain an estimate of the dissociation energy with an accuracy on par with published SDCI calculations in the literature, despite our relatively crude wavefunctions. By use of correlated sampling there was a factor of seven gain in efficiency relative to sampling CuH independent of Cu.

Direct calculation of selected eigenvalues in quantum molecular dynamics: Application to vibrations and reaction rates

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We present a study of methods designed to calculate eigenvalues in a range of interest. Applications to a one-dimensional Morse oscillator and to HCN/HNC (in 3-d) were our first test cases (*J. Chem. Phys.* (1995), in press). Levels in the chosen range are computed using the filter-diagonalisation method proposed by Neuhauser (*J. Chem. Phys.* (93), 2611 (1990)), a spectral transform approach, and our own guided Lanczos. In the latter method, convergence of levels of interest is favoured by choosing a starting vector exhibiting a substantial overlap only with eigenvectors in the chosen range. This biased starting vector is calculated from a solution of the time-dependent Schroedinger equation. Of the three methods, the guided Lanczos is the most efficient for both test cases. None of the methods designed to favour a chosen energy range are, however, (for the two problems considered) as efficient as a straightforward Lanczos method. We are presently calculating reaction rates using the cumulative reaction probability method of Miller (*Acc. Chem. Res.*, (26) , p.174 (1993)) and various schemes to favour converge of eigenvalues in a given range.

# Structure, Properties, and Reactivity of Clusters and Surfaces from Density Functional Theory

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Recent advances in non-local density functional theory will be reviewed from the perspective of chemisorption and catalysis problems. A chemist's (gaussian function) approach has been taken and is embodied in the molecular/cluster code deMon and its periodic counterpart Bloch-deMon. Selected applications from cluster science (e.g. Fe, Co, Ni, Cu clusters, Nb<sub>3</sub>O, etc.) and from surface science (e.g. NO and CO adsorption on nickel and rhodium, and on Pd-Cu alloys, adsorption of diazine on Pd, etc. ) will illustrate the possibilities and present limitations of the methodology.



# **Competitive Atomic Two-Colour, Two-Photon Absorption in the Presence of a Static Electric Field**

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The laser control of atomic and molecular species has recently been the subject of much experimental and theoretical investigation. Control manifests itself through the interference between probability amplitudes for two or more coherent optical excitation routes from an initial state to a desired final state. This can be achieved in processes such as multi-photon absorption, for example, by varying laser field parameters such as field strength, pulse duration, frequency, polarisation direction and phase.

Specifically, two-colour, two-photon absorption in (a three - level model of) atomic Sodium is studied using both semi-classical time-dependent perturbation theory and the exact Riemann Product Integral technique. In addition to the transition dipole moments already present within Sodium, diagonal dipole moments are induced by the application of a static electric field. Two-photon absorption occurs via two competing pathways; one involving absorption through a permanent dipole mechanism and the other in which the transition proceeds via the participation of a virtual state. The transfer of population from initial to final state is controlled by varying laser field parameters. The effect of the nature of the atom is also discussed.

# Theoretical Studies of Protein Folding

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Empirical potential functions and associated computer algorithms are used to calculate the stable structures of polypeptides and proteins. The main difficulty that has to be overcome arises from the existence of many minima in the multi-dimensional energy surface, i.e., the so-called multiple-minima problem. Several procedures have been developed, and solve the multiple-minima problem for small open-chain and cyclic peptides and for models of fibrous proteins such as collagen. Most of the procedures developed so far are not efficiently extendible to larger polypeptides, specifically globular proteins. The recently-developed diffusion equation method, however, does seem to scale efficiently with polypeptide size, and this procedure is currently under investigation to determine whether it can solve the multiple-minima problem for a globular protein containing of the order of 50 amino acid residues. The procedure works well with clusters of individual atoms, and attempts are now being made to adapt it to a chain molecule whose atoms are connected by bonds that also satisfy bond-angle restrictions.

# The Interaction Representation and Non-Adiabatic Corrections to Adiabatic Evolution Operators

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This paper presents a new approach to operator resummation corrections to adiabatic evolution operators. It is shown that an infinite order correction produces an operator that is equivalent to a propagator in the interaction representation. For a problem in which the adiabatic approximation assumes that certain degrees of freedom are held fixed, the interaction representation correction is just the interaction propagator of the coupling for these degrees of freedom. This formulation allows simple physical interpretation and simple mathematical evaluation of the full correction. No power series or cumulant methods are needed. Application to double well splitting when coupled to a bath oscillator shows the approach to be highly accurate.

# The Stereochemical Fit of Carcinogenic PAH Triol Carbocations to B-DNA

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The equilibrium structures of intercalated physical complexes of "bay region" triol carbocations (TC) of different polycyclic aromatic hydrocarbons (PAH) with the dGG/dCC fragment of B-DNA are obtained by the AMBER and FLEX force field calculations. The most important structural feature of the complexes with highly potent ultimate carcinogens is their "preorganization" for the subsequent covalent bonding. The complexes are stabilized by two hydrogen bonds between quasi-axial OH groups of TC and N3 atoms of the adjacent guanine residues of the dinucleotide, with only minor conformational changes taking place upon complexation. The stabilities of the diaxial conformers of different TC are proven by *ab initio* calculations. A new explanation for the stereochemical and shape selectivity in PAH carcinogenesis is presented.

Publications: L.v.Szentpaly, I.L.Shamovsky, *Molec. Pharmacol.* 47, 624 (1995); *Intern. J. Quant. Chem.; Quant. Biol. Symp.*, 1995, accepted.

# **Stabilizing and Tracking Stationary States and Periodic Orbits in Chaotic Systems**

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Major strides have been made over the past few years in controlling chaos in low dimensional systems. Unstable periodic orbits have been stabilized in magnetoelastic strips, electronic circuits, laser systems and chemical reactions, and recent reports of stabilizing periodic rhythms in heart tissue and inducing periodic and chaotic behavior in hippocampal brain tissue have stimulated widespread interest. It is clear that new developments in controlling dynamical systems offer opportunities for potentially important practical applications.

Stabilizing and tracking states with more than one unstable direction remains an important challenge. Such states are common in spatially extended systems, and techniques beyond those developed for low-dimensional systems are required for controlling spatiotemporal chaos. We present a general method for stabilizing and characterizing states with many unstable degrees of freedom and possibly an infinite number of stable degrees of freedom. This generalization provides an explicit connection between the OGY and related phase space approaches and the linear control routines of classical single-input, single-output (SISO) systems.

# Chemically Incorrect Molecular Structures

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It has become common for quantum chemical calculations to be carried out on molecules and reactions of great interest to experimental chemists. This is good but it is by no means among the most important contributions for theory to make to chemical science. In this presentation, I will discuss several of my coworkers' studies of species in which unusual electronic structures occur - Rydberg bonds, doubly charged anions, dipole-bound anions, and double-Rydberg anions. These species not only present special challenges to the theoretician but they represent, I assert, good examples of what theoreticians should be focusing on to optimize opportunities for gaining new knowledge.

# On the Conversion of Cyclopropane Radical Cation to Propene Cation

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*Ab initio* techniques at the UMP2/6-31G\*\*//UMP2/6-31G\* level has been used to study the conversion of cyclopropane cation to propene radical cation. The process has been found to have a one-step mechanism. The reactant has a  $C_{2v}$  symmetry and a  $2A_2$  electronic state. The barrier to conversion is 29.6 kcal/mol, approximately half the value of the corresponding value for the neutral analogues. There is no evidence of a stable trimethylene system.

# Structural Aspects of a Possible Transannular Interaction in Silatranes and Azasilatranes. An *Ab Initio* Study

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Complete geometry optimizations using *ab initio* SCF/3-21G\* calculations have been performed on silatrane and azasilatrane, on their fluoro derivatives, and on methyl-silatrane. By comparison with optimized geometries obtained for a series of model systems the predicted transannular internuclear distances have been interpreted in terms of the combined effects of electronegative substituents on Si and the anomeric interaction in the silatranes. The predicted geometries indicate that there is a weak transannular interaction in silatrane, and a more significant one in azasilatrane, the predicted equilibrium distances being 2.66 Å and 2.15 Å, respectively.



## Vibrational-rotational spectra of $H_2O$ in space-fixed coordinates using the Lanczos algorithm

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Excited ro-vibrational states provide information on the potential energy surface (PES) not available from ( $J=0$ ) vibrational states. Ro-vibrational states are observed up to high  $J$ -values. To assign transitions and refine the potential energy surface, efficient and exact procedures are needed to calculate many ro-vibrational states. Highly excited ro-vibrational states probe regions of the PES where body-fixed (BF) kinetic energy operators are singular. In our investigation we use a space-fixed (SF) coordinate system and formulate the exact kinetic energy operator in (SF) Radau coordinates. This kinetic energy operator contains no cross terms and has no difficult singularities. In a mixed DVR-FBR basis (Discrete variable representation DVR for stretches and finite basis representation FBR for the bend) the kinetic energy matrix is simple but each potential matrix element is an integral over (for a triatomic) four angles. By using the Lanczos algorithm and evaluating the sums of the matrix-vector product sequentially we calculate energy levels without storing the Hamiltonian matrix and without explicitly calculating potential matrix elements. We report ro-vibrational energy levels of  $H_2O$ .

# Investigation of the Geometric and the Electronic Structure in Novel Organic Polymers Possessing Very Small Intrinsic Bandgaps\*

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Conducting polymers such as polythiophene and polycyclopentadiene and their derivatives exhibit small intrinsic bandgaps. We have found that a new organic conducting polymer, polydicyanomethylene-cyclopenta[-1,1'-methylene-dicyclopentadiene], has a lower bandgap than either one of the above polymers. The precursor of this new polymer is polydicyanomethylene-cyclopenta-dicyclopentadiene in which the two cyclopentadiene rings are connected by a dicyanomethylene group. The polydicyanomethylene-cyclopenta [-1,1'-methylene-dicyclopentadiene] is a planar polymer. We believe that its lower bandgap is due to the additional conjugation as well as the increased planarity of the monomers. The electron withdrawing cyano group stabilizes the polymer by increasing the intermolecular interactions and the additional conjugation perpendicular to the chain axis makes the monomer very rigid. With the use of symmetry, the band structure calculations using full semi-empirical molecular orbital theory (MNDO,AM1) were performed for the new polymer, its precursors and the polythiophene based polymer systems. The trends in the bandgaps will be discussed.

\*Work supported in part by the Natural Science and Engineering Research Council

# Topological Entanglement in Polymers

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During the last decade, experimental scientists have become increasingly aware that geometry and topology can be used in the interpretation and design of experiments. Molecular biologists use differential geometry and knot theory in the analysis of experiments on circular DNA molecules which elucidate spatial conformation (helical twist and supercoiling) and the mechanism of life-sustaining enzymes (topoisomerases and recombinases).

Chemists synthesize molecular knots and links, and study the chemical and physical ramifications of random topological entanglement in polymers. Polymer entanglement in dilute solution can take the form of linking between two or more circular polymers and knotting (self-entanglement) of a single circular polymer; analogs of these entanglement phenomena occur in constrained linear polymers. Entanglement can be caused by random chain conformation or by the intervention of chemical or biological agents. Entanglement is believed to influence crystallization behavior and rheological properties, and is directly observable in large biopolymers by electron microscopy. This talk will discuss the mathematical quantization of entanglement and its relation to experiments.

## **First Computer Simulations of Crystallization in Molecular Systems: Water and Carbon Dioxide**

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Although the crystallization of a simple Lennard-Jones fluid was first studied almost 20 years ago, only recently has the crystallization of a molecular fluid been observed in computer simulations. In a recent MD simulation study (Phys.Rev.Lett. 73 (1994) 975) we succeeded in crystallizing a bulk sample of supercooled liquid water, the liquid-to-solid phase transition being induced with a homogeneous static electric field. The resulting polar crystal had the structure of cubic ice I. In this paper we present a detailed microscopic picture of the field-induced crystallization (electrofreezing) of supercooled liquid water and discuss some important implications of this phenomenon in nature, such as cyclic tropospheric responses to solar variations (sunspot cycles), etc... We also describe the mechanism of the homogeneous crystallization of a nonpolar molecular liquid in the absence of any externally applied field. We have carried out a series of extensive MD simulations of carbon dioxide and have observed the spontaneous nucleation of a nonpolar fcc crystal from supercooled liquid CO<sub>2</sub> on a time-scale of a few nanoseconds over a narrow range of temperatures. Directional anisotropy in the local molecular diffusion is found to be an important feature of the nucleation process.

**m-BRANCHING LIMIT to DETERMINACY in (Cayleyan)  $SU(m) \times \mathcal{S}-10 \supset \mathcal{D}-5$  SPIN SYMMETRY EMBEDDING in RO-VIBRATIONAL STATISTICS of (1,12)-CARBORANE CAGE ISOTOPOMERS.**

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In context of the automorphic NMR spin group[1] and its associated mappings onto rotational symmetries of isotopmeric cage structures, a view of Cayley's theorem in purely geometric terms is of much value in discussing dual group spin algebras and the nature of their indeterminacy as  $SU(m < n) \mathcal{S}-n \downarrow \mathcal{S}$  models[2] of cage isotopomers, - compared to Casimir invariants under a  $\mathcal{S}-6 \supset \mathcal{O}$  natural embedding[3]. Here knowledge of the specific Module decompositions[4] yield a subset (of a more general highest- $n$   $(\lambda|-n)(\mathcal{S}-n)$  limit) of Kostka co-efficients, from which the detailed mapping  $\{[\lambda] \rightarrow \Gamma(\mathcal{S}-10 \downarrow \mathcal{D}-5)\}$  follows directly, as the system has "determinacy of the first kind" as  $n=\mathcal{S}/$ . The highest  $SU(m)$  branching limit for  $(\lambda|-n)(\mathcal{S}-10)$  models free of "indeterminacy of the second kind" is investigated-i.e. comparable to ref.[3]- to verify the mappings. By focussing on the automorphic relationships[5] to regular cage polyhedra, new insight is obtained into the physics associated with Cayley's theorem and the ro-vibrational spin statistical properties of trans-(1,12) car-11-B(10-B)-boranes[6].

**METHODS: Specific Koska  $(\lambda|-n)(\mathcal{S}-10)$ - decomposition coeffs. for  $\mathcal{S}-10 \downarrow \mathcal{D}-5$  Modelling.** The  $\{:\lambda:\equiv(\lambda|-n)\}(\mathcal{S}-n)$  Modules yield specific  $\{\Lambda-\lambda[\lambda']\}$  Kostka coeffs. over  $\{[\lambda]\}(\mathcal{S}-10)$

$$\begin{pmatrix} :532: \\ :442: \\ :4411: \\ :433: \end{pmatrix} \equiv \begin{pmatrix} 1\ 2\ 3\ 1; & 3\ 2\ -; & 2\ 2\ 1\ -\ -; & 1\ 1\ 1 \\ 1\ 2\ 3\ 1; & 3\ 2\ -; & 3\ 2\ 1\ -\ -; & \underline{1}\ 2\ 1\ -\ -\ -; & \rightarrow 1 \\ 1\ 3\ 4\ 3; & 4\ 4\ 1; & 4\ 4\ 1\ 1\ -; & \underline{2}\ 4\ 1\ 1\ -\ -; & 1\ 1 \\ 1\ 2\ 4\ 1; & 3\ 3\ -; & 3\ 3\ 1\ -\ -; & \underline{2}\ 3\ 1\ -\ -\ -; & 1\ -\ 1 \end{pmatrix} \{[\lambda]\} \quad (1)$$

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 3] J.Sullivan & T.H.Siddall-III, 1992, J.Math.Phys., 36, 1964.  
 4] F.P.Temme, 1994, Physica A202, 595; A210, 435; 1995, Co-ord Ch.Rev., 143; Math.C.M. (III)  
 5] F.P.Temme, 1994/5, Molec.Phys. (I/II) (in press); F.P.T., C.E.Mitchell & M.S. Krishnan, *ibid.*, 78, 1385. [6] F.P.Temme, 1995/6, J.Math.Phys, (to be Publ'd).

# **Algebraic Methods in Quantum Mechanics**

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We investigate a time-dependent Landau system. A general algebraic technique is outlined for the study of a charged, spin one-half quantum particle in a time-varying electromagnetic field. The case of a time-varying uniform magnetic induction is examined and shown to provide a physical realization of a supersymmetric quantum mechanical system. Algebraic methods are used to factorize the relevant Schroedinger equations and obtain eigensolutions.

# **Kinetics and Reaction Dynamics and their Interface with Potential Energy Surfaces**

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Advances in computer technology and algorithms in recent years have made the computer an extremely powerful tool for studying the dynamical behavior of chemical systems. With increasing computational power, larger and more complicated systems can be studied with higher accuracy.

In classical and semiclassical dynamics methods, the accuracy and efficiency are usually largely determined by the quality and the computational cost of the potential energy function used in the calculations. Traditionally, dynamical studies are based on analytical potential energy functions fitted to experimental or electronic data. However, the process of fitting an analytical potential energy surface for a polyatomic system is usually very lengthy and difficult. Furthermore, the choice of a functional form for the fitting process is usually arbitrary, but the dynamical behavior of the system can be sensitive to this choice. These difficulties, in many cases, have prevented interesting applications of modern dynamical theory to organic and biochemical reactions.

Recently, however, a new approach to carrying out dynamics calculations, called direct dynamics, has appeared in a variety of contexts in physics, materials science, and chemistry. In a direct dynamics study the potential energy information needed in a dynamics calculation is obtained directly from electronic structure calculations, without the intermediary of an analytic fit to the potential energy surface. Since there are usually many electronic structure calculations involved, this method can be computationally expensive, especially if applied naively, and accurate calculations are only possible in recent years with improved computer speed and algorithms.

In this paper, the evolution of this method as applied to chemical reaction dynamics will be emphasized, with special attention to dual-level techniques, recent applications, and future prospects.

Studies of  $C_{28}H_4$  and  $Hf@C_{28}H_4$

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Ab initio restricted Hartree-Fock and configuration interaction calculations were performed on the ground and excited states of  $C_{28}H_4$ ,  $Hf@C_{28}H_4$ , and their positive and negative ions. Relativistic core potential and spin-orbit operators were included in the calculations to take account of the relativistic effects of the heavy atom. Symmetry-adapted functions were used to reduce the time and effort of the computation. Ionization potentials, electron affinities, and excitation energies of the systems were obtained and compared with experimental data or other theoretical values where available. These results and those from our previous studies of  $Hf@C_{28}$  were used to discuss the bonding in  $C_{28}H_4$  and  $Hf@C_{28}H_4$  in terms of the MO interaction diagrams, population analyses, and the flow of electrons between Hf, 4H and  $C_{28}$ . The mutual weakening of the bonding of Hf and 4H to  $C_{28}$  will be discussed. The factors that affect the bonding can also shed light on the characteristics of the bonding of endohedral and exohedral complexes of fullerenes in general.



# **Effect of Solvent on Semiconductor Surface Electronic States: A First-Principles Study**

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The first step is taken toward a first-principles molecular theory of the liquid-semiconductor interface. The focus is on the degree of rigor that must be applied to the solvent in order to obtain a realistic description of the interfacial electronic properties. To accomplish this, various water solvent geometries on the H/Si(111)1X1 surface are assumed, and the electronic structure of the system is calculated using two different models for the water molecules, one which includes the electrons of water explicitly and one which does not. It is found that for a realistic description of the surface electronic structure it is necessary to use a first-principles description of the solvent molecules for at least the first layer due to the electronic state mixing. The issues of broken symmetry of the crystal surface and possible dissociation of the solvent molecules are also discussed.

# The Influence of Hindered Rotations in the Recombination Kinetics of Radicals

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The recombination of radicals typically proceeds along a barrier-less reaction path. Large amplitude excursions from that path are sampled by hindered rotational tumbling of the reactants about each other. Variational Flexible Transition State Theory (FTST) incorporates such motion classically in determining the recombination rate constant. We have been able to recast canonical FTST theory into a relatively simple expression containing factors for the kinematics and for the potential energy surface (PES) sensitivity. Dialing the PES model from a harmonic torsion to a free rotation of the reactants tumbling about each other causes calculated rate constants to smoothly vary between the harmonic oscillator and free rotor limits of variational transition state theory. Between those limits the same FTST expression can accommodate any kind of hindered rotation mandated by the PES model. The effect of such rotations on rate constants will be illustrated for systems whose PES for hindered rotations have been studied using electronic structure theory. Examples will be drawn in part from the  $CX_3 + Y$  system where  $X$  and  $Y = H, D, F,$  and  $Cl$ .

# **Clusters - interpolations and surprises in the science between molecules and bulk phases**

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Understanding the physics and chemistry of clusters requires theoretical techniques capable of handling large numbers of particles without the benefits of periodicity. This often results in hybrid molecular and bulk approaches, with the particular contribution of each determined by the size and type of aggregate considered. I shall outline recent theoretical advances in the treatment of van der Waals and covalently bonded clusters ranging from 2 to 10,000 atoms (3 - 100 Angstrom), illustrating the kinds of structural, dynamical and electronic properties which are of interest, and demonstrating the novel information which these can provide on the nature of matter in the mesoscopic size domain.

# A Re-investigation of Sixth-Row Relativistic Effective Potentials

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Recent benchmark studies by both Dyll and Clementi on PbO have made possible the investigation of the practicality of relativistic effective core potentials (RECPs) for sixth-row elements. Previous use of RECPs has resulted in substantial discrepancies from expected values for molecular properties associated with the use of Rydberg states in the generation of pseudo-orbitals. We have made a small adjustment to the method for deriving RECPs and preliminary results indicate good correlation with the benchmark studies.

# **The Intermolecular Interaction Energy of the Helium Dimer Using a Monomer-Centered Plus Basis Set**

**Hayes L. Williams**

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The most effective method of locating basis functions for calculations of intermolecular interaction energies using the Symmetry-Adapted Perturbation Theory (SAPT) is to apply the so-called "monomer plus" approach. This approach utilizes basis sets which contain, in addition to the monomer-centered functions, bond functions and a small number of functions centered on the interacting partner. The intermolecular potential for the helium dimer has been first computed using such a basis set. Next, for the major interaction energy components saturated values have been obtained using Gaussian-type geminals. These values are substituted for the components obtained in orbital bases. Finally, the higher-order terms in the perturbation expansion, which are not included in the present general SAPT codes, have been computed using the full configuration interaction many-electron basis built from a small set of orbitals. The potential obtained in this way is significantly deeper than the recent literature potentials. Literature claims about the accuracy of some published potentials cannot be valid in view of the fact that basis sets used in that work give interaction energy components far from the saturated values.

**The effect of the methyl group in thymine on the stability of the thymine - adenine base pair compared with the uracil - adenine base pair**

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The use of thymine in DNA as opposed to uridine as in RNA has puzzled scientists for many years. One possible reason for this is that the methyl group affects the hydration pattern in the vicinity of the base pairs and that this in turn effectively increases the T-A interaction energy relative to the U-A interaction energy. A number of techniques have been used to investigate this. Analysis of X-ray crystal data, GRID maps and quantum chemical calculations have indeed shown that the hydration pattern is different in these two cases.

Using the supermolecule approach, quantum chemical calculations were used to derive the charge distributions of the individual bases in the gas phase, in the complex and in the hydrated complex. The electrostatic interaction energies show that the methyl group results in the T-A pair being less stable than the U-A pair in the gas phase but when solvation is taken into account the T-A base pair becomes more stable. The results are discussed in terms of ideas on cooperativity and anti-cooperativity. Further studies involving molecular dynamics including polarisation are in progress.

# Optimization of the Gradient-Corrected Exchange Term in DFT

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In the most frequently used implementations of density functional theory (DFT) parameterization of the exchange and correlation functionals has been based upon reproducing experimental thermodynamic data. This preliminary investigation of the parameterization of the gradient-corrected exchange term focuses on reproducing the electronic density of a molecule. Calculations were done using Gaussian 92/DFT's user defined five-parameter expression and the electron densities obtained from these calculations were compared to QCISD densities, since experimental electron densities are not readily available. Properties obtained using this new parameterization for the gradient-corrected exchange term were then compared to experimental and other DFT values.

# Potential Energy Models for Closed Shell Atom or Ion - Closed Shell Atom or Molecule Interactions

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Applications of the exchange-coulomb (XC) potential energy model to interactions involving closed shell atoms or atomic ions with closed shell atoms or molecules will be discussed. These potential energy models are based on previous work involving the interaction of rare gas atoms. The repulsive part of the model is a modification of the Heitler-London interaction energy (first order Coulomb and exchange energies) which requires only the ground state wave functions for the interacting species. The attractive portion of the potential energy model is developed from multipolar dispersion and/or induction energies by the incorporation of higher order charge overlap and electron exchange effects. Illustrative examples will be discussed that involve Rg-CO interactions, Rg = He, Ne, Ar with the inclusion of CO bond stretch dependencies, and the  $\text{Li}^+$ -Rg and  $\text{Na}^+$ -Rg interactions.



# Linear Scaling Methods for Electronic Structure Calculations: The Divide-and-Conquer Strategy

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Conventional approaches for electronic structure calculations are limited in the size of systems because of the cubic scaling with the number of atoms. Recently, we have developed the divide-and-conquer density functional approach for large systems. This method uses electron density as the basic computational variable and uses a divide-and-conquer strategy. Its computational cost increases linearly with the size of molecules. Progress in the divide-and-conquer method, including the analytical energy gradients, geometry optimization, a density matrix variant, and extension and applications to solid-state systems will be presented. An overview of the development of various linear scaling methods will be offered and the keys to achieve such scaling will be addressed.

1. Weitao Yang, "Direct Calculation of Electron Density in Density-Functional Theory", *Phys. Rev. Letts.* 66, 1438 (1991).
2. Weitao Yang and Tai-Sung Lee, "A Density-Matrix Divide-and-Conquer Approach for Electronic Structure Calculations of Large Molecules", submitted to *J. Chem. Phys.* (1995).

# A Generalized Formulation of the Chemical Potential Equalization Principle from Density-Functional Theory

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## ABSTRACT

A generalized formulation of the chemical potential (electronegativity) equalization principle is presented from the perspective of density-functional theory. The resulting equations provide a linear-response framework for describing the redistribution of electrons upon perturbation by an applied field. The equations can be solved using a finite set of basis functions to model the density response. In this formulation, atomic dipole and bond polarization arises naturally. The method provides high accuracy in the presence of relatively strong perturbations such as those arising from interactions with other molecules or applied fields, and is "exact" in the limit that these interactions vanish. The method has the advantage that accuracy can be systematically improved by inclusion of more complete basis functions. Applications at two basis set levels demonstrate the method can accurately reproduce induced dipole moments and estimated chemical potentials obtained from density-functional calculations. It is demonstrated that inclusion of basis functions beyond the conventional spherical-atom type is essential in some instances. The present formulation provides the foundation for a promising semi-empirical model for polarization and charge transfer in molecular simulations.

**Computational Modelling at the University of Calgary. A  
Density Functional Approach to Transition Metal Chemistry.  
Parts I-III**

**Attila Berces, Liqun Deng, Ross M. Dickson, Liangyou Fan, Yunzhu Han,  
Heiko Jacobsen, John C.W. Lohrenz, Peter Margl, Yosadara Ruiz-Morales,  
georg Schreckenbach, David Swerhone, Tom K.Woo and Tom Ziegler**

**Contribution from the University of Calgary, Calgary, Alberta, Canada  
T2N 1N4**

Developments, implementations and applications will be presented in the fields of :  
(a) DFT studies on Ziegler-Natta olefin polymerization by metallocenes, (b) Car-Parrinello investigations of C-H activation by rhodium complexes, (c) examinations of hydride migration in organometallic chemistry, (d) the calculation of NMR shifts and spin-spin coupling constants by DFT, (e) force fields of metal complexes, (f) the application of DFT to excited states, (g) DFT for large molecules.



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## Additional Abstracts and Participants

# Variational Study of Atomic Information Entropies

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The variational behavior of atomic informational entropies (Shannon and Kullback-Leibler) in position space is the subject of this study. Several independent particle models are explored: the bare Coulomb field (BCF), the effective potential (EP) generated by the interelectronic repulsion, and the Hartree-Fock method (HF). The configuration interaction (CI) method is also employed. For the BCF and EP models, variational expressions for one-particle densities of two electron-model atoms are given by using first-order Schroedinger perturbation theory. For comparison, variational HF- and CI-densities for He-series are also computed. The variational paths of the entropies and several expectation values show a remarkable similarity to that of the total energy. Except for the BCF model, it is observed that none of the variational extrema of the entropies and the properties coincides with the minimum of the energy. The role of the informational entropies as complementary variational criteria for atomic properties other than the energy is considered.

*Ab initio* investigation of the spectroscopic and reactive properties of FCO radical

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**ABSTRACT**

An *ab initio* MRD-CI study is carried out to obtain the potential surfaces governing the dissociation of FCO in the ground and excited states ( $2^2A'$ ,  $1^2A''$  and  $2^2A''$ ). In order to obtain a complete understanding of the possible processes for dissociation of FCO in the upper atmosphere, a calculation of the dissociations rate constant was made, using the reaction rate theory.

# Ferroelectric Liquid Crystal Phases of Dipolar Cut-Spheres

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Results for computer simulations of dipolar cut spheres where the dipole is modelled by two circular charge distribution of opposite charge are presented. It is found that this dispersion of charge results in a stable ferroelectric nematic phase.

Recently, systems of dipolar hard and soft spheres have been found to possess a stable ferroelectric nematic phase [1,2]. In this phase, the sample is polarized, but it is also a fluid in the sense that there is particle mobility. The orientational order comes from purely dipole dipole interactions. This result answers a question that has persisted for a long time [3], and opens up the possibility that a real ferroelectric (FE) nematic liquid crystal could be constructed in the laboratory. However, fluids of dipolar prolate ellipoids [4], and cut spheres [5] were found to not have to a ferroelectric phase. Either disordered, as in the case of dipolar ellipsoids, or antiferroelectric columnar phases, as in the case of cut spheres, were found. These results suggest that the stability of the FE phase is strongly affected by the nature of the short range interactions, and that only dipolar models with nearly spherical repulsive cores could have a ferroelectric nematic. If a more realistic model of a FE nematic is to be found, it would be advantageous to find a more robust model that would not be as sensitive to details of the molecular shape. In all these models, a single point dipole was placed at some location within the repulsive core, however, it is unknown what is the effect of dispersing the interaction throughout, effectively using a number of weak dipolar sites instead of one point site. The short range interactions could be drastically changed due to this dispersion. In this Letter, we present results of computer simulations of dipolar cut-spheres, where many small dispersed dipolar sites are modelled by a charge density  $\sigma^+$  and another  $\sigma^-$  distributed within the core of the cut-sphere. We find that this dispersion results in a stable FE nematic, where the point dipole model is predicted to have an antiferroelectric columnar phase.

The model we consider is cut spheres with length  $L = 1$  and diameter  $D = 10$  with two charge distributions  $\sigma_+$  and  $\sigma_-$ , separated by a distance  $L'$ , and placed within the core of the cut sphere. The distributions are disc shaped with a diameter  $D' = 9$ . The cut sphere is simply a hard repulsive core that prevents two particle's charge distributions from overlapping. The total dipole moment of the particle is  $\mu$  and is calculated in the limit that the distance between the two distributions  $\sigma_+$  and  $\sigma_-$  goes to zero, but the product  $\mu = \sigma L'$  is constant. This can be written as

$$\mu = \int_A \sigma r dr \hat{d}. \quad (1)$$

the pair potential can be written as

$$u(12) = u_{cs}(12) + u_{DD}(12), \quad (2)$$

# **PHASE TRANSITION IN THE MONOLAYER STRUCTURE OF CO/NaCl(001)**

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A Monte Carlo study of a monolayer of CO/NaCl(001) was carried out at low temperatures (1K-40K). At higher T a 1x1 structure is observed, while at lower T a 2x1 structure emerges in accordance with experiment. The low T phase consists of alternating rows of tilted ( $\sim 15^\circ$ ) molecules.

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