

Third  
Canadian  
Computational  
Chemistry  
Conference

University of Alberta  
Edmonton  
Alberta

19-23 July, 1997

The Organizing Committee of the 3rd CCCC

André Bandrauk

Christopher Bayly

Ken Edgecombe (Associate Chairman)

Paul Mezey

Mariusz Klobukowski (Chairman)

Vedene H. Smith, Jr.

Contents

Acknowledgments .....	2
Program .....	3
Detailed Program .....	4
Poster Schedule .....	8
Collected Abstracts .....	11
List of Participants .....	73

The Organizing Committee of the 3rd CCCC acknowledges the material assistance, contributions, and sponsorship from the following organizations:

- Department of Chemistry, University of Alberta
- Public Affairs Office, University of Alberta
- Technical Services, University of Alberta
- Economic Development Edmonton
- Canadian Society for Chemistry
- IBM Canada Ltd.
- Sun Microsystems, Inc.
- Tripos, Inc.
- Merck Frosst Canada
- Bio-Mega
- SGI/Cray Canada

The assistance of the following people was indispensable to the organization of the Conference:

- Christine Otter
- Scott Delinger
- Ron Gardner
- Cathy Grant
- Glen Donald
- Steve Decker
- Alan Clement
- Arnold Adam
- Joanne Gainsforth
- Wendy Garinther
- Anna Jordan

## Program

	Sunday July 20	Monday July 21	Tuesday July 22	Wednesday July 23
8:20 AM	W.A.G. Graham			
	<u>Session 1-1</u> V.H. Smith	<u>Session 2-1</u> K. Edgecombe	<u>Session 3-1</u> P. Mezey	<u>Session 4-1</u> M. Barysz
8:40 AM	R.J. Boyd	H.F. Schaefer	A.J. Sadlej	J. Karwowski
9:25 AM	A.D. Becke	M. Head-Gordon	K. Hirao	M.C. Zerner
10:10 AM	Refreshment Break			
10:30 AM	E.R. Davidson	P. Taylor	A.M. Chaka	M.A. Whitehead
11:15 AM	D. Salahub	M. Dupuis	D.F. Feller	J.M. Coffin J. Himer
12:00 AM	Lunch Break			V.H. Smith Closing Remarks
	<u>Session 1-2</u> J. Wright	<u>Session 2-2</u> D. Cameron	<u>Session 3-2</u> M. Klobukowski	
1:40 PM	R. Kapral	C. Bayly	R.J. Boyd	
2:25 PM	G.N. Patey	D.F. Weaver	D.P. Chong	
3:10 PM	Refreshment Break			
3:30 PM	T.N. Truong	D.A. Case	P. Margl	
4:15 PM	J.S. Tse	T.R. Cundari	O.N. Ventura	
5:00 PM	Poster Session A Evening Social	Poster Session B Evening Social		
Saturday, July 19, 1997				
4:15 PM	Registration Desk Opens (Timms Centre)			
5:00 PM	Opening Social (Timms Centre)			

## Detailed Program

---

Sunday, July 20, 1997

---

8:20 AM	<b>W.A.G. Graham</b> Faculty of Science	Opening Remarks
	Session 1-1. Chair: V.H. Smith	
8:40 AM	<b>R.J. Boyd</b> Dalhousie	History of computational chemistry in Canada
9:25 AM	<b>A.D. Becke</b> Queen's	Systematic generation of density functionals
10:10 AM		Refreshment Break
10:30 AM	<b>E.R. Davidson</b> Indiana	A comparison of conventional ab initio and DFT results for some problems in structure, reactions and spectroscopy
11:15 AM	<b>D. Salahub</b> Montréal	Density functionals in the hydrogen-bonding arena
12:00 AM		Lunch Break
	Session 1-2. Chair: J. Wright	
1:40 PM	<b>R. Kapral</b> Toronto	Condensed phase reaction dynamics: Simulating reactions when they occur once in a blue moon
2:25 PM	<b>G.N. Patey</b> UBC	Computer simulation studies of fluids with interesting phase transitions
3:10 PM		Refreshment Break
3:30 PM	<b>T.N. Truong</b> Utah	Predicting kinetics of chemical reactions from first principles: A robust and practical ab initio direct dynamics methodology
4:15 PM	<b>J.S. Tse</b> NRC	First principles calculation of the electronic and structural properties of condensed matters
5:00 PM	Poster Session A	

---

---

Monday, July 21, 1997

---

Session 2-1. Chair: K. Edgecombe

- 8:40 AM **H.F. Schaefer**  
Georgia Molecular anions: A wealth of important, uncharacterized systems
- 9:25 AM **M. Head-Gordon**  
UCB A new approach to local electron correlation using nonorthogonal orbitals
- 10:10 AM Refreshment Break
- 10:30 AM **P. Taylor**  
SDSC Gaussian-type geminal basis sets in quantum chemical calculations
- 11:15 AM **M. Dupuis**  
PNL Spin multiplicities and ab initio methods : A comparative study of molecular orbital theory and density functional theory
- 12:00 AM Lunch Break

Session 2-2. Chair: D. Cameron

- 1:40 PM **C. Bayly**  
Merck Frosst Predicting a ligand binding mode in cyclooxygenase-2
- 2:25 PM **D.F. Weaver**  
Queen's Applications of large-scale computations to the design of neurologic drugs
- 3:10 PM Refreshment Break
- 3:30 PM **D.A. Case**  
Scripps Quantum mechanical and molecular mechanical approaches to aqueous solvation energetics
- 4:15 PM **T.R. Cundari**  
Memphis Approaches to computer-aided design of f-element complexes
- 5:00 PM Poster Session B
-

---

Tuesday, July 22, 1997

---

Session 3-1. Chair: P. Mezey

- 8:40 AM **A.J. Sadlej**  
Lund Recent developments in non-singular two-component relativistic theories
- 9:25 AM **K. Hirao**  
Tokyo Multireference based perturbation theory - Accuracy and interpretation
- 10:10 AM Refreshment Break
- 10:30 AM **A.M. Chaka**  
Lubrizon Understanding the reactivity of chlorine with hydrocarbons
- 11:15 AM **D.F. Feller**  
PNL How accurately can we compute molecular properties? More lies, damned lies and statistics
- 12:00 AM Lunch Break

Session 3-2. Chair: T.W. Dingle

- 1:40 PM **R.J. Boyd**  
Dalhousie A density functional theory study of electron density distributions and the electronic properties of molecules
- 2:25 PM **D.P. Chong**  
UBC Accurate DFT calculation of core-electron binding energies
- 3:10 PM Refreshment Break
- 3:30 PM **P. Margl**  
Calgary Applications of density functional molecular dynamics in homogeneous catalysis
- 4:15 PM **O.N. Ventura**  
Montevideo Theoretical study of oxygen fluorides
-

---

Wednesday, July 23, 1997

---

Session 4-1. Chair: M. Barysz

8:40 AM	<b>J. Karwowski</b> Torun	Statistical theory of atomic and molecular spectra
9:25 AM	<b>M.C. Zerner</b> Florida	Environmental effects on molecular electronic spectroscopy
10:10 AM		Refreshment Break
10:30 AM	<b>M.A. Whitehead</b> McGill	A computational study of nitrogen heterocyclic compounds: Molecular mechanics, ab-initio and semi-empirical calculations
11:15 AM	<b>J.M. Coffin</b> IBM	Computational chemistry on the IBM SP
11:40 AM	<b>J. Himer</b> SUN	High performance computing in computational chemistry
12:05 AM	<b>V.H. Smith</b> Queen's	Closing Remarks

---



# Poster Session A

## Sunday, July 20, 5 - 7 PM

- |      |                            |  |
|------|----------------------------|--|
| A-01 | <b>Maria Barysz</b>        | Relativistic corrections to expectation values in approximate 2-component theories   |
| A-02 | <b>Maxwell D. Cummings</b> | Comparative Modeling of the Ubiquitin Conjugating Enzyme UBC1  |
| A-03 | <b>Stephen A. Decker</b>   | Bonds, Points, and Blobs: Analysis of Metal-Acetylene Complexes  |
| A-04 | <b>Oreola Donini</b>       | Modelling of voltage-gated ion channels  |
| A-05 | <b>Eva Fadrna</b>          | AAA RNA trimer using computational chemistry tools   |
| A-06 | <b>Dean Goddette</b>       | Hologram QSAR: A Highly Predictive QSAR Technique Based on Molecular Holograms   |
| A-07 | <b>Serge Gorelskii</b>     | Charge Transfer in Ion Associates: Semiempirical Calculations  |
| A-08 | <b>George L Heard</b>      | Quantum theoretical studies of quadrupole moments of polycyclic aromatic hydrocarbons: Applications to chromatography                  |
| A-09 | <b>Dylan Jayatilaka</b>    | Wavefunctions from X-ray Diffraction Data  |
| A-10 | <b>Jana Khandogin</b>      | Density Functional Study of Nuclear Spin-Spin Coupling for Transition Metal Systems  |
| A-11 | <b>Heidi M. Muchall</b>    | A search for a calculational method for the reliable prediction of the first adiabatic and vertical ionization potentials of carbenes. |
| A-12 | <b>Cory C. Pye</b>         | Implementation of COSMO Solvation Model in the Amsterdam Density Functional Package  |
| A-13 | <b>Cory C. Pye</b>         | An ab Initio Study of cis-5,6-Disubstituted Cyclohexadienes  |
| A-14 | <b>Isabel Rozas</b>        | Inverse Hydrogen-Bonded Complexes  |
| A-15 | <b>Irina Vedernikova</b>   | Quantum mechanical evaluation of the anodic oxidation  |
| A-16 | <b>Chung Wong</b>          | Brownian Dynamics Simulations of the Ionic Atmospheres around Biomolecules   |
| A-17 | <b>Tom K. Woo</b>          | A combined QM/MM ab initio molecular dynamics simulations of transition metal catalysts  |

Note: Please set up your poster anytime on the day of your poster presentation, before the Poster Session begins. Please take it down the same day, after the session ends.

# Poster Session B

## Monday, July 21, 5 - 7 PM

- B-01 **Maria Barysz** Perturbation theory of relativistic effects:  
Relative inaccuracies of approximate results
- B-02 **Alwin Cunje** Inert gases as catalysts in 1,2-shifts in cations  $\text{RCO}^+$  ( $\text{R}=\text{H}, \text{CH}_3$ )
- B-03 **Ken Edgecombe** Protein Structure Determination Through A Topological Analysis  
of the Density
- B-04 **Joanne L. Gainsforth** DFT
- B-05 **Serge Gorelskii** Metal-Ligand Mixing in Ru Diimino Complexes
- B-06 **Trevor Hart** DockVision: an Integrated Software Package for Molecular Docking
- B-07 **Araz Jakalian** Molecular Dynamics Simulations of the  $c(4 \times 2)$  Superstructure of  
Octanethiol Adsorbed on Au(111)
- B-08 **Dylan Jayatilaka** Electron Spin Resonance  $g$  Tensor Calculations
- B-09 **Kereen Monteyne** Density Functional Study of the [2+2] Addition of Ethylene to the  
 $\text{Mo}=\text{E}$  Bond in  $\text{Mo}(\text{E})(\text{O})\text{Cl}_2$  ( $\text{E} = \text{O}, \text{NH}, \text{CH}_2$ )
- B-10 **Yosadara Ruiz-Morales** A theoretical study of 13-C and 17-O NMR shielding tensors in transition  
metal carbonyls based on density functional theory and gauge-including  
atomic orbitals
- B-11 **Cory C. Pye** Geometry Optimization in Ab Initio Theory.  
Part II. Natural Internal Coordinates
- B-12 **Hartmut Schmider** Orthogonal polynomials from atomic charge densities
- B-13 **Stephen K. Wolff** The inclusion of spin-orbit and Fermi-contact in a DFT calculation of  
NMR shielding tensors
- B-14 **Chung Wong** Density functional calculations of  $^1\text{H}$  and  $^{15}\text{N}$  chemical shifts in the  
catalytic triad of serine proteases
- B-15 **Tom K. Woo** A theoretical study of the mechanism of hydroxylation  
in methane monooxygenase
- A-16 **James S. Wright** Dodecahedral Molecular Nitrogen ( $\text{N}_{20}$ ) and Related Structures
- B-17 **Liqiu Yang** Effective Medium Theory including Perturbation Electron Density  
Changes

Note: Please set up your poster anytime on the day of your poster presentation, before the Poster Session begins. Please take it down the same day, after the session ends.



# Relativistic corrections to expectation values in approximate 2-component theories

Maria Barysz (\*)

*Theoretical Chemistry*  
*University of Lund*  
*P.O.Box 124, S-221 00 Lund*  
*Sweden*

The definition of the expectation value of different operators in approximate 2-component relativistic theories is analysed with reference to exact results of the Direct Perturbation Theory [1,2]. The relativistic correction to the  $\frac{1}{r}$  operator is calculated through the first order in  $\alpha^2$  by using 2-component wave functions of the Douglas-Kroll method [3,4], the Regular Hamiltonian Approximation [5], and of the newly developed non-singular approaches [6]. The magnitude of the error is evaluated and indicates that the operators need to be transformed to the appropriate representation prior to the calculation of their expectation values [7].

---

(\*) Permanent address: Department of Chemistry, University of Silesia, ul. Szkolna 9, 40-006 Katowice, Poland

[1] A. Rutkowski, *J. Phys. B* **19**, 141 (1986).

[2] W. Kutzelnigg, *Z. Phys. D* **11**, 15 (1989); W. Kutzelnigg, *Z. Phys. D* **15**, 27 (1990).

[3] M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).

[4] J. Sucher, *Phys. Rev. A* **22**, 348 (1980).

[5] E. van Lenthe, R. van Leeuwen, E. J. Baerends and J. G. Snijders, *Int. J. Quantum Chem.* **57**, 281 (1996).

[6] M. Barysz, A. J. Sadlej, and J. G. Snijders, *Int. J. Quantum Chem.*, in the press.

[7] M. Barysz and A. J. Sadlej, *Theor. Chem. Acc.*, in the press.

# Perturbation theory of relativistic effects: Relative inaccuracies of approximate results

Maria Barysz (\*)

*Theoretical Chemistry*  
*University of Lund*  
*P.O.Box 124, S-221 00 Lund*  
*Sweden*

The first-order relativistic corrections to energies can be determined either from the direct perturbation expansion of the Dirac equation or by using the so-called Pauli operator. The two formulae are equivalent for exact non-relativistic reference functions but lead to different results for approximate solutions. The analysis of a model problem with controlled deviation from the exact non-relativistic solution clearly shows a preference for the first-order relativistic energy formula derived from direct perturbation theory. The use of the Pauli approximation with inaccurate non-relativistic reference functions may introduce significant inaccuracies in the calculated relativistic corrections for low-lying s-states [1].

---

(\*) Permanent address: Department of Chemistry, University of Silesia, ul. Szkolna 9,  
40-006 Katowice, Poland

[1] M. Barysz, Chem. Phys. Lett., in the press.

## Predicting a ligand binding mode in cyclooxygenase-2

Christopher Bayly,\* Gary O'Neill, Joe Mancini, David Percival,  
Diane Ethier, and Lison Bastien

*Merck Frosst Centre for Therapeutic Research  
Box 1005, Pointe Claire-Dorval  
Quebec H9R 4P8.*

The starting point for structure-based drug design is in general a lead structure bound in the active site of the macromolecule of interest. Usually an experimentally-determined structure for the complex is used, however, if this is not known experimentally, this too must be modelled. In the case of human cyclooxygenase-2 (hCOX2), a therapeutic target for the treatment of inflammation, an experimental structure was not available although an X-ray structure of the closely-related sheep cyclooxygenase-1 (sCOX1) was. The modelling studies leading to the prediction of the binding mode of lead structure L-584095 in a homology-built hCOX2 structure will be presented, together with comparison to the subsequent experimental X-ray crystal structure.

# Systematic refinement of exchange-correlation density functionals

Axel D. Becke

*Department of Chemistry  
Queen's University  
Kingston, Ontario  
CANADA K7L 3N6*

An automatic and systematic procedure for refining gradient corrections in exchange-correlation density functionals will be presented. It involves least-squares fitting to accurate thermochemical benchmark data, such as the G2 data set of Pople and coworkers. The flexibility of our fitting model suggests that we have found the limits of precision of gradient corrections in Kohn-Sham density-functional theory.

# History of computational chemistry in Canada

Russell J. Boyd

*Department of Chemistry  
Dalhousie University  
Halifax, Nova Scotia  
Canada, B3H 4J3*

This paper will outline the history of computational chemistry in Canada. The emphasis will be placed on the strong link between the development of theoretical chemistry and the subsequent emergence of computational chemistry as a complementary research field. Particular attention will be paid to some key historical events and to some of the leading personalities, past and present, of the Canadian community of theoretical and computational chemistry.



# A density functional theory study of electron density distributions and the electronic properties of molecules

Russell J. Boyd

*Department of Chemistry  
Dalhousie University  
Halifax, Nova Scotia  
CANADA, B3H 4J3*

Several aspects of our recent research under the general heading of the electronic properties of molecules and density functional theory will be summarized. Particular attention will be paid to the comparison of the electron densities of small molecules calculated by use of various exchange and correlation functionals with the results of quadratic configuration interaction methods [1]. An orbital-based density difference for the comparison of two density distributions will be described and representative results reported for a few small molecules [2]. Recent progress in the calculation [3] of isotropic hyperfine coupling constants by means of density functional methods will be reviewed. Also, the ability of density functional methods to accurately describe the molecular quadrupole moments of polycyclic aromatic hydrocarbons will be outlined [4]. And finally, a few comments will be made on the prospects for the development and parameterization of new functionals for use in density functional methods from high-level ab initio electron densities.

---

[1] J. Wang, B.G. Johnson, R.J. Boyd and L.A. Eriksson, *J. Phys. Chem.* 100, 6317-6324 (1996); J. Wang, L.A. Eriksson, B.G. Johnson and R.J. Boyd, *J. Phys. Chem.* 100, 5274-5280 (1996).

[2] S.K. Worsnop, J. Wang and R.J. Boyd, submitted.

[3] S.D. Wetmore, R.J. Boyd and L.A. Eriksson, *J. Chem. Phys.*, 102, 7738-7748 (1997); J.M. Martell, R.J. Boyd and L.A. Eriksson, *J. Phys. Chem.* 99, 623-629 (1995); J. Wang, A. Laaksonen, L.A. Eriksson and R.J. Boyd, *J. Chem. Phys.* 103, 8166-8173 (1995).

[4] G.L. Heard and R.J. Boyd, *J. Phys. Chem.*, in press.

This research is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Swedish National Science Research Council (NFR) and the Killam Trust.

# Quantum mechanical and molecular mechanical approaches to aqueous solvation energetics

David A. Case

*The Scripps Research Institute  
10666 N. Torrey Pines Rd.  
La Jolla, CA 92037, USA*

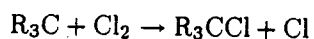
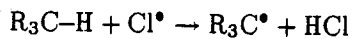
Quantum mechanical treatments are frequently necessary to understand the nature of active sites of enzymes and electron transport proteins. Continuum electrostatic models can be used to provide a realistic yet computationally tractable approach to simulate the protein/solvent environment. In this model, the protein is considered to be a medium of low dielectric, with embedded charges and dipoles, and the solvent a medium of high dielectric. We have coupled this model to modern density functional theory, using the Amsterdam Density Functional codes, and have made applications protonation of amino acid sidechains, and to the metal-hexaquo complexes of the first transition row. Analogous models can be made in which the solute is represented by atomic partial charges derived from force fields. Approximate schemes allow the Poisson-Boltzmann equations to be solved very quickly for this model. I will discuss tests of this idea to folding/unfolding transitions in peptides and to the A/B transition in DNA and RNA oligonucleotides.

# The reaction of chlorine with hydrocarbons

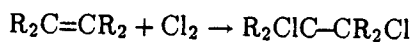
Anne M. Chaka

Research Division MS 151-C,  
The Lubrizol Corporation,  
29400 Lakeland Blvd, Wickliffe, OH 44092-2298

Organochlorine compounds have received considerable attention in recent years due to increasing environmental concern and regulation. Hence it is essential to better understand the formation and degradation of these compounds. Organochlorine compounds can result from hydrogen abstraction by chlorine atoms:



or by addition of chlorine molecules to double bonds:



*Ab initio* post-Hartree Fock (HF) and density functional theory calculations are used to characterize the reaction pathways of chlorine with hydrocarbons in the gas phase and in nonpolar solvents. For the first time a pathway for the electrophilic addition of Cl<sub>2</sub> to ethylene has been determined which does not require a high dielectric solvent to proceed.

# Accurate DFT calculation of core-electron binding energies

Delano P. Chong

*Department of Chemistry  
University of British Columbia  
Vancouver, BC, V6T 1Z1*

A simple procedure was developed for the accurate computation of core-electron binding energies (CEBEs) of C, N, O, and F in small molecules. The method was based on the unrestricted generalized transition-state (uGTS) model and the exchange-correlation functional B88-P86, a combination of Becke's 1988 exchange functional with Perdew's 1986 correlation functional. Small relativistic corrections were estimated from Pekeris' accurate results for two-electron atomic ions. Over fifty cases were studied with the deMon density functional program, with a truncated version of Dunning's cc-pV5Z basis set (s,p, and d-components only). The average absolute deviation (aad) from experiment for our uGTS/pV5Z method was found to be 0.23 eV.

Recently, a more efficient basis set was proposed and tested. This new basis set consisted of Dunning's cc-pVTZ for the parent and scaled pVTZ for the partial core-hole cation (again without f-type functions). The Slater-like screening constants were taken from the 1963 paper of Clementi and Raimondi. With this much smaller basis set, the aad was maintained at 0.22 eV for 66 cases studied.

The reduced computational demands enabled us to extend such calculations to larger molecules and to model polymers and solids. Examples include amines, nitriles,  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Mn}(\text{CO})_4\text{NO}$ ,  $\text{Co}(\text{CO})_3\text{NO}$ ,  $\text{Fe}(\text{CO})_2(\text{NO})_2$ ,  $\text{Mn}(\text{NO})_3\text{CO}$ ,  $\text{Cr}(\text{NO})_4$ , ethyl perfluoroacetate, 2-methylglutaronitrile (to model polyacrylonitrile), gamma-aminopropyltrihydroxysilane (to model gamma-aminopropyltriethoxysilane),  $\text{C}_6\text{H}_6$  isomers, etc.

All together over 100 cases have been studied and many predicted CEBEs obtained. The aad from experiment for our uGTS/B88-P86/scaled pVTZ method remains at 0.2 eV. The reasons for such accuracy, as well as future extensions, will be discussed in this talk.

## Computational chemistry on the IBM SP

James M. Coffin

*IBM Higher Education Industry Solution Unit  
1505 LBJ Freeway, 5th Floor  
Dallas, TX 75234*

This talk will give an overview of distributed memory computer architectures, in particular the IBM SP. With over 350 installations in universities worldwide, the SP has been found to be a very high quality machine for research problems in chemistry, physics, biology, engineering, seismic and weather modelling. The IBM SP is the fastest and most scalable machine for problems in computational chemistry. In the area of quantum chemistry, the IBM SP has close to 60% market share due to the highly compute intensive floating point nature of these problems. The SP will be discussed in detail including design specifications and future product directions.

## Comparative modeling of the ubiquitin conjugating enzyme UBC1

Maxwell D. Cummings,\* Rajeev Pannu, and Michael J. Ellison

*Department of Biochemistry  
University of Alberta  
Edmonton, AB, Canada T6G 2H7*

Using comparative modeling techniques a model of a catalytically competent truncated form of the ubiquitin conjugating enzyme UBC1 from *S. cerevisiae* ( $\Delta$ UBC1) was constructed, based on the three-dimensional structure of a related enzyme. The modeled structure was analyzed using a variety of criteria, including comparison with the published structures of four related enzymes. Our analyses indicate that the final model of the  $\Delta$ UBC1 monomer represents a reasonable protein structure. We are using the modeled  $\Delta$ UBC1 structure to study different protein-protein interactions. One protein-protein system of interest is the  $\Delta$ UBC1 homodimer, and some early results in this area are also presented.

## Approaches to computer-aided design of f-element complexes

Michael T. Benson, Thomas R. Cundari,\* Eddie W. Moody,  
Leah C. Saunders, Shaun O. Sommerer

*Department of Chemistry,  
University of Memphis,  
Memphis, TN 38152*

The unique chemical and physical properties of the lanthanides have been increasingly exploited by experimentalists for a variety of catalytic, advanced materials, and biomedical applications. Computational chemistry is the least well-developed for the lanthanides in comparison to other families of elements. The large number of electrons, relativistic effects, large ligands, and highly ionic bonding serve to make modeling of lanthanide complexes a challenge. This contribution will discuss our efforts in efficient modeling of the bonding, structure and reactivity of lanthanide complexes using a variety of classical and quantum approaches.

Inert gases as catalysts in 1,2-shifts in cations  $\text{RCO}^+$   
( $\text{R} = \text{H}, \text{CH}_3$ )

A. Cunje,\* A.C. Hopkinson, and C.F. Rodriguez

*York University  
Department of Chemistry  
4700 Keele Street  
North York, Ontario, M3J 1P3*

The barrier to the intramolecular 1,2-shift of a hydrogen atom or a methyl group in a cation in the gas phase is often large. In solution such rearrangements are often catalyzed by the solvent and in principle a similar process can occur in the gas phase. Relative methyl cation and proton affinities provide a guide as to what molecules might function as catalysts. In this study inert gases such as argon and molecular nitrogen were found to be satisfactory. Optimizations and subsequent characterizations have been performed using Density Functional Theory (at B3LYP/6-311++G(d,p)) followed by single point calculations at QCISD(T)/6-311++G(2df,p). Catalytic effects are largest in the smallest ion,  $\text{HCO}^+$ , where the barrier is lowered appreciably (from  $\sim 35$  kcal/mol to 10-20 kcal/mol depending on the catalyst used). By comparison, in  $\text{CH}_3\text{CO}^+$  the barrier to methyl transfer shift is reduced by somewhat smaller amounts.



A comparison of conventional *ab initio*  
and DFT results for some problems in structure,  
reactions and spectroscopy

Ernest R. Davidson

*Department of Chemistry  
Indiana University  
Bloomington, IN 47405*

We will compare CASSCF and DFT results for the structure of [2.2.2] propellane, the 1,3 shift of vinylcyclopropane, and the ESR spectra of some metal oxide diatomics. We will also discuss (e,2e) and photoelectron spectra for some simple molecules. For (e,2e), DFT gives a good description of primary hole state cross-sections. But DFT is generally unable to predict satellite state intensities. DFT generally performs better than limited CI for ESR hyperfine parameters and is more stable as the basis set is improved. For molecules involving singlet biradical intermediates, broken spin UDFT often gives reasonable results while spin-restricted DFT fails. In this respect, DFT retains some of the fallacies of similar SCF calculations.

# Bonds, points, and blobs: Analysis of metal-acetylene complexes

Stephen A. Decker\* and Mariusz Klobukowski

*Department of Chemistry  
University of Alberta  
Edmonton, AB, T6G 2G2*

In a recent kinetics study members of the Jordan and Takats groups, here at the University of Alberta, have shown that the rate of carbonyl substitution in complexes of the type  $M(\text{CO})_4(\text{C}_2\text{R}_2)$ , where  $M=\text{Fe, Ru, Os}$ , is accelerated by factors of  $10^2$ - $10^{13}$  over the respective pentacarbonyl complexes. These substitution reactions have been shown to be dissociative in nature and the following metal dependence has been observed:  $\text{Fe} > \text{Os} > \text{Ru}$ .

We employed non-local density functional theory (Becke's 1988 exchange functional coupled with Lee, Yang and Parr's correlation functional, commonly referred to as the BLYP functional), with both effective core potential and all electron basis sets, in conjunction with the charge decomposition analysis (CDA) scheme of Frenking et. al. and Bader's atoms in molecules (AIM) analysis in order to probe the origin of the increased reactivity of these alkyne complexes. We found that the BLYP/ECP method used here predicted geometries very close to experiment for both the parent carbonyl and alkyne (in this study  $\text{C}^2\text{H}^2$  was used) complexes. The calculated CO bond dissociation energies (BDEs) were also found to agree well with experiment and mirrored the trends observed experimentally for both  $M(\text{CO})_5$  and  $M(\text{CO})_4(\text{C}_2\text{H}_2)$ .

With Frenking's CDA scheme we were able to characterize the nature of the acetylene ligand in the reactant,  $M(\text{CO})_4(\text{C}_2\text{H}_2)$ , and unsaturated dissociation product,  $M(\text{CO})_3(\text{C}_2\text{H}_2)$ , complexes. This analysis showed that acetylene acts as a 2e donor in the reactant complex (with only the  $\pi_{\parallel}$  orbitals of  $\text{C}_2\text{H}_2$  actively donating to the metal), while it acts as a 4e donor (both  $\pi_{\parallel}$  and  $\pi_{\perp}$  orbitals of  $\text{C}_2\text{H}_2$  active) in order to stabilize the 16e unsaturated dissociation product. Bader's AIM analysis supports this result.

At the BLYP/ECP level the observed metal dependence of the rate may be rationalized in terms of the metal dependence of the molecular orbital energy gap of the  $\text{C}_2\text{H}_2 \rightarrow M \pi_{\perp}$  interaction.

## The modeling of voltage-gated ion channels

O. Donini<sup>†\*</sup> and D.F. Weaver<sup>‡</sup>

*Departments of Chemistry<sup>†</sup> and Medicine<sup>‡</sup>  
Queen's University  
Kingston, Ontario, K7L 3N6*

The modeling of voltage-gated ion channels requires protein force fields which are parameterized for both ion - amino acid and electric field interactions. The parameterization of ion - amino acid interactions is particularly problematic due to the multiple atom dependency of the interaction and to the computational expense of the analytic mathematical equations required. We examine the interaction of a potassium ion with various amino acids using *ab initio* (DFT-BLYP, 6-311G\*) calculations and compare them to predictions of a widely used force field (CHARMm22.0). We also assess the usefulness of empirically derived equations and coefficients to "adjust" the protein force field in a robust and computationally inexpensive manner. These empirical terms allow us to comment on the ability of CHARMm22.0 to model cation -  $\pi$  interactions.

Spin multiplicities and ab initio methods:  
A comparative study of molecular orbital theory  
and density functional theory

Michel Dupuis\* and D.A.Dixon

*Pacific Northwest National Laboratory  
Environmental And Molecular Sciences Laboratory (\*)  
Richland, WA 99352*

The design of selective separation ligands and function-specific and efficient enzymes are two of several key aspects of innovative approaches to address the challenge of the management of radioactive and non-radioactive wastes from the production of nuclear materials. Theoretical studies can play a key role in advancing molecular-level understanding of the physical, chemical, and biological processes that underlie environmental remediation. We have recently undertaken a comparative study of available ab initio methods for the calculation of the electronic structure of organometallic complexes as well as porphyrins. We have focussed our effort on assessing the relative performance of molecular orbital-based methods and density functional-based methods in yielding accurate electronic structure and energetics for such complexes in different spin states. Our initial efforts has dealt with Fe(III) species, ferri-cyanide, hexa-aquo-iron, and iron- porphyrin complexes. It was found that molecular orbital-based methods favor high spin states while density-based methods favor low spin states. Details of the results will be presented and prospects for obtaining accurate energy and structure data will be discussed.

---

(\*) The Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE- AC06-76RLO 1830.

# Topological analysis of x-ray protein relative density maps utilizing the eigenvector following method

K.E. Edgecombe,\* A. Ableson, K. Baxter, T. Chiverton, S. Fortier and J. Glasgow

*Molecular Scene Analysis Group  
Depts. of Computing and Information Science and Chemistry  
Queen's University at Kingston  
Kingston, ON  
Canada K7L 3N6*

Crystallographic studies play a major role in protein structure determination. Despite significant effort and advances in the computational tools available, constructing a protein model from medium and low resolution crystallographic data remains problematic. In this report, the preliminary results of the application of the technique of modeling the experimentally derived relative density utilizing cubic splines followed by a topological analysis of the resulting scalar field are discussed. Note that the topological analysis makes use of Popelier's eigenvector following algorithm and the fifth-order Cash-Karp-Runge-Kutta gradient path tracing algorithm in a specially adapted version of Popelier's MORPHY program.

# A detailed analysis of conformational behavior of AAA RNA trimer using computational chemistry tools

Eva Fadrná\* and Jaroslav Koča

Laboratory of Biomolecular Structure and Dynamics  
and Department of Organic Chemistry,  
Faculty of Science, Masaryk University,  
Kotlářská 2, 611 37 Brno  
Czech Republic

In our Laboratory an effective method of conformational behavior exploration has been developed. The method is a combination of a pseudosystematic search with molecular dynamics simulated annealing. The potential energy is calculated by means of molecular mechanics. The method is called CICADA [1] and is interfaced [2] with AMBER 4.1 [3] force field.

We have made calculations on the AAA RNA trimer. Crystallographic structure [4] and data obtained by theoretical methods [5] on AAA are known. Using our methodology we have found all structures described in literature, and also several additional ones.

The CICADA-AMBER combination appears to be a promising tool for the study of larger biologically interesting polymers.

---

[1] Koča J.: *J. Mol. Struct. (Theochem)* 1994, 308, 13.

[2] Fadrná E.; Koča J.: *J. Biomol. Struct. Dynam.* 1996, 14, 137.

[3] Pearlman D.A.; Case D.A.; Cadwell J.C.; Ross W.S.; Cheatham III T.E.; Ferguson D.M.; Seibel G.L.; Singh U.Ch.; Weiner P.; Kollman P.: *AMBER Version 4.1*, University of California, San Francisco, 1995.

[4] Suck D.; Manor P.C.; Saenger W.: *Acta Crystallogr.* 1976, B32, 1727.

[5] Ghomi, M.; Victor, J.M.; Henriët, Ch.: *J. Comput. Chem.* 1994, 15, 433.

How accurately can we compute molecular properties?  
More lies, damned lies and statistics

David Feller

*Environmental Molecular Sciences Laboratory  
Battelle Pacific Northwest National Lab (\*)  
Mail Stop K1-90  
906 Battelle Blvd  
Richland, WA 99352*

As the power of computer hardware and software has continued to double every 12 - 18 months, computational chemists have grown increasingly ambitious in applying their tools to a ever wider range of molecular properties. As a result, it has become more difficult for an individual scientist to stay informed of the typical accuracy to be expected from commonly-used basis sets and levels of theory in areas of chemistry outside of their own area of expertise. The impact of an on-line database of electronic structure properties on experts and novice users of these applications is discussed in light of a prototype.

---

(\*) The Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Let's Twist Again!  
Origin of the inverse isotope effect  
in the addition of Br and S to ethylene

Joanne L. Gainsforth\* and Mariusz Klobukowski

*Department of Chemistry  
University of Alberta  
Edmonton, AB, T6G 2G2*

Using Density Functional Theory, the geometries of reactant, product (bromine), and transition state (sulfur) were optimized and Hessians calculated. Vibrational mode analysis and subsequent breakdown of the overall isotope effect into contributions associated with individual vibrational modes led to a single isotope-sensitive mode in both systems that is responsible for the inverse effect.



## HQSAR: A new highly predictive QSAR technique based on molecular holograms

David Lewis,\* Trevor Heritage, and Tad Hurst

*Tripos, Inc.*  
1699 S. Hanley Road  
St. Louis, MO 63144

The CoMFA technique has proven to be an extremely valuable tool in pharmaceutical research. The necessity of conformer generation and structural alignment in preparation for CoMFA makes use of the technique non-trivial. This is emphasised particularly for large datasets such as those now being generated by combinatorial chemistry and high throughput screening. Hologram QSAR (HQSAR) is a new technique which employs specialised fragment fingerprints (molecular holograms) as predictive variables of biological activity. By removing the necessity of molecular alignment, HQSAR models can be obtained much more rapidly making the technique readily applicable to both small and large datasets. HQSAR models are comparable in predictive ability to those derived from CoMFA studies and allow extension to database searching capability.

## Outer-sphere charge transfer transitions: MO approach

S. I. Gorelskii\*, V. Yu. Kotov, A. B. P. Lever

*Chemistry Department, York University,  
4700 Keele St., North York,  
Ontario, M3J 1P3*

A large amount of experimental data on the outer-sphere charge transfer (OSCT) transitions in ion associates has been collected and rationalised in the terms of the molecular-orbital approach. The quantum chemical method has been suggested for calculation the OSCT energies. There is a good agreement between the experimental and calculated OSCT energies (the average deviation is only 0.07 eV).

## Metal-ligand orbital mixing in Ru(II) diimino complexes

S. I. Gorelskii,\* E. S. Dodworth, A. B. P. Lever

*Chemistry Department, York University,  
4700 Keele St., North York,  
Ontario, M3J 1P3*

Electronic structure of Ru(II) diimino complexes has been studied by INDO/S-CI semiempirical method. Deviations from the standard relationship between metal-to-ligand charge-transfer energies and the difference in complex reduction and oxidation potentials arise from extensive metal-ligand orbital mixing in these systems. The traditional molecular orbital model introduced by Magnuson and Taube [J. Am. Chem. Soc., 1975, 97, 5129] does not appear to be accurate within terms of modern understanding of electronic structure of these complexes. The electron transition energies calculated by the INDO/S method agree well with the experimental data in solution.

# A new approach to local electron correlation using nonorthogonal orbitals

Martin Head-Gordon

*Department of Chemistry  
University of California, Berkeley  
Berkeley, CA 94720*

While there have been tremendous advances in the theory of electron correlation over the past several decades, one particular problem with standard many-body theory approaches is that their computational complexity increases in an unphysical way with the size of the molecule. This dependence typically goes as either the fifth, sixth or seventh power of the molecule size, and is a fundamental obstacle to applying these electron correlation methods to large molecules. Attempts to remedy this problem typically seek to describe electron correlations in terms of spatially localized functions, such as localized MO's.

We have developed a new approach to local electron correlation, which is based on applying techniques of tensor analysis to many-body theory. The keystone of the new formalism is that the tensor approach permits the use of sets of nonorthogonal functions to describe the occupied and virtual subspaces, which can be redundant. This opens the door for the first time to formulate electron correlation theories entirely in terms of local atom-centered quantities. Since the tremendous efficiency of simpler mean-field methods arises from using local atom-centered functions this is a potentially significant development.

To develop practical theoretical models for local electron correlation from this formalism is the next step, which we have now completed at the level of second order Moller-Plesset (MP2) theory. Our new local MP2 method will be discussed and assessed in this talk. In particular, I shall discuss and highlight the following key features:

- 1) Occupied and virtual functions are described by nonorthogonal atomic functions, which in the first implementation are simply projected atomic orbitals.
- 2) The normally quartic number of MP2 double excitations are reduced to a number which is strictly quadratic by a covalent diatomic ansatz. Retained substitutions are the direct product of an intra-atomic excitation from an occupied to a virtual function on one atom, with a similar excitation on another atom.
- 3) The inherent computational complexity of conventional MP2 theory is reduced from quintic in molecular size to cubic in this new approach.
- 4) Unlike previous local MP2 models (which were not fully atom-centered), our method is non-iterative, just like conventional MP2.
- 5) In initial tests, recovery of the canonical MP2 correlation energy is in the vicinity of 99.9%.

# Quantum theoretical studies of the quadrupole moments of polycyclic aromatic hydrocarbons: Applications to chromatography

George L. Heard\* and Russell J. Boyd

*Department of Chemistry,  
Dalhousie University  
Halifax, NS B3H 4J3*

The molecular quadrupole moment is the first non-vanishing multipole moment of many polycyclic aromatic hydrocarbons (PAHs), and is hence an important quantity in electrostatically-driven phenomena such as aromatic stacking, enzyme-substrate binding and solid-liquid phase equilibria.

A variety of *ab initio* and DFT techniques using a series of basis sets as large as aug-CC-PVTZ have been considered in the calculation of the quadrupole moment of benzene and naphthalene. It is shown that hybrid functionals (incorporating Becke's three-parameter exchange functional with gradient-corrected correlation functionals) and a large basis set compute quadrupole moments which are within experimental error.

The quadrupole moments calculated using density functional theory for PAHs up to four rings in size are presented, and their relationship to the retention factor on a dinitrobenzene column is shown. There is excellent correlation between the quadrupole moment and the log of the retention factor (which is proportional to the binding energy between the PAH and the dinitrobenzene). This indicates that the quadrupole moment can be used as a predictive tool in determining the retention factor of polycyclic aromatic hydrocarbons.

High performance computing in computational  
chemistry

James Himer

*Sun Microsystems of Canada  
SunLife Plaza III 9th Floor  
112 - 4th Ave SW  
Calgary, AB, T2P 0H3*

Multireference based perturbation theory:  
Accuracy and interpretation

Kimihiko Hirao,\* Haruyuki Nakano, Tomohiro Hashimoto,  
Kenichi Nakayama, and Yukio Kawashima

*Department of Applied Chemistry,  
Graduate School of Engineering,  
The University of Tokyo, Tokyo, Japan 113*

Multireference Møller-Plesset perturbation theory (MRMP) provides a powerful framework for accurate, correlated quantum chemical calculations. MRMP has proven to be especially useful in application calculations of potential energy surfaces of chemical reactions and molecular electronic excited states. Illustrative and chemically interesting examples will be presented.

# Molecular dynamics simulations of the c(4x2) superstructure of octanethiol adsorbed on Au(111)

A. Jakalian\* and D.B. Jack

*Dept. of Chemistry and Biochemistry, Concordia University,  
1455 de Maisonneuve Blvd. W., Montreal, QC, H3G 1M8.*

Results of a computational study of the structure and orientation of octanethiols adsorbed on a Au(111) surface are presented. In particular, at full monolayer coverage, our simulations show that the molecules form a c(4x2) superstructure in agreement with He diffraction work (Camillone et al.) and STM imaging (Poirier et al.). Our MD simulations demonstrate that the c(4x2) superstructure arises mainly from chain-chain interactions. Two distinct molecular orientations with differing heights above the surface are present. The molecules are tilted towards their next-nearest-neighbor at an angle of 33 degrees from the surface normal and are twisted by approximately 90 degrees relative to each other. The molecular dynamic simulations were performed using a modified version of AMBER which included molecule-surface interactions. All-atom potentials which contain various bonding, electrostatic, van der Waals and surface interaction (including corrugation) terms were used. Point charges located on atomic sites were derived with the RESP methodology (Bayly et al.).



# Wavefunctions directly from experiment

Dylan Jayatilaka

*The University of Western Australia  
Department of Chemistry  
Nedlands 6009  
Australia*

The problem of extracting a reasonable wavefunction directly from experimental measurements has had a long history. In this poster we describe a procedure to extract a single determinant wavefunction from X-ray charge density structure factors. The orbitals obtained are either viewed as approximate Kohn-Sham-Wannier orbitals or as Hartree-Fock orbitals constrained to give the experimental charge density to a prescribed accuracy. Unlike previous work, the problem of having sufficient experimental data does not arise.

The method is applied to Beryllium metal. Observed experimental features are reproduced. From our fitted wavefunction we can extract the binding energy of the crystal and the workfunction, which are both in qualitative agreement with independent experiments.

We also present density plots for an experimental wavefunction for oxalic acid dihydrate. It is observed that hydrogen bonding in the crystal environment is enhanced compared to a supermolecule described by the SCF approximation.

# Electron Spin Resonance $g$ tensor calculations

Dylan Jayatilaka

*The University of Western Australia  
Department of Chemistry  
Nedlands 6009  
Western Australia*

Little attention has been given to calculating the  $g$  tensor, which is a basic property for radicals defining the magnetic moment of a molecule in an applied external magnetic field.

In this poster we outline a new way to calculate the  $g$  tensor as a derivative of the energy. Interestingly, the formula involves derivatives of the square of the energy. A General Hartree Fock method is implemented to deal non-perturbatively with the required one and two electron spin-orbit interactions.

We will present results for selected molecules, including the ion  $\text{CoCl}_4^{2-}$ .

Condensed phase reaction dynamics:  
Simulating events that occur once in a blue moon

Raymond Kapral

*Chemical Physics Theory Group  
Department of Chemistry  
University of Toronto  
Toronto, ON M5S 3H6*

Methods used to simulate classical, rare, reactive events in condensed phases will be described. This will serve as an introduction to the main topic: the simulation of non-adiabatic dynamics in mixed quantum-classical systems. An outline of the approximations needed to arrive at the equations of motion will be given, along with the computational schemes that are used to simulate the dynamics. Applications to proton transfer and electron diffusion will be described.

# Statistical theory of atomic and molecular spectra

Jacek Karwowski

*Instytut Fizyki*  
*Uniwersytet Mikołaja Kopernika*  
*Grudziądzka 5, 87-100 Toruń*  
*Poland*

Studies of the eigenvalue spectrum of a Hamiltonian in a finite-dimensional model space belong to the most common tasks of computational chemistry. In the traditional approach to the problem, the individual eigenvalues are evaluated either by diagonalizing the Hamiltonian matrix or by using approximate methods to estimate the locations of the eigenvalues of interest. This approach is most useful when only a few eigenvalues are needed, as it is in the case of electronic molecular states. If the number of energy levels is very large, as e.g. in spectra of molecular vibrations or of complex atomic configurations, this approach becomes prohibitively inefficient. In such a case the set of eigenvalues may be treated as a statistical ensemble and its description may be derived from a knowledge of the spectral density distribution moments, closely related to the traces of powers of the Hamiltonian matrix. The resulting approach is often referred to as *statistical spectroscopy*. Spectra of atoms and of nuclei, spectral distributions of eigenvalues of some model Hamiltonians, vibronic spectra of molecules belong to the areas where the statistical spectroscopy is useful. Problems handled by this theory are, in most cases, complementary to those studied within the traditional approach. The global description of a spectrum frequently reveals new features and characteristics.

In this presentation several applications of methods of statistical spectroscopy to solving some problems of computational chemistry are reviewed. In particular methods in which, from a knowledge of appropriate moments, one may determine the envelopes of bands in molecular spectra, spectral density distributions and, finally, locations of individual energy levels, are discussed. Some rather exotic problems, like searching for the quantum chaos or for some hidden constants of the motion using methods of statistical spectroscopy are also addressed.

# Density functional study of nuclear magnetic resonance spin-spin coupling constants

J. Khandogin\* and T. Ziegler

*Department of Chemistry,  
University of Calgary,  
T2N 1N4 Calgary, Alberta, Canada*

The NMR spin-spin coupling constants for first row transition metal systems have been studied using the perturbed Density Functional method. The results for  $^1J(\text{M-C})$  and  $^1J(\text{M-O})$  couplings are presented. The MO analysis shows that the core orbitals of the light atom play a dominant role while contributions from the core part of the heavy atom are in most cases negligible. Further studies using frozen core approximation conform this relationship. Indeed, by applying the frozen core and quasi-relativistic method the calculations of coupling constants for some third row transition metal systems yield very good results.

## Applications of density functional molecular dynamics in homogeneous catalysis

Peter M. Margi,\* Tom Ziegler, Tom K. Woo and Liqun Deng

*Department of Chemistry,  
University of Calgary,  
T2N 1N4 Calgary, Alberta, Canada.*

Recent developments in the area of density-functional molecular dynamics have made it possible to study the sub-picosecond, nano-scale dynamics of homogeneous catalytic reactions on a first-principles level. In this talk, we describe how we incorporate Car-Parrinello molecular dynamics simulations into our quantum chemist's toolbox and present recent results derived from simulations of several catalytic organometallic reactions. We will also analyse how they match up against conventional ("static") DFT calculations both in terms of accuracy and scientific content. We demonstrate for a number of chemical systems of current interest that first-principles molecular dynamics is not only a viable alternative to conventional methods but also considerably extends our reach into the realm of sub-picosecond events.

Density functional study of the [2+2] addition of  
ethylene to the Mo=E bond in Mo(E)(O)Cl<sub>2</sub>  
(E = O, NH, CH<sub>2</sub>)

Kereen Monteyne\* and Tom Ziegler

*Department of Chemistry  
The University of Calgary  
T2N 1N4*

The [2+2] addition of ethylene to the Mo=E bond in Mo(E)(O)Cl<sub>2</sub> for E = O, NH, CH<sub>2</sub> was studied using density functional theory (DFT). All stationary points have been characterized for each choice of ligand E. The reaction was seen to be endothermic for the case of E=O with  $\Delta H_{rxn} = 12.0$  kcal/mol and had a high activation barrier of 26.7 kcal/mol. In the cases of E=NH and CH<sub>2</sub>, the reaction enthalpies were -0.8 kcal/mol and -15.6 kcal/mol, respectively. The amide had an activation barrier of 21.0 kcal/mol while the carbene had a small barrier of only 4.4 kcal/mol. The [2+2] reactions were further studied using the intrinsic reaction coordinate (IRC) method to determine the geometric changes along the cycloaddition path.

A search for a calculational method for the reliable prediction of the first adiabatic and vertical ionization potentials of carbenes.

H.M. Muchall,\* N.H. Werstiuk\* and B. Choudhury

*Department of Chemistry  
McMaster University  
Hamilton, ON L8S 4M1, Canada*

For photoelectron (PE) spectroscopic studies, carbenes have been generated in the gas phase from suitable precursors by techniques such as pyrolysis. Because other primary and secondary products are likely to produce a complex PE spectrum and make the carbene's detection difficult, it is imperative to have a procedure which allows easy, accurate prediction of its first ionization as this is the most likely not to be covered by other ionizations.

We have calculated the first adiabatic and vertical ionization potentials (IPs) for eight carbenes - whose PE spectra are available - using *ab initio* methods and have compared them to those taken from the PE spectra to evaluate their quality. We have found that Becke3LYP gives excellent predictions for both adiabatic and vertical IPs even for relatively big carbenes in a reasonably short time. Experimental data for two stable carbenes is given for the first time.



# Computer simulation studies of fluids with interesting phase transitions

Gren N. Patey

*Department of Chemistry  
University of British Columbia  
Vancouver, BC, V6T 1Z1*

The talk will focus upon computer simulation studies of interesting phase transitions. Monte Carlo methods which are convenient for investigating phase transitions will be briefly described. Phase transitions (or their absence where expected in some cases) in dipolar systems and model liquid crystals will be considered in some detail. Field induced transitions in electrorheological fluids will also be discussed.

An *ab initio* study of *cis*-5,6-disubstituted  
cyclohexadienes.

Cory C. Pye,\* Raymond A. Poirier, D. Jean Burnell,  
Dieter Klapstein

*Department of Chemistry*  
*Memorial University of Newfoundland,*  
*St. John's NF A1B 3X7*

Several *cis*-5,6-disubstituted 1,3-cyclohexadienes have been studied. A full comparison between experimental and theoretical structures and inversion barriers is made for 1,3-cyclohexadiene. The effect of basis set and conformation on the structure of *cis*-3,5-cyclohexadiene-1,2-diol is discussed. The predicted and actual photoelectron spectra are compared for several diol derivatives. A correlation between the square of the twisting mode frequency and the C-O-X angle is noted. The Diels-Alder transition states of cyclohexadiene with ethylene and acetylene are compared.

Geometry optimization in *ab initio* theory.  
Part II. Natural internal coordinates

Cory C. Pye,\* Raymond A. Poirier

*Department of Chemistry,  
Memorial University of Newfoundland,  
St. John's NF A1B 3X7*

A connectivity-based scheme for generating natural internal coordinates for use in optimization is presented. The flexibility in the connectivity definition allow for easy customization of the coordinates. An efficient graph theoretical algorithm for finding rings, and thus ring coordinates, is given. Coordinates for fused polycyclic ring assemblies and weakly interacting complexes are suggested. Some general observations of Z-matrix and natural internal coordinate optimizations are discussed. The coordinate generation is mostly automatic and implemented in our *ab initio* program MUNGAUSS. [R. A. Poirier, Y. Wang and C. C. Pye, MUNGAUSS 1.0, (OSIPE Version), Chemistry Department, Memorial University of Newfoundland, St. John's, Newfoundland, Canada; F. Colonna, L.-H. Jolly, R. A. Poirier, J. G. Ángyán, G. Jansen, *Comp. Phys. Comm.*, **81**, 293 (1994)]

# An implementation of the COSMO solvation model in the density functional package ADF

Cory C. Pye,\* Yunzhu Han, and Tom Ziegler

*Department of Chemistry,  
The University of Calgary,  
Calgary, Alberta T2N 1N4*

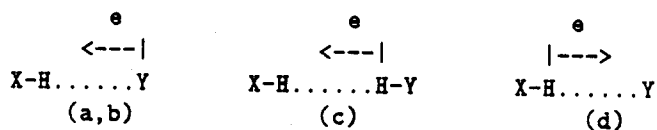
An implementation of the Conductorlike Screening Model (COSMO) within the ADF density functional package is presented. The COSMO theory [A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 799 (1993)] treats the solute as being embedded in a cavity surrounded by a solvent of dielectric  $\epsilon$ . The induced charges  $q$  are found by solving a linear equation, assuming a conductor-like solvent response, followed by a dielectric-dependent scaling. The cavity can be generated as either a van der Waals, solvent-excluding, or solvent-accessible surface. Features of our implementation include the iterative solution of the COSMO equation and the use of an adaptive disc potential to avoid singularities during numerical integration.

## Inverse hydrogen-bonded complexes

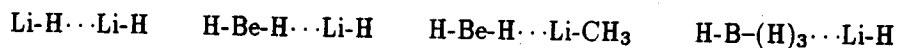
Isabel Rozas,\* Ibon Alkorta and Jose Elguero

*Instituto de Química Médica (C.S.I.C.)*  
*c/ Juan de la Cierva 3,*  
*28006-Madrid*  
 SPAIN

Most published works of hydrogen bonds (HBs) are of the type O-H...B or N-H...B in which the HB acceptor 'B' possesses O or N lone pairs responsible for the HB formation. These classical HBs have been generalized in other directions such as: a) HBs with unconventional H donors such as C-H, b) HBs with unconventional H acceptors as (pi)-bonded functional groups, halogens or C atoms, and c) dihydrogen bonds X-H...H-Y. In the HBs aforementioned, the H atom plays the role of electron acceptor, except for type c) (dihydrogen bonds) where one of the H atoms accepts the electrons while the other provides them. Following this sequence we propose the study of a new class of unconventional HBs (type d) where the H atom will provide electrons and another non-hydrogen atom will accept them.



Thus, a theoretical study of the linear and multiple approximation in a series of complexes formed by molecules with electron-rich hydrogen atoms and electron-poor heavy atoms (LiH, LiCH<sub>3</sub>, BeH<sub>2</sub>, BH<sub>4</sub><sup>-</sup>, LiF and BeF<sub>2</sub>) has been carried out. The interaction energy (taking into account the zero point energy and the basis set superposition error), the atomic charges and the electron density of the monomers and complexes have been evaluated at MP2/6-311++G\*\* level. The linear complexes (see below) which show a strong similarity with the standard hydrogen bonds except for the reverse direction of the electron transfer, could be defined as inverse HBs and the nature of these interactions has been verified to be that of a HB given their geometric, electronic and energy features.



Origin of the hydridic  $^1\text{H}$  NMR chemical shift  
in low valent transition metal hydrides  
and the calculation of  $^{125}\text{Te}$  chemical shifts  
using gauge including atomic orbitals  
and density functional theory.

Yosadara Ruiz-Morales,\* Georg Schreckenbach and Tom Ziegler.

*Department of Chemistry, University of Calgary  
2500 University Drive, N.W. Calgary, Alberta, Canada, T2N 1N4*

We will present the results from theoretical studies of the  $^1\text{H}$  NMR chemical shifts in low valent transition metal hydrides and calculations of  $^{125}\text{Te}$  nuclear magnetic resonance chemical shifts of a number of organic, inorganic and organometallic tellurium-containing complexes, both studies based on density functional theory and gauge-including atomic orbitals (DFT-GIAO). Calculations have been carried out on the representative hydrides  $\text{HM}(\text{CO})_5$  ( $\text{M} = \text{Mn}, \text{Tc}, \text{Re}$ ),  $\text{H}_2\text{Fe}(\text{CO})_4$ ,  $\text{HCo}(\text{CO})_4$ ,  $[\text{HCr}(\text{CO})_5]^-$ , and  $[\text{HCr}_2(\text{CO})_{10}]^-$ . In general, the calculated chemical shifts are in good agreement with the available experimental data. The paramagnetic and diamagnetic contributions to the  $^1\text{H}$  chemical shielding have been analyzed in detail. Our calculations show that the paramagnetic current localized in the adjacent metal fragment,  $\text{ML}_n$ , is responsible for the negative 'hydridic' shift observed in transition metal hydrides  $\text{H-ML}_n$ .

The calculated Te-containing systems cover almost the complete spectrum of known  $^{125}\text{Te}$  chemical shifts with a range of about 3000 ppm. It is concluded that the DFT-GIAO method is able to reproduce the observed trends in  $^{125}\text{Te}$  chemical shifts for organic, inorganic and organometallic tellurium containing compounds.

# Recent developments in non-singular two-component relativistic theories

Andrzej J. Sadlej

*Theoretical Chemistry*  
*Chemical Center*  
P.O.Box 124, S-221 00 Lund  
Sweden

The majority of relativistic effects relevant for chemistry of heavy atoms and molecules can be well described in terms of what is known as the two-component approximation for single-particle wave functions. As long as the genuine quantum electrodynamic effects can be neglected, the two-component theories can be considered as a hidden way of handling the 'small' component of 4-spinors. The corresponding methods range from the Pauli approximation to more advanced theories which follow from the use of different (approximate) unitary transforms of the Dirac hamiltonian. Their usefulness is largely determined by analytic features of the respective two-component hamiltonians.

Different methods for the reduction of the 4-component formalism in relativistic quantum chemistry are reviewed [1,2,3]. Particular attention is given to methods leading to *non-singular* two- and one-component relativistic hamiltonians which can be used in the framework of variation techniques. The analysis of the so-called Douglas-Kroll approximation [1,2] indicates the possibility of an alternative approach and brings about a series of two-component relativistic hamiltonians [4] of increasing accuracy in the fine structure constant  $\alpha$ . In comparison with other methods currently in use the present approach is manifestly open-ended. Moreover, increasing the order of accuracy with respect to  $\alpha^2$  does not essentially affect the computing times. Several formal and computational aspects of the derived two-component hamiltonians will be discussed.

---

[1] M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).

[2] J. Sucher, *Phys. Rev. A* **22**, 348 (1980).

[3] E. van Lenthe, R. van Leeuwen, E. J. Baerends and J. G. Snijders, *Int. J. Quantum Chem.* **57**, 281 (1996), and references therein.

[4] M. Barysz, A. J. Sadlej, and J. G. Snijders, *Int. J. Quantum Chem.*, in the press.

# Density functionals in the hydrogen-bonding arena

Dennis R. Salahub

*Departement de Chimie, Universite de Montreal, C.P. 6128, Succursale  
Centre-ville, Montreal, Quebec H3C 3J7, CANADA*

*and*

*CERCA - CEntre de Recherche en Calcul Applique, 5160, boul. Decarie,  
bureau 400, Montreal, Quebec, H3X 2H9 CANADA*

Over the last few years, Density Functional methodology and computer programs have improved to the point where they are now very serious contenders for the first-principles description of complex hydrogen-bonded systems. In this lecture, an overview of Kohn-Sham DFT and its Gaussian implementation, deMon-KS, will be given. The performance of various functionals will be put in perspective with that of traditional correlated quantum chemical methods. Emphasis will be placed on results from the Generalized Gradient Approximation and from the newer LAP correlation functionals which are the most accurate at this moment. Validation systems will include simple dimers and complexes, the intramolecular hydrogen bonds that determine the delicate conformational balance in gas-phase glycine, the tautomeric structure of malonaldehyde, and the proton-transfer barrier in this latter system.

DFT calculations using deMon-KS and other tools can now be applied with reasonable confidence to a wide variety of complex systems and models. Current and future possibilities will be discussed using as examples some of the following:

- The structure and vibrational frequencies of hydrated proton clusters, containing up to eight water molecules. Structures have been found by using a variant of simulated annealing, using the forces from deMon-KS calculations.

- Very large cooperative hydrogen-bonding effects (nonadditivities) have been found in biochemical models involving negative ions (carboxylates) interacting with polarizable groups (histidine residues, peptide links). The case of the enzyme TIM (Triosephosphate Isomerase) will be discussed as an illustration.

- NMR chemical shifts provide a very sensitive probe of the interactions such as those in TIM. Models of the serine proteases are shedding light on the role of strong hydrogen bonding involving ions in enzymatic catalysis.

- For systems of modest size (15 or 20 atoms) it is possible to perform short Molecular Dynamics simulations using the forces from deMon-KS, thus avoiding empirical potentials. We have performed such simulations for an alanine dipeptide model. Comparisons with simulations using standard nonpolarizable force fields are providing insight into the limitations of such approaches and will, hopefully, help to formulate improvements.



Molecular anions:  
A wealth of important, uncharacterized systems

H. F. Schaefer III

*Center for Computational Quantum Chemistry  
University of Georgia  
Athens, GA 30602-2556*

As a general rule, molecular negative ions are far more difficult to characterize experimentally than are either neutral molecules or positive molecular ions. Traditionally, negative ions have proven equally treacherous for theoretical methods. However, the use of high level theoretical methods, for example coupled cluster theory or Brueckner theory, in conjunction with large basis sets, allows truly quantitative predictions for small molecular anions. A careful assessment has also been made of the reliability of theoretical methods that are applicable to much larger anions. Formal (i.e. mathematical) objections to the application of density functional methods to negative ions are examined. It is concluded that recent theoretical advances now make reliable predictions possible for molecular anions as large as  $C_{60}^-$ , but with no requirements of high symmetry.

# Orthogonal polynomials from atomic charge densities

Hartmut Schmider\* and Robin P. Sagar

*Department of Chemistry, Queen's University,  
Kingston, Ontario, CANADA K7L 3N6*

Orthogonal polynomials may be constructed with respect to any positive integrable weight function, using techniques such as the discretized Stieljtes procedure. These polynomials provide powerful tools for numerical analysis. In this work, we suggest the construction of such polynomials using atomic charge densities as the weight functions. The resulting functions serve a twofold purpose: their properties provide a means of characterizing the underlying densities, and their nodal structure allows the construction of "tailored" Gaussian quadratures specific for that atomic density. Convergence studies indicate that although such quadratures achieve a relatively high degree of accuracy with a very small number of points, a greater degree of precision does not seem to be attainable with higher order quadratures. Reasons for this behavior are given and we address the problem by "smoothing" the weight function beforehand and limiting the integration range. Such a procedure yields atom-specific radial quadrature rules that may be used for numerical integrations of charge-density related quantities, e.g., in the framework of Density Functional Theory. We assess the performance of these rules on simple test systems.

# Gaussian-type geminal basis sets in quantum chemical calculations

Peter R. Taylor,\* B. Joakim Persson, and Pål Dahle

*Department of Chemistry and Biochemistry  
University of California, San Diego*

*and*

*San Diego Supercomputer Center  
P. O. Box 85608, San Diego, CA 92186-5608*

We have begun to explore the use of two-electron basis functions to augment traditional one-electron basis sets in the calculation of correlation energies. The two-electron functions have a Gaussian dependence on the interelectronic distance — the so-called Gaussian-type geminals. We show that only a few such Gaussian correlation factors are necessary to drastically reduce the error in the correlation energy obtained with orbitals alone.

Predicting kinetics of chemical reactions  
from first principles: A robust and practical  
*ab initio* direct dynamics methodology

Thanh N. Truong

*Department of Chemistry*  
*University of Utah*  
*Salt Lake City, Utah 84112*  
*USA*

One of the most severe limitations for quantitative predictions of thermal rate constants of polyatomic reactions is the availability of accurate potential energy functions. *Ab initio* direct dynamics approach circumvents this problem by calculating potential energy information needed for the dynamics directly from electronic structure theories. Progress in our efforts to develop a robust methodology for predicting accurate thermal rate constants of chemical reaction from first principles will be presented. Applications to several important gas-phase processes will also be discussed.

# First Principles calculations of the electronic and structural properties of condensed matter

John S. Tse

*Steacie Institute for Molecular Sciences  
National Research Council of Canada  
100 Sussex Drive  
Ontario K1A 0R6  
Canada*

Recent advances in the First Principles plane-wave based density functional computational methods now enable the study of the electronic structure, structural stability and dynamical properties of large crystalline solids. In this presentation, the capabilities of these new techniques are demonstrated through several applications related to material research. The optimization of crystal structures and the molecular dynamics simulations and the mechanism for pressure-induced transformations in silica systems will be discussed. The electronic and optical properties of encapsulated metal and semiconductor clusters in zeolites will be presented.

# Quantum mechanical evaluation of the anodic oxidation of phenolic compounds

A. Haemers,<sup>a</sup> J. Tollenaere,<sup>b</sup> and I. Vedernikova<sup>a\*</sup>

<sup>a</sup>Department of Pharmaceutical Chemistry, Universiteitplein 1,  
Universitaire Instelling Antwerpen, Antwerpen 2610, Belgium;

<sup>b</sup>Janssen Research Foundation, Turnhoutseweg 30, Beerse 2340, Belgium.

Oxidation and reduction processes are very important in biochemistry and medicine. Phenolic compounds can interfere with these redox reactions and are interesting tools in biochemical studies or as antioxidant in medicine. The oxidation potential of some phenolic compounds correlate well with their antioxidant activity [1-3].

In order to study the antioxidant activity of a series of phenols we investigated the correlation between their halfpeak oxidation potential ( $E_p/2$ ) and some theoretical parameters.

As mechanism for the anodic oxidation of phenolic compounds we suggest an electron abstraction followed by proton loss (single electron transfer).

All calculations were performed with the semiempirical AM1 method in the MOPAC 6.0 software [Stewart] in InsightII. The geometry of the parent compounds, their cation-radicals and radicals are optimized using UHF followed by RHF calculation.

Correlations of  $E_p/2$  with different parameters are discussed:

1. The ionization potential as ability of phenol to donate electrons.
2. Absolute electronegativity as indicator for Lewis acid strength and hardness.
3. The energy of activation corresponding to the intermediate cation-radicals and relative stability of the formed free radicals.
4. The comparison of molecular diagrams of HOMO and SOMO of neutral and radical forms.
5. The spin densities of the intermediate cation-radicals and the phenoxy radicals.

---

[1] V. Misik; K. Ondrias.; D. Gergel; D. Bullova; V. Suchy; M. Nagy.; *Fytoterapia*, 62, 215-220 (1991).

[2] S.A.B.E. van Acker, L.M.H. Koymans and A. Bast, *Free Radical Biology & Medicine*, 15, 311-328 (1993).

[3] K. Mukai; K. Fukuda K. Tajima; K. Ishizu, *J. Org. Chem.* 53, 430-432 (1988).

# Theoretical study of oxygen fluorides

Oscar N. Ventura

*MTC-Lab,  
Universidad de la Republica  
CC 1157, 11800 Montevideo  
Uruguay*

The recently recommended NIST-JANAF values for the thermochemical properties of oxygen fluorides are examined critically on the basis of high level density functional and ab initio G2 calculations. Especial attention is given to the heats of formation, and it is concluded that, although the proposed values for OF(g), FOO(g) and FOF(g) are reasonable and in agreement with our previously recommended values [Chem. Phys. Letters 245 (1995) 488], the heat of formation recommended for FOOF is too low. A value about 50% larger is proposed, and it is recommended that the original, 1959 experimental determination of this heat of formation be reexamined.

# Applications of large scale computational techniques to the design of neurologic drugs

D. Weaver

*Departments of Chemistry and Medicine (Neurology)  
Queen's University  
Kingston, Ontario, K7L 3N6*

Large scale computational techniques are used to develop therapeutics for epilepsy and Alzheimer's dementia. Epilepsy affects 1.2% of the general population. Using semi-empirical molecular orbital calculations, 40 hydantoins, 36 barbituates, 45 oxazolinediones and 48 succinimides were studied for anticonvulsant activity. Using these results, a pseudoreceptor model was devised for the receptor site on the sodium channel protein. These calculations are augmented by empirical calculations on the Na<sup>+</sup> channel protein. Alzheimer's Disease affects 15% of the population greater than 65 years. Modeling of the  $\beta$ -amyloid peptide suggests mechanisms of toxicity and potential therapeutic approaches.



# A computational study of nitrogen heterocyclic compounds: Molecular mechanics, *ab initio* and semi-empirical calculations

M.A. Whitehead\* and C.I. Williams

Quantum Theory Laboratory,  
Chemistry Department,  
McGill University,  
801, Sherbrooke Street West,  
Montreal, Quebec, H3A 2K6

The structures, energies and reactivities of nitrogen containing heterocyclic compounds were studied using a selection of computational methods.

A method to calculate azole, azine and benzoazole heats of formation using *ab initio* total energies and isolobal reaction schemes was developed, to give heats of formation within 0-4 kcal/mol of the experimental values. Systematic errors in the semi-empirical MNDO, AM1 and PM3 heats of formation of azoles, azines and benzoazoles are discussed, and correction terms suggested. Pentazole, pentazine, hexazine, pyrazepine, indazine, purine, azolotriazine and diazoazole heats of formation were then predicted. Isocyanate equilibrium geometries calculated with these semi-empirical and *ab initio* methods were compared to the experimental values.

The cycloaddition reaction of isocyanates with alkenes was modelled using MNDO, AM1 and PM3 semi-empirical methods. Localized bonding in diazoazole ring systems, and flexibility in the diazo group C=N=N bond angle were demonstrated. Thermolytic and photolytic 4-diazo-1,2,3-triazole reaction products were then predicted by comparing the computed relative energies of the azolydene intermediate singlet and triplet states.

Possible mechanisms for diazoazole cycloaddition reactions with ethyne, ynamine and cyanoethyne are discussed and modelled with these semi-empirical methods. The regio-specificity of diazoazole cycloaddition reactions with ynamine, and the lack of diazoazole cycloaddition with cyanoethyne, are predicted and correlated with experimental results.

Molecular Mechanics (MM+), used throughout to calculate starting geometries in all calculations, semi-empirical and *ab initio* methods were used to generate benztetrazepinone equilibrium geometries. The racemization of chiral benztetrazepinone occurs through a concerted mechanism involving a chiral transition state.

Mechanisms for the acid-induced ring opening of benztetrazepinone (BTZ) are proposed and investigated using the PM3 semi-empirical method. The computational results are compared with UV/VIS spectral evidence for the ring-opening. The tendency for benztetrazepinone to ring open is correlated with the Hammett constants of the aryl-ring substituents using PM3 relative energies. The pKa of protonated benztetrazepinone is estimated.

# The inclusion of spin-orbit and Fermi-contact in a DFT calculation of NMR shielding tensors.

S. K. Wolff,\* T. Ziegler, and G. Schreckenbach

*Department of Chemistry  
The University of Calgary  
Calgary, Alberta, Canada T2N1N4*

The inclusion of spin-orbit and Fermi-contact into a DFT calculation of NMR shielding tensors has been formulated and is currently being implemented within the framework of the ADF package [1]. This work is an extension of G. Schreckenbach and T. Ziegler's scalar-relativistic DFT calculations of NMR shielding tensors [2]. The formulation of the theory together with the method of implementation is presented here.

- 
- [1] Amsterdam Density Functional (ADF), Version 2.0.4, Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands; <http://tc.chem.vu.nl/SCM/>  
[2] G. Schreckenbach and T. Ziegler, *J. Phys. Chem.* 1995, 99, 606-611

## Brownian dynamics simulations of the ionic atmosphere of biomolecules

Wenbin Yu,<sup>a†</sup> Chung F. Wong,<sup>a\*</sup> and John Zhang<sup>b</sup>

<sup>a</sup>*Department of Physiology and Biophysics,  
Mount Sinai School of Medicine, New York, NY 10029-6574.*

<sup>b</sup>*Department of Chemistry, New York University, NY, NY 10003.*

<sup>†</sup>*Current address: Photon Research Associates, Inc.,  
1911 N Fort Myer Dr., Ste. 408, Arlington, VA 22209.*

Since it is very expensive to carry out molecular dynamics simulations with explicit-solvent models to study the ionic atmosphere of biomolecules, we have explored the use of the Brownian dynamics simulation method in studying the distribution and dynamics of ions surrounding biomolecules, using a 13-residue polyalanine as a test case. We found that a very large nonbonded cutoff was needed to give reliable structural and dynamical properties of the ionic atmosphere around the polypeptide. At a NaCl concentration of 0.1 M, a long microsecond-simulation was required to give reliable statistics for studying the ion distribution around the polyalanine at resolution comparable to the size of the ions. Preferential binding of sodium ions was also observed and the degree of this preferential binding was found to depend on the conformation of the polyalanine and the ion concentration.

# Density functional calculations of $^1\text{H}$ and $^{15}\text{N}$ chemical shifts in the catalytic triad of serine proteases

Michaela Flock,<sup>a†</sup> Chung F. Wong,<sup>b\*</sup> Hong Guo,<sup>a</sup> and  
Dennis Salahub<sup>a</sup>

<sup>a</sup>*Département de chimie, Université de Montréal,  
Montréal, Québec, Canada H3C 3J7.*

<sup>b</sup>*Department of Physiology and Biophysics,  
Mount Sinai School of Medicine, New York, NY 10029-6574.*

<sup>†</sup>*Current address: Department of Chemistry, Catholic University of Leuven,  
Belgium*

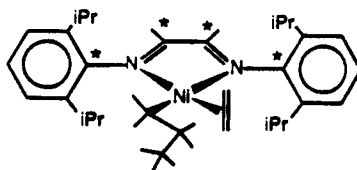
Sum-over-states density functional perturbation theory has been used to study the contributing factors to the  $^1\text{H}$  and  $^{15}\text{N}$  shifts of the catalytic histidine of serine proteases. The interactions among the three residues of the catalytic triad appear to account for most of these shifts; the environment of the catalytic triad has little influence on these shifts. The relative  $^{15}\text{N}$  shift between the two nitrogens in the catalytic histidine agrees well with experimental measurement. However, the  $^{15}\text{N}$  absolute shifts differ from the experimental values by  $\sim 20$  ppm. We have therefore carried out additional calculations on  $\text{CH}_3\text{NO}_2$  and N-methylacetanilide using the IGLO and GIAO methods with several exchange-correlation functionals in order to identify a better computational model for calculating  $^{15}\text{N}$  shifts.

# A combined QM/MM *ab initio* molecular dynamics simulations of transition metal catalysis

Tom K. Woo,\* Peter M. Margl, Liqun Deng, and Tom Ziegler

Department of Chemistry,  
University of Calgary,  
2500 University Drive N.W.,  
Calgary, AB, T2N 1N4,  
CANADA

In this paper, we will describe our implementation of a combined Car-Parrinello DFT and molecular mechanics method for the *ab initio* molecular dynamics simulations of large systems. We have applied the method to determine the free energy barrier of the chain termination in a Ni-diimine based ethylene polymerization catalyst, **1**. In this simulation the Ni diimine core was treated at the Becke88-Perdew86 DFT level while the large ortho substituted aryl rings were treated with a molecular mechanics force field (The atoms with the asterisk in structure **1** are the capping atoms). We have performed a 40000 time step (7 ps) simulation of the termination process at 300 K giving a free energy barrier of 15 kcal/mol which is in excellent agreement with the experimental termination barrier of 16 kcal/mol. Without the bulky aryl ligands, the analogous pure QM simulation provided a barrier of 9.7 kcal/mol.



**1**

# A theoretical study of the mechanism of hydroxylation in methane monooxygenase

Tom K. Woo,<sup>a\*</sup> Ann M. Valentine,<sup>b</sup> Stephen J. Lippard,<sup>b</sup>  
and Tom Ziegler<sup>a</sup>

<sup>a</sup> *Department of Chemistry,  
University of Calgary,  
2500 University Drive N.W.,  
Calgary, AB, T2N 1N4, CANADA*

<sup>b</sup> *Department of Chemistry,  
Massachusetts Institute of Technology,  
Cambridge, Massachusetts, 02139, USA*

Methane monooxygenase (MMO) is an enzymatic system which catalyzes the conversion of methane to methanol in methanotropic bacteria ( $\text{CH}_4 + \text{NADH} + \text{H}^+ + \text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{NAD}^+ + \text{H}_2\text{O}$ ). At the heart of the metalloenzyme is a non-heme diiron unit which reacts with oxygen through a series of discrete intermediates. These intermediates of the catalytic cycle have been defined to some extent by various biophysical techniques, but details of the mechanism of hydroxylation still remain elusive. With various model systems for the diiron core of the metalloenzyme, we have examined the intermediates and the hydroxylation mechanism with density functional theory.

# Dodecahedral molecular nitrogen ( $N_{20}$ ) and related structures

J.S. Wright,\* D.J. McKay, G.A. DiLabio

*Ottawa-Carleton Chemistry Institute,  
Department of Chemistry,  
Carleton University,  
Ottawa, ON, K1S 5B6*

The stability of a dodecahedral cage of nitrogen atoms ( $N_{20}$ , or "dodecahedrazane") is examined using semiempirical and density functional methods. In agreement with earlier work, it is shown that the nitrogen cage is stable in all vibrational modes. Protonation of the  $N_{20}$  structure allow hydrogen bonding with another similar unit, leading to the possibility of extended structures. Endohedral systems including an enclosed hydrogen atom, hydride ion and hydrogen molecule are all stable. Polymeric systems with covalent bonds can be built by substitution of CH for N and subsequent formation of an  $N_{19}C-CN_{19}$  linkage, and other organic connecting groups (acetylene, ethylene) also form stable structures. The fuel value of  $N_{20}$  to form dinitrogen is enhanced by recombination of trapped hydrogen in the cage. The decomposition barrier for  $N_{20}$  is studied along several symmetric paths, and suggests that these structures may be isolated experimentally. Several possible methods of synthesis are discussed.

# Effective medium theory including perturbation electron density changes

Liqu Yang,\* Thiele L. Wetzel, and Andrew E. DePristo

*Ames Laboratory,  
Iowa State University,  
Ames, Iowa 50011,  
U.S.A.*

A recent paper [1] presented an exact implicit Poisson equation for the spatial change in the system electron density from summed atomic Kohn-Sham densities. We have implemented the first-order perturbation solution for the change in density and the resultant change in interaction energies into the corrected effective medium (CEM) [2] theory. This new theory describes two bonding effects that were beyond the reach of the previous CEM theory: weak charge transfer and weak directional bonding. Results selected from the bulk structural energy differences, alloy heats of mixing, surface energies, surface diffusion barriers, and the energetics of small clusters will be discussed for a number of transition metals.

---

[1] A. E. DePristo, *Phys. Rev. A* **54**, 3863 (1996).

[2] A. E. DePristo, in *Recent Advances in Density Functional Theory*, edited by D. Chong (World-Scientific, Singapore, 1996), Vol. 1, Part 1, Chap. 6, pp. 193-218.



# Environmental effects on molecular electronic spectroscopy

Michael C. Zerner

*Quantum Theory Project  
University of Florida  
Gainesville, FL 32611*

We examine the effects that condensed phases have on the electronic spectroscopy of molecules and ions. We first examine the simple reaction field models that seem successful in estimating solvent shifts in very many systems, and that consider in a reasonably systematic way the electronic, polarization and dispersion effects.

We will examine the the spectroscopy of  $[\text{Ru}(\text{NH}_3)_5 \text{py}]^{2+}$  where the reaction field theory fails due to charge transfer. We will examine simulations that pick up the subtle red shifts associated, for example, with benzene in benzene liquid and benzene solid.

We will also discuss the emission spectroscopy of lanthanide ions in alkaline earth calcogin lattices in an attempt to predict the optical properties of potential flat screen display panels that depend on  $f \leftarrow d$  transitions. These systems are studied as large supermolecule containing many quantum chemical atoms embedded in a periodic lattice of point atoms.



Maria Barysz  
Institute of Chemistry  
Silesian University  
Szkolna 9, 40 006 Katowice  
Poland  
mb@tc3.ich.us.edu.pl

Christopher Bayly  
Merck Frosst Centre  
for Therapeutic Research  
P.O. Box 1005  
Pointe Claire-Dorval, QC, H9R 4P8  
Canada  
bayly@merck.com  
phone 514-428-3403  
fax 514-695-0693

Axel D. Becke  
Department of Chemistry  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
beckea@qucdn.queensu.ca  
phone 613-545-2634  
fax 613-545-6669

Peter Boyd  
Chemistry Department  
The University of Auckland  
Auckland  
New Zealand  
cheboyd@ccul.auckland.ac.nz  
phone 3737599 ext. 8283

Russell J. Boyd  
Department of Chemistry  
Dalhousie University  
Halifax, NS, B3H 4J3  
Canada  
boyd@ac.dal.ca  
phone 902-494-3707  
fax 920-494-1310

Dale R. Cameron  
Bio-Mega Research Division  
Boehringer Ingelheim (Canada) Ltd.  
2100 rue Cunard  
Laval, QC, H7G 2G5  
Canada  
dcameron@bio-mega.boehringer-ingelheim.ca  
phone 514 682-4640  
fax 514 682-8434

David A. Case  
Scripps Research Institute  
10666 N. Torrey Pines Rd.  
La Jolla, CA 92037  
U.S.A.  
case@scripps.edu  
phone 619-554-9768  
fax 619-554-6602

Anne M. Chaka  
Research Division  
The Lubrizol Corp.  
29400 Lakeland Blvd.  
Wickliffe, OH 44092-2298  
U.S.A.  
chaka@lubrizol.com  
phone 216-943-1200 ext. 2027  
fax 216-943-9020

Delano P. Chong  
2026 Main Mall  
Department of Chemistry  
University of British Columbia  
Vancouver, BC, V6T 1Z1  
Canada  
chong@chem.ubc.ca  
phone 604-822-5754  
fax 604-822-2487

James M. Coffin  
Scientific and Technical Computing Manager  
IBM Higher Education Industry Solution Unit  
1505 LBJ Freeway, 5th Floor  
Dallas, TX 75234  
U.S.A.  
jmcoffi@us.ibm.com  
phone (972) 432-9701

Maxwell D. Cummings  
Department of Biochemistry  
University of Alberta  
Edmonton, AB, T6G 2H7  
Canada  
max@crack.biochem.ualberta.ca

Thomas R. Cundari  
Department of Chemistry  
The University of Memphis  
Memphis, TN 38152  
U.S.A.  
cundarit@cc.memphis.edu  
phone 901-678-2629  
fax 901-678-3447

Alwin Cunje  
Department of Chemistry  
York University  
Toronto, ON, M3J 1P3  
Canada  
alwin@yorku.ca  
phone 416-736-2100 ext. 77839

Ernest R. Davidson  
Department of Chemistry  
Indiana University  
Bloomington, IN 47405  
U.S.A.  
davidson@indiana.edu  
phone 812-855-6013  
fax 812-855-8300

Stephen A. Decker  
Department of Chemistry  
University of Alberta  
Edmonton, AB, T6G 2G2  
Canada  
decker@jcvsparc.chem.ualberta.ca  
fax 403-492-3281  
phone 403-492-2546

Tom Dingle  
Department of Chemistry  
University of Victoria  
Box 3065  
Victoria, BC, V8W 3V6  
Canada  
chemgrad@uvvm.uvic.ca  
fax (250) 721-7147

Oreola Donini  
Department of Chemistry  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
oreola@chem.queensu.ca

Michel Dupuis  
Pacific Northwest National Laboratory  
EMSL / mail stop K1-90  
Battelle Blvd  
Richland WA 99352  
U.S.A.  
mdupuis@hondo.emsl.pnl.gov  
phone 509-375-6784

Ken Edgecombe  
Dept. of Computer and Information Science  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
edgecomk@qucdn.queensu.ca  
fax (613)542-2279  
phone (613)545-6000 ext.5710

Eva Fadrna  
Laboratory of Biomolecular Structure and Dynamics  
Faculty of Science  
Masaryk University  
611 37 Brno  
Czech Republic  
evaf@chemi.muni.cz  
fax +420-5-41211214  
phone +420-5-41129581

David F. Feller  
Pacific Northwest National Laboratory  
P.O. Box 999, K1-90  
Richland WA 99352  
U.S.A.  
d3e102@emsl.pnl.gov  
phone 509-375-6784

Joanne L. Gainsforth  
Department of Chemistry  
University of Alberta  
Edmonton, AB, T6G 2G2  
Canada  
joanne@om.chem.ualberta.ca  
fax 403-492-3281  
phone 403-492-2546

Dean Goddette  
Tripos, Inc.  
1699 S. Hanley Road  
St. Louis, MO 63144  
U.S.A.  
goddette@tripos.com  
phone 314-647-1099  
fax 314-647-9241

Serge Gorelskii  
Chemistry Department  
York University  
4700 Keele St.,  
North York, ON, M3J 1P3  
Canada  
serge@yorku.ca  
phone (416)736-2100 ext. 77720

Trevor Hart  
Department of Medical Microbiology  
and Immunology  
University of Alberta  
Edmonton, AB, T6G 2H7  
Canada  
trevor.hart@ualberta.ca

Martin Head-Gordon  
Department of Chemistry  
University of California  
Berkeley, CA 94720  
U.S.A.  
mhg@bastille.cchem.berkeley.edu  
phone 510-642-5957  
fax 510-642-9675

George L Heard  
Department of Chemistry  
Dalhousie University  
Halifax, NS, B3H 4J3  
Canada  
gheard@is.dal.ca  
phone 902-494-7021  
fax 902-494-1310

James Himer  
Sun Microsystems of Canada  
SunLife Plaza III 9th Floor  
112 - 4th Ave SW  
Calgary, AB, T2P 0H3

Kimihiko Hirao  
Department of Applied Chemistry  
School of Engineering  
University of Tokyo  
7-3-1- Hongo, Bunkyo-ku  
Tokyo 113  
Japan  
hirao@qcl.t.u-tokyo.ac.jp  
phone +1-03-5802-3335

Araz Jakalian  
Dept. of Chemistry and Biochemistry  
Concordia, University  
1455 de Maisonneuve Blvd. W.  
Montreal, QC, H3G 1M8  
Canada  
araz@planck.concordia.ca  
phone (514) 848-3387

Dylan Jayatilaka  
The University of Western Australia  
Department of Chemistry  
Nedlands 6009  
Western Australia  
fax (09) 380 1005  
phone (09) 380 3515  
dylan@crystal.uwa.edu.au

Ray Kapral  
Department of Chemistry  
University of Toronto  
80 St. George Street  
Toronto, ON, M5S 1A1  
Canada  
rkapral@chem.utoronto.ca  
phone +1-416-978-6106  
fax +1-416-978-1631

Jacek Karwowski  
Institute of Physics  
N. Copernicus University  
ul. Grudziadzka 5/7  
87-100 Torun  
Poland  
jka@phys.uni.torun.pl  
phone 48-56-21065  
fax 48-56-25397

Jana Khandogin  
Department of Chemistry  
University of Calgary  
Calgary, AB, T2N 1N4  
Canada  
khan@zinc.chem.ucalgary.ca  
phone 403-220-5069

Mariusz Klobukowski  
Department of Chemistry  
University of Alberta  
Edmonton, AB, T6G 2G2  
Canada  
mariusz@qc.chem.ualberta.ca  
fax 403-492-3281  
phone 403-492-2568

David Lewis  
Tripos, Inc.  
1699 S. Hanley Road  
St. Louis, MO 63144  
U.S.A.  
dlowis@tripos.com  
phone 314-647-1099  
fax 314-647-9241

Peter Margl  
Department of Chemistry  
University of Calgary  
2500 University Drive N.W.  
Calgary, AB, T2N 1N4  
Canada  
pmargl@acs.ucalgary.ca  
phone 403-220-8204

Charles H. Martin  
Department of Chemistry  
Syracuse University  
Syracuse NY 13244  
U.S.A.  
cmartin@rainbow.uchicago.edu  
fax (315) 443-4070  
phone (315) 443-3754

Paul Mezey  
Mathematical Chemistry Research Unit  
Department of Chemistry  
University of Saskatchewan  
Saskatoon, SK, S7N 5C9  
Canada  
mezey@sask.usask.ca  
phone 306-966-4661  
fax 306-966-4730

Kereen Monteyne  
Department of Chemistry  
University of Calgary  
Calgary, AB, T2N 1N4  
Canada  
kmonteyn@acs.ucalgary.ca  
phone 220-5069

Heidi M. Muchall  
Department of Chemistry  
McMaster University  
Hamilton, ON, L8S 4M1  
Canada  
muchall@mcmaster.ca  
fax (905) 522-2509  
phone (905) 525-9140

Oswald G Parchment  
Department of Chemistry  
University of Surrey  
Guildford, Surrey  
United Kingdom GU2 5XH  
chslop@surrey.ac.uk

Gren N. Patey  
Department of Chemistry  
University of British Columbia  
Vancouver, BC, V6T 1Z1  
Canada  
patey@theory.chem.ubc.ca  
phone 604-822-2996  
fax 604-822-2847

Cory C. Pye  
Department of Chemistry  
University of Calgary  
Calgary, AB, T2N 1N4  
Canada  
cory@zinc.chem.ucalgary.ca  
phone (403)-220-3232

Isabel Rozas  
Instituto de Quimica Medica (CSIC)  
C/ Juan de la Cierva 3  
28006-Madrid  
Spain  
rozas@pinar1.csic.es  
fax 34-1-564 4853  
phone 34-1-562 2900

Yosadara Ruiz-Morales  
Department of Chemistry  
University of Calgary  
2500 University Drive, N.W.  
Calgary, AB, T2N 1N4  
Canada  
yruizmor@zinc.chem.ucalgary.ca  
phone 220-3232  
fax (403) 289-9488

Andrzej J. Sadlej  
Dept. of Theoretical Chemistry  
Chemical Center  
POB 124  
S-221 00 Lund  
Sweden  
teoajs@garm.teokem.lu.se  
phone +46-46-222 82 42  
fax +46-46-222 45 43

Dennis Salahub  
Université de Montréal  
Département de chimie  
C.P. 6128, Succ. Centre-Ville  
Montréal, QC, H3C 3J7  
Canada  
salahub@ERE.UMontreal.CA  
phone 514-343-6755  
fax 514-343-2468

H. F. Schaefer III  
Center for Computational Quantum Chemistry  
University of Georgia  
Athens, GA 30602-2556  
U.S.A.  
hfsiii@uga.cc.uga.edu  
phone 706-542-2067

Hartmut Schmider  
Department of Chemistry  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
hasch@ct3a.chem.queensu.ca

Vedene H. Smith, Jr.  
Department of Chemistry  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
smithvh@qucdn.queensu.ca  
phone 613-545-2650  
fax 613-545-6669

Peter Taylor  
San Diego Supercomputer Center  
POB. 85608  
San Diego, CA 92186-9784  
U.S.A.  
taylor@sdsc.edu  
phone +1-619-534 5153  
fax +1-619-534 5117

Thanh N. Truong  
Department of Chemistry  
University of Utah  
Salt Lake City, UT 84112  
U.S.A.  
truong@mercury.chem.utah.edu

John S. Tse  
Steacie Institute for Molecular Science  
National Research Council of Canada  
100 Sussex Drive, Ottawa, ON, K1A 0R6  
Canada  
tse@ned1.sims.nrc.ca  
phone 613-991-1237

Irina Vedernikova  
Department of Pharmaceutical Sciences  
University of Antwerpen  
Universiteiplein 1  
B-2610 Antwerpen  
Belgium  
veder@uia.ua.ac.be

Oscar N. Ventura  
MTC-Lab  
Facultad de Química  
C.C.1157, 11800 Montevideo  
Uruguay  
oscar@bilbo.edu.uy  
phone 598-2-941860  
fax 598-2-941906

Donald F. Weaver  
Department of Chemistry  
Queen's University  
Kingston, ON, K7L 3N6  
Canada  
weaverd@qucdn.queensu.ca  
phone 613-545-6521  
fax 613-545-6669

Michael Anthony Whitehead  
Department of Chemistry  
McGill University  
801 Sherbrooke St. NW  
Montreal, QC, H3A 2K6  
Canada  
tony@maw.chem.mcgill.ca  
phone 514-398-6239  
fax 514-398-3797

Stephen K. Wolff  
Department of Chemistry  
The University of Calgary  
Calgary, AB, T2N 1N4  
Canada  
swolff@acs.ucalgary.ca  
phone (403) 220 8204

Chung Wong  
Mount Sinai School of Medicine  
Department of Biology and Biophysics  
Box 1218  
1 Gustave L. Levy Place  
New York, NY 10029-6574  
U.S.A.  
wong@msvax.mssm.edu

Tom K. Woo  
Department of Chemistry  
Calgary, AB, T2N 1N4  
Canada  
tkwoo@zinc.chem.ucalgary.ca  
phone (403) 220 8204

James S. Wright  
Ottawa-Carleton Chemistry Institute  
Department of Chemistry  
Carleton University  
Ottawa, ON, K1S 5B6  
Canada  
jwright@ccs.carleton.ca

Liqu Yang  
303C Wilhelm Hall  
Ames Laboratory  
Iowa State University  
Ames, Iowa 50011-3020  
U.S.A.  
LYang@ameslab.gov

Michael C. Zerner  
Department of Chemistry  
University of Florida  
P.O. Box 117200  
Gainesville, FL 32611  
U.S.A.  
zerner@qtp.ufl.edu  
phone 904-392-1597  
fax 904-392-8758



