

**7<sup>th</sup> CERMM Annual Symposium**

**Program and  
Book of Abstracts**

**May 4-6, 2007**

**Richard J. Renaud Science Complex,  
Concordia University**

## CERMM Director's Foreword

Envisioning the growing importance of computational and theoretical chemistry in modern research, the Concordia Faculty of Arts & Science supported and encouraged the establishment of the Centre for Research in Molecular Modeling (CERMM) in 2000. CERMM is now a multi-institutional research centre with 14 senior members from 6 institutions with diverse interests, and it will soon expand to count 21 senior members from 7 institutions. These are exciting times for computational physicists, chemists and biochemists! The Canada Foundation for Innovation has announced the funding of *Compute Canada* along with provincial and industrial partners, a project that will allow Canada to remain at the forefront of computer-simulation-based research, and in particular, will provide Québec computational chemists with access to a state-of-the-art computing infrastructure which will be deployed in CERMM as part of the Réseau Québécois de Calcul Haute Performance.

The infrastructure available in CERMM has supported in the past the research of over 10 postdoctoral fellows, 40 graduate students and numerous undergraduate students in atmospheric, biological, inorganic, macromolecular, materials, medicinal, organic, physical, and polymer chemistry. The mission of CERMM is to promote excellence in research and graduate education in computational chemistry and biochemistry, to foster collaborations between researchers in different institutions, and to provide an interdisciplinary forum for experimentalists, modelers and theoreticians to combine their expertise to reach new frontiers in the molecular sciences. Accordingly, the CERMM annual symposium is the annual regional event where researchers and students with interests in computational physics, chemistry and biochemistry have the opportunity to showcase their work in the field.

I would like to thank the sponsors for their generous support, my CERMM colleagues and the CERMM students and postdocs for helping organize the symposium. As usual, they did a terrific job! I hope you will all enjoy a fruitful and stimulating symposium.



Gilles H. Peslherbe, CERMM Director

## Reception Sponsors



Division of Physical,  
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Chemistry

## Book Prizes for Best Oral and Poster Presentations



Taylor & Francis Group / CRC Press is a premier publisher of scientific and technical books, journals, and electronic databases. They publish a number of titles in chemistry, including their flagship title, *CRC Handbook of Chemistry and Physics*, now in its 88<sup>th</sup> edition. In addition to the traditional disciplines, they offer titles in proteomics, computational chemistry, catalysis, and drug discovery. They have generously sponsored book prizes for the best oral presentation and for the best poster presentation by students and postdoctoral fellows at the CERMM symposium. Each awardee will receive one copy of the latest edition of the *CRC Handbook of Chemistry and Physics*. We are grateful for the unwavering support from Taylor & Francis Books/CRC Press to our symposium.



# Symposium Program

## Friday, May 4, 2007 - Science Pavilion S110

**17:00** Welcoming remarks

**Graham Carr**, Associate Dean, Research & Graduate Studies, Arts & Science

**Louise Dandurand**, Vice-President, Research & Graduate Studies, Concordia University

Discussion Leader: **Gilles H. Peslherbe** (Concordia University)

**Sharon Hammes-Schiffer** (Pennsylvania State University)

Hydrogen Tunneling and Protein Motion in Enzyme Reactions

**18:15** Reception - Department of Chemistry & Biochemistry - Science Pavilion Atrium

Sponsored by *Azuris Technologies* and the *Canadian Society for Chemistry* (Division of Physical, Theoretical and Computational Chemistry)

## Saturday, May 5, 2007 - Science Pavilion S110

Discussion Leader: **Tucker Carrington** (Université de Montréal)

**9:30** **André Bandrauk** (Université de Sherbrooke)

TDDFT for Intense Laser Fields - the Route to Attosecond Science

**10:10** **Sergei Manzhos** and Tucker Carrington (Université de Montréal)

Improved Neural Network Methods for Solving the Schroedinger Equation

**10:30** **Xiaogang Wang** and Tucker Carrington (Université de Montréal)

A Quantum Full Dimensional Calculation of Vibrational Levels of  $\text{CH}_5^+$

**10:50** Coffee Break - Science Pavilion Atrium

Discussion Leader: **Marcel Nooijen** (University of Waterloo)

**11:20** **Alex Brown** (University of Alberta)

Laser Control of Molecular Processes

- 12:00** Reza Rajaie Khorasani and **Randall S. Dumont** (McMaster University)  
Long Time Wavepacket Dynamics from Energy Eigenfunctions; Nonuniform Energy Resolution via Adaptive Bisection Fast Fourier Transformation
- 12:20** **Lisandro Hernández de la Peña**, Ramses van Zon, Jeremy Schofield and Sheldon B. Opps (Concordia University; University of Toronto; University of Prince Edward Island)  
Discontinuous Molecular Dynamics for Semi-flexible and Rigid Bodies: Method and Applications
- 12:40** Lunch - Science Pavilion Atrium
- Discussion Leader: **Bob LeRoy** (University of Waterloo)
- 14:00** **Christopher I. Bayly**, Matthew Cooper, Claude Dion, Manuel Smeu and Sishi Tang (Merck Frosst)  
Progress Towards AM1-BCC Version 2, an Improved Charge Model for Biomolecular Simulations
- 14:40** **Jean-François Truchon** and Christopher I. Bayly (Merck Frosst)  
GLARE: A New Approach for Filtering Large Reagent Lists in Combinatorial Library Design Using Product Properties
- 15:00** **Christopher Corbeil**, Pablo Englebienne, Nicolas Moitessier (McGill University)  
FITTED 1.5, Docking to Flexible and Solvated Macromolecules.
- 15:20** **Guillaume Lamoureux**, Michael L. Klein, Simon Bernèche (University of Pennsylvania; University of Basel)  
The Pore of the AmtB Ammonium Transporter: Ammonia versus Water
- 15:40** **Qadir K. Timerghazin**, Chen Liang, Haley Carlson, Robert Campbell and Alex Brown (University of Alberta)  
Photoabsorption Properties of the *Aequorea* Fluorescent Protein Chromophores
- 16:00** Poster Session - Science Pavilion Atrium
- 18:15** Banquet - Macao Tapas Bar, 2070 rue Saint-Denis, Montreal, QC H2X 3K7.  
Phone: 514-223-6411. Metro: Sherbrooke (Orange Line)

**Sunday, May 6, 2007 - Science Pavilion S110**

Discussion Leader: **Matthias Ernzerhof** (Université de Montréal)

- 9:30 Tom K. Woo** (University of Ottawa)  
The High Pressure World of Quantum Chemistry
- 10:10 Radu Iftimie**, Vibin Thomas and Patrick Ayotte (Université de Montréal; Université de Sherbrooke)  
The Mechanism of Weak Acid Dissociation in Liquid and Amorphous Water
- 10:30 Lei Zhang**, Gilles H. Peslherbe and Heidi M. Muchall (Concordia University)  
Calculation and Interpretation of Absorption Spectra of Phenol Radical Species
- 10:50 Dominika Zgid** and Marcel Nooijen (University of Waterloo)  
Orbital Optimization with Monotonically Convergent Density Matrix Renormalization Group in the Active Space
- 11:10 Patrick Laflamme**, Armand Soldera and Wes Capehart (Université de Sherbrooke; GM Research & Development Center)  
Characterization and Validation of Parameter for Perfluorinated Acid Ionomers
- 11:30 Tony M.A. Whitehead**, Thomas Lazzara, Rami Hourani and Adrian Villegas-Jimenez (McGill University)  
Modelling Can Sometimes Tell You What to Do, Even if it Cannot Tell What You Did

# Poster Presentations

Saturday, May 5, 4:00 – 6:00 PM SP-S Atrium

- 1 **Daniel J. McKay** and Christopher I. Bayly (Merck Frosst)  
Charge-ELF: Addressing Conformational Dependency of Small-molecule Atomic Charge for Biomolecular Simulations
- 2 **Jason Cooper** and Tucker Carrington, Jr. (Université de Montréal)  
High-dimensional Wavepacket Methods using Lanczos Propagation
- 3 **Elena V. Ivanova** and Heidi M. Muchall (Concordia University)  
On the Electronic Structure of N-sulfinyl Amines, Hydrazines and Hydrazides, and the Relationship to their Hydrolysis Reaction
- 4 **Petrina R.N. Kamy** and Heidi M. Muchall (Concordia University)  
A Quantum Chemical Investigation into the Observation of NA Tautomers in Isolated Base Pairs
- 5 **In S. Koo**, Kiyull Yang, Dildar Ali, Gary W. vanLoon and Erwin Buncel (Gyeonsang National University, Korea; Queen's University)  
Investigation into the  $^{31}\text{P}$  NMR Chemical Shifts for Organophosphorus Esters and Organophosphorus-metal Complexes
- 6 **Noureddine Metatla** and Armand Soldera (Université de Sherbrooke)  
Molecular Modeling of the Glass Transition of Stereoregular Vinyl Polymers
- 7 **Francois Goyer** and Matthias Ernzerhof (Université de Montréal)  
Applications of the SSP (Source-Sink Potentials) Method to Molecular Electronics Devices
- 8 **Hui Li** and Robert J. Le Roy (University of Waterloo)  
An Analytic 3-Dimensional Potential Energy Surface for  $\text{CO}_2\text{-He}$  and its Predicted Infrared Spectrum
- 9 **Ondrej Demel**, K. R. Shamasudhar and Marcel Nooijen (University of Waterloo; University of Stuttgart, Germany)  
Generalization of Equation of Motion Coupled Cluster Method to a State-Selective Internally Contracted Multireference Coupled Cluster Approach

- 10 **Hilke Bahmann** (Université de Montréal)  
Correlation Factor Model
- 11 Lisandro Hernández de la Peña and **Gilles H. Peslherbe** (Concordia University)  
Quantum Effects on the Solvation Structure of I-(H<sub>2</sub>O)<sub>n</sub> Clusters
- 12 **Denise M. Koch** and Gilles H. Peslherbe (Concordia University)  
Role of Polarization in Simulations of Excited-State Dynamics: NaI(H<sub>2</sub>O)<sub>n</sub> Photodissociation as a Case Study
- 13 **Yan Li**, Qadir Timerghazin, Ann English and Gilles H. Peslherbe (Concordia University)  
A Density-Functional Theory Investigation of Cu(I) Complexes



# TALKS

## Hydrogen Tunneling and Protein Motion in Enzyme Reactions

*Sharon Hammes-Schiffer  
Pennsylvania State University*

Theoretical studies of proton, hydride, and proton-coupled electron transfer reactions in enzymes will be presented. We have developed a theoretical formulation for proton-coupled electron transfer reactions. The quantum mechanical effects of the active electrons, transferring proton, and donor-acceptor mode are included in this formulation, and analytical nonadiabatic rate expressions have been derived in various limits. The application of this approach to proton-coupled electron transfer in the enzyme lipoyxygenase will be discussed. The experimentally measured deuterium kinetic isotope effect of 80 at room temperature is found to arise from the small overlap of the reactant and product proton vibrational wavefunctions. Our calculations illustrate that the proton donor-acceptor vibrational motion plays a vital role in the proton-coupled electron transfer reaction. We have also developed a hybrid quantum/classical molecular dynamics approach that includes electronic and nuclear quantum effects, as well as the motion of the entire solvated enzyme. The application of this approach to hydride transfer in the enzyme dihydrofolate reductase will be discussed. An analysis of the simulations leads to the identification and characterization of a network of coupled motions that extends throughout the enzyme and represents conformational changes that facilitate the charge transfer process. Mutations distal to the active site are shown to significantly impact the catalytic rate by altering the conformational motions of the entire enzyme and thereby changing the probability of sampling conformations conducive to the catalyzed reaction.

## TDDFT for Intense Laser Fields - the Route to Attosecond Science

*André Bandrauk  
Université de Sherbrooke*

Current laser technology enables for the first time for the synthesis of ultrashort ( $< 5$  fs) intense ( $I > 10^{14}$  W/cm<sup>2</sup>) laser pulses. Molecules exposed to such pulses undergo nonlinear nonperturbative response such as high order harmonic generation [1], imaging molecular orbitals by tunneling ionization [2]. "Attosecond" science is a main spin-off of intense field physics [3] in which nonperturbative effects dominate. TDDFT approaches have had mitigated success [4] especially since electron recollision is an essential dynamical effect controlled by the laser pulse leading to strong 2-electron and thus correlation effects [5]. Exact numerical solutions of H<sub>2</sub> in an intense laser pulse will be presented and compared to various TDDFT methods such as OEP,TDKLI approaches. TDEHF methods based on 2 nonorthogonal determinants give excellent 2-electron ionizations and thus point out the possibility of using multideterminant KS-schemes [6].

[1] A. D. Bandrauk, S. Barmaki-in "Progress in Ultrafast Intense Laser Science", edit K Yamanouchi (Kluwer Press, Amsterdam, 2007), 35 pges.

[2] G. Lagmago Kamta, A. D. Bandrauk, Phys Rev A 74,033415(2006).

[3] G. Yudin, A. D. Bandrauk, P. B. Corkum, Phys Rev Lett 96,063002(2006).

[4] C. Ullrich, A. D. Bandrauk, in "Time Dependent Density Functional Theory", edit K Burke et al, (Springer, N Y 2006), p 357-374.

[5] N. A. Nguyen, A. D. Bandrauk, Phys Rev A 73,032708(2006).

[6] N. A. Nguyen, A. D. Bandrauk, in preparation.

Talk

Sat. 10:10 AM

## **Improved Neural Network Methods for Solving the Schroedinger Equation**

*Sergei Manzhos and Tucker Carrington*  
*Université de Montréal*

We use a neural network (NN) based algorithm to calculate vibrational energies and wavefunctions. Improvement over previous work is achieved by combining a neural network representation of the wavefunction with methods of linear algebra to find the network parameters of the external layer of neurons (coefficients of the basis of neurons). The NN representation is equivalent to an expansion over basis functions whose number is moderate as a direct product is avoided. Using linear algebra on a subspace of NN parameters reduces the dimensionality of the space of NN parameters in which non-linear optimisation is done permitting the treatment of systems of a higher dimensionality.

Talk

Sat. 10:30 AM

## **A Quantum Full Dimensional Calculation of Vibrational Levels of CH<sub>5</sub><sup>+</sup>**

*Xiaogang Wang and Tucker Carrington Jr.*  
*Université de Montréal*

The vibrational levels of CH<sub>5</sub><sup>+</sup> are very difficult to compute because the five protons move almost freely around the carbon center and the dimensionality is high (12 dimensions). We take a divide-and-conquer approach by first solving a 7-dimension bend problem and a 5-dimension stretch problem and then solving the full problem by coupling the lowest wavefunctions of both sub-problems to form a basis whose size is orders of magnitude smaller than that of the primitive basis. Wavefunctions and energies are obtained by diagonalizing the Hamiltonian matrix using the symmetry-adapted Lanczos method. Converged excited vibrational levels are obtained by starting from  $1.3 \times 10^{12}$  primitive basis functions. Due to the flexibility of this ion, a rich structure of the low-lying bending energy levels are revealed for the first time.

**Laser Control of Molecular Processes**

*Alex Brown*  
*University of Alberta*

The use of tailored laser pulses to control chemical processes has received much attention recently, in part due to the rapid development of experimental pulse shaping techniques. In this talk, I will provide a general introduction to laser control. I will discuss some of our recent theoretical/computational work using optimal control theory (OCT) to determine the tailored laser pulses needed to achieve a desired excitation. A new method that we have proposed to design optimized control fields with desired temporal and/or spectral properties will be outlined. Results for this new method will be contrasted with those obtained using chirped laser fields optimized with a genetic algorithm. The control of vibrational excitation of OH (anharmonic) and ClO (nearly harmonic) will be used as simple examples. If time permits, I will highlight our use of the Multi-Configurational-Time-Dependent-Hartree (MCTDH) method combined with OCT for examining laser control in polyatomic molecules.

**Long Time Wavepacket Dynamics from Energy Eigenfunctions; Nonuniform Energy Resolution via Adaptive Bisection Fast Fourier Transformation**

*Reza Rajaie Khorasani and Randall S. Dumont*  
*McMaster University*

This article presents a new approach to long time wavepacket propagation. The methodology relies on energy domain calculations and an on-the-surface straightforward energy to time transformation to provide wavepacket time evolution. The adaptive bisection Fourier transform method employs selective bisection to create a multiresolution energy grid, dense near resonances. To implement fast Fourier transforms on the nonuniform grid, the uniform grid corresponding to the finest resolution is reconstructed using an iterative interpolation process. By proper choice of the energy grid points, we are able to produce results equivalent to grids of the finest resolution, with far fewer grid points. We have seen savings 20-fold in the number of eigenfunction calculations. Since the method requires the computation of the energy eigenfunctions, it is best suited for situations where many wavepacket propagations are of interest at a fixed small set of points - as in time dependent flux computations. The FFT algorithm used, is an adaptation of the Danielson-Lanczos FFT algorithm to sparse input data. A specific advantage of ABFFT is the possibility of long time wavepacket propagations showing slow resonant decay. A method is discussed for obtaining resonance parameters by least squares fitting of energy domain data. The key innovation presented is the means of separating out the smooth background from the sharp resonance structure.

## **Discontinuous Molecular Dynamics for Semi-flexible and Rigid Bodies: Method and Applications**

*Lisandro Hernández de la Peña  
Concordia University*

*Ramses van Zon, Jeremy Schofield  
University of Toronto*

*Sheldon B. Opps  
University of Prince Edward Island*

A general framework for performing event-driven simulations of systems with semi-flexible or rigid bodies interacting under impulsive forces will be outlined. The method consists of specifying a means of computing the free evolution of constrained motion, evaluating the times at which interactions occur, and determining the consequences of interactions on subsequent motion. Algorithms for computing the times of interaction events and carrying out efficient event-driven simulations will be discussed.

As an illustration of the method, the results of event-driven molecular dynamics simulations of two rigid-body systems (which differ in the symmetry of their molecular mass distributions) will be presented. First, simulations of methane in which the molecules interact via discontinuous potentials will be compared with simulations in which the molecules interact through standard continuous Lennard-Jones potentials. It will be shown that under similar conditions of temperature and pressure, the rigid discontinuous molecular dynamics method reproduces the essential dynamical and structural features found in continuous-potential simulations at both gas and liquid densities. Moreover, it will be demonstrated that the discontinuous molecular dynamics approach is between 3 and 100 times more efficient than the standard molecular dynamics method depending on the specific conditions of the simulation. The rigid discontinuous molecular dynamics method will be also applied to a discontinuous-potential model of a liquid composed of rigid benzene molecules, and equilibrium and dynamical properties will be shown to be in qualitative agreement with more detailed continuous-potential models of benzene.

## **Progress Towards AM1-BCC Version 2, an Improved Charge Model for Biomolecular Simulations**

*Christopher I. Bayly, Matthew Cooper, Claude Dion, Manuel Smeu and Sishi Tang  
Merck Frosst Centre for Therapeutic Research*

The AM1-BCC charge model (AM1 charges with Bond Charge Corrections) was introduced in 2002 as a relatively quick method to approximate ab initio-based Restrained ElectroStatic Potential (RESP) fit charges. It has seen increasing usage in the small-molecule-ligand protein biomolecular simulations community and has shown good performance in free energy calculations. Still, some defects have been identified; these will be described followed by a progress report on a free-energy-centric version 2 for this model.

Talk

Sat. 2:40 PM

## **GLARE: A New Approach for Filtering Large Reagent Lists in Combinatorial Library Design Using Product Properties**

*Jean-François Truchon and Christopher I. Bayly*  
*Merck Frosst Canada & Co.*

We present a novel computer algorithm, called GLARE (Global Library Assessment of REagents), that addresses the issue of optimal reagent selection in combinatorial library design. This program reduces or eliminates the time a medicinal chemist spends examining reagents which a priori cannot be part of a "good" library. Our approach takes the large reagent sets returned by standard chemical database queries and produces often considerably reduced reagent sets that are well-behaved with respect to a specific template. The pruning enforces "goodness" constraints such as the Lipinski rule of five on the product properties such that any reagent selection from the resulting sets produces only "good" products. The algorithm we implemented has three important features: (i) As opposed to genetic algorithms or other stochastic algorithms, GLARE uses a deterministic greedy procedure that smoothly filters out nonviable reagents. (ii) The pruning method can be biased to produce reagent sets with a balanced size, conserving proportionally more reagents in smaller sets. (iii) For very large combinatorial libraries, a partitioning scheme allows libraries as large as  $10^{12}$  to be evaluated in 0.25 s on an IBM AMD Opteron processor. This algorithm is validated on a diverse set of 12 libraries. The results that we obtained show an excellent compliance to the product property requirements and very fast timings.

Talk

Sat. 3:00 PM

## **FITTED 1.5, Docking to Flexible and Solvated Macromolecules**

*Christopher R Corbeil, Pablo Englebienne and Nicolas Moitessier*  
*McGill University*

In response to the continual increase in the number of new potential therapeutic targets newly discovered targets, cost and time efficient designs and syntheses must be devised for active enzyme inhibitors, receptor antagonists/agonists, nucleic acid binders,.... The low hit rate observed with the expensive HTS of large combinatorial libraries has contributed proportionally less in the identification of novel leads compared with traditional rational or semi-rational design and synthesis. This weakness of conventional methods has led to the development of computational tools to virtually screen libraries of compounds.

A method of interest in the field of virtual screening is molecular docking. Even though molecular docking has potential to guide the researcher to find new drug leads all docking methods still treat the ligand-protein binding as partially rigid. Within the Moitessier Research Group we have developed a novel program, FITTED (Flexibility Induced Through Targeted Evolutionary Description), which is the first to treat this interaction as a fully dynamic system. The validation of FITTED1.0 and improvement to create FITTED1.5 will be discussed along with an application in virtual screening.

## The Pore of the AmtB Ammonium Transporter: Ammonia versus Water

*Guillaume Lamoureux and Michael L. Klein*  
*University of Pennsylvania*

*Simon Bernèche*  
*University of Basel, Switzerland*

Although lipid membranes are relatively permeable to ammonia ( $\text{NH}_3$ ), bacteria, yeast, and plants under too low ammonium concentrations express transmembrane proteins from the Amt/MEP family that have a high affinity for ammonium and facilitate its transport across the membrane. In mammals, a similar function is performed by the analogous Rhesus (Rh) proteins (present in red blood cells, liver cells and kidney cells). The first X-ray structures of a protein from the Amt/MEP/Rh family have been obtained only very recently, for the bacterial ammonium channel AmtB and for the archaeal channel Amt-1. Although the structures provide a lot of insight into the general conduction mechanism of Amt proteins, confusion remains on the nature of the permeant species. Depending on the specific Amt protein (in bacteria or in plants), experiments suggest a net transport of either  $\text{NH}_3$  or  $\text{NH}_4^+$ .

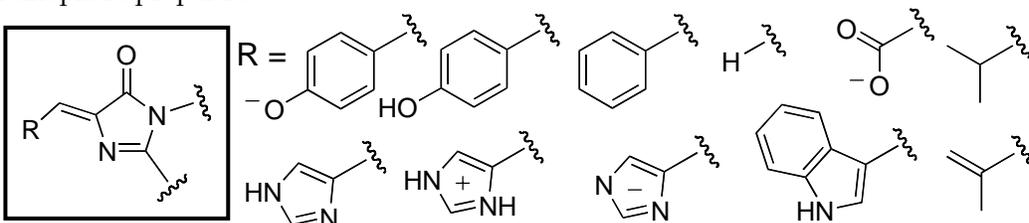
For the bacterial AmtB protein the prevailing model, initially proposed by Khademi et al. (Science 2004, vol. 305, p. 1587), involves the binding of ammonium ( $\text{NH}_4^+$ ) in the periplasmic vestibule of the protein, which gets deprotonated and then diffuses as ammonia ( $\text{NH}_3$ ) through a hydrophobic pore according to a single-file diffusion mechanism reminiscent of ion permeation in potassium channels. This model relies on the assumption that water molecules are excluded from the pore. However, water and ammonia being isoelectronic species, one cannot draw a definitive conclusion on the molecular species occupying the pore from the X-ray data alone.

Using classical molecular dynamics simulations, we have studied the competition between water and ammonia molecules for the occupation of the pore of AmtB. The simulations show (1) that the so-called hydrophobic pore can stabilize a chain of water molecules, and (2) that a chain (or "file") of ammonia is highly improbable at physiological concentrations. These results suggest that an ammonium or ammonia molecule permeating into the narrow pore of AmtB is likely to encounter water, and go against the view of single-file diffusion of ammonia molecules.

## Photoabsorption Properties of the *Aequorea* Fluorescent Protein Chromophores

*Qadir K. Timerghazin, Chen Liang, Haley Carlson,  
Robert Campbell and Alex Brown  
University of Alberta*

Fluorescent proteins derived from *Aequorea victoria* jellyfish green fluorescent protein (GFP) are widely used in cell and molecular biology as fluorescent labels and reporter molecules. Protein engineering allows creating a number of fluorescent proteins with various photophysical properties by changing the structure of the chromophore and/or protein environment around the chromophore. We are interested in computational modeling of the photochemical processes in fluorescent proteins to gain mechanistic insights necessary to improve and extend their utility in molecular biology. Our initial work has concentrated on the properties of isolated chromophores in solution. Photoexcitation wavelengths were calculated using various quantum chemistry methods for a number of chromophores (Figure 1) and compared to the experimental data. Computational methods have been benchmarked for determining the absorption properties of the chromophores in gas- and liquid-phase. The results provide insight into the reliability of each computational method and an understanding of the effect of the protein environment on chromophore properties.



## The High Pressure World of Quantum Chemistry

*Tom K. Woo  
University of Ottawa*

Quantum chemical calculations have had an enormous impact on all areas of chemistry. Density Functional Theory (DFT) calculations are becoming common tool used in experimental and synthetic laboratories. Here, calculations are typically performed on small molecules in the gas-phase. In our lab, quantum chemical simulations of liquids and solids under high pressure are often performed. In this talk, an introduction to such simulations will be given along with details of two of our most recent studies of materials under extremely high pressure conditions. First, a study of how anti-wear engine oil additives function at the molecular level in automobile engines will be provided (*Science*, **2005**, *207*, 1612-1615). Our simulations show that high pressures induce cross-linking in the pads, increasing the hardness of the film and its ability to accommodate applied loads. The resultant anti-wear mechanism explains a myriad of experimental observations and points toward pathways for the rational design of new anti-wear additives that are effective on materials other than steel. Second, a study of how nitrogen under extremely high pressure can polymerize to form a meta-stable solid that can be used for energy storage will be given. Recently, a non-molecular, polymeric form of nitrogen composed solely of single bonds, in analogy to carbon in diamond, has been synthesized (*Nature Mat.* **2004**, *3*, 558) by compressing molecular nitrogen to over 110 GPa and heating it to over 2000 K. Three single-bonded phases of polymeric nitrogen have been proposed to exist, two based known structures of nitrogen's group 15 congeners and a new so-called *cubic gauche* structure not seen in any other element. We have performed an *in silico* search for new polymeric phases of nitrogen, using a combination of high pressure quantum chemical calculations, a new systematic approach, and genetic algorithms. (*Phys. Rev. Lett.* **2006**, *97*, 155503).

## The Mechanism of Weak Acid Dissociation in Liquid and Amorphous Water

*Radu Iftimie and Vibin Thomas*  
*Université de Montréal*

*Patrick Ayotte*  
*Université de Sherbrooke*

The mechanism of dissociation of weak acids in aqueous solutions is investigated by taking the hydrofluoric acid as an example. The various ion pairs that appear along the dissociation pathway are identified by means of molecular beam studies and computational *ab initio* molecular dynamics IR spectroscopy. The roles of enthalpy vs. entropy effects are quantized by investigating the dissociation at 300 and at 80 K, the later measurements/calculations corresponding to low-density amorphous water solutions. The role and the magnitude of nuclear quantum effects are investigated by means of isotopic labelling experiments in conjunction with centroid molecular dynamics.

Our conclusions point to the importance of Zundel-like symmetric contact ion pairs that form easily between one molecule of hydrofluoric acid and another molecule of water. This dissociation intermediate appears to be favoured by entropy effects, suggesting it could be an ubiquitous species in environments that prohibit 3D spatial diffusion, such as ion channels or protein surfaces.

## Calculation and Interpretation of Absorption Spectra of Phenol Radical Species

*Lei Zhang, Gilles H. Peslherbe and Heidi M. Muchall*  
*Concordia University*

Since the phenolic structure of organic compounds is widely distributed in nature, their radical derivatives, phenol radical cations and phenoxyl radicals, are involved in many photooxidative processes occurring naturally. These radical species can not be observed in a routine manner due to their short lifetime, and have been a subject of intense experimental and theoretical work for many years. In this work, Time-Dependent Density-Functional Theory, which we have proven reliable for phenolic systems, [1] is employed to calculate the electronic structure and absorption spectra of methoxy- and methyl-substituted phenol radical cations and the corresponding phenoxyl radicals. The observed "anomalously" long wavelength of the maximum in the absorption spectrum of the 3,5-dimethoxyphenol radical species ( $\lambda_{\max}$  580 nm for the radical cation and 510 nm for the phenoxyl radical), compared to that of the other substituted phenol radical species (between 370 and 460 nm), [2] is qualitatively reproduced by our calculations. The results of the calculations are scrutinized to explore tentative explanations for this finding.

<sup>1</sup> Zhang, L.; Peslherbe, G.H.; Muchall, H.M. *Photochem. Photobiol.* **2006**, 82, 324.

<sup>2</sup> Gadosy, T. A.; Shukla, D.; Johnston, L. J. *J. Phys. Chem. A* **1999**, 103, 8834. Ganapathi, M. R.; Hermann, R.; Naumovb, S.; Brede, O. *Phys. Chem. Chem. Phys.* **2000**, 2, 4947.

## Orbital Optimization with Monotonically Convergent Density Matrix Renormalization Group in the Active Space

*Dominika Zgid and Marcel Nooijen*  
*University of Waterloo*

Despite the success of modern quantum chemistry in addressing organic molecules the treatment of many inorganic systems revealing many close lying states is still not within quantitative reach for current methods. In order to treat the non-dynamical correlation we take advantage of the density matrix renormalization group (DMRG) method which became a very successful method in the field of solid state physics. Our prime goal is to develop a DMRG-SCF approach, analogous to CASSCF, but dealing with large active spaces, which are too demanding for FCI. As a first step towards the DMRG-SCF procedure we present a spin-adapted DMRG algorithm designed to target spin- and spatial-symmetry states which are hard to obtain while using an unrestricted algorithm. We show that the spin-adapted energies can be lower than the unrestricted ones, which is intuitively surprising based on the analogy with restricted vs. unrestricted Hartree-Fock approach. Our next step is modification of the DMRG algorithm in order to make the obtained energy lower at every step during sweep. The monotonically convergent DMRG (MC-DMRG) scheme lets us obtain a two-body density matrix as a byproduct of the existing procedure without any additional cost in storage. Additionally, a two-body density matrix produced at convergence using this scheme is free from N-representability problem which is present when producing the 2-body density matrix with two-site DMRG scheme without additional storage cost. Finally, taking advantage of the developed modifications we present the results from the DMRG-SCF method. We also take the advantage of the two-body density matrix obtained within MC-DMRG scheme and optimize geometry on the DMRG-SCF level. At last, we discuss possible ways of incorporating the dynamical correlation into the DMRG scheme which can lead to a modern multireference approach.

## Characterization and Validation of Parameter for Perfluorinated Acid Ionomers

*Patrick Laflamme and Armand Soldera*  
*Université de Sherbrooke*

*Wes Capehart*  
*GM Research & Development Center*

Despite numerous years of active research, the structure of the polyelectrolyte membrane, Nafion®, remains unsolved. A computational simulation is proposed through a hierarchical approach dealing with information gained on the structure at three different levels: atomic, molecular and mesoscale levels. As the system grows, longer simulation times can be performed which provide a greater portion of phase space to be explored. Consequently, properties can be regarded at each scale of the simulation.

An intimate link between the different scales exists: the information gained at one level is used to carry out the simulation at the others scales. This method is called the 'bottom up' approach and can be performed since each local phenomenon of the 'up' level will be an approximation of the 'bottom' level. The 'top down' approach consists in assigning molecular properties to a specific atom. This method could not be considered for application on a chemistry approach.

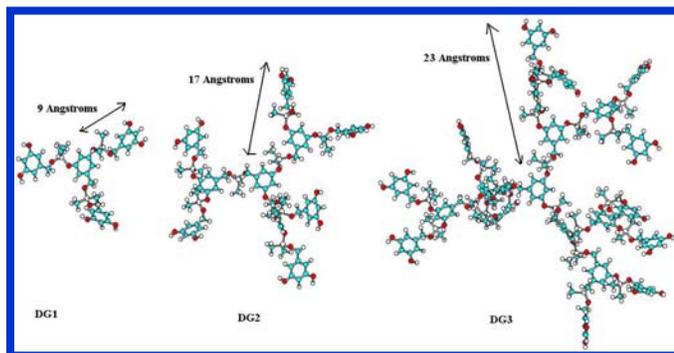
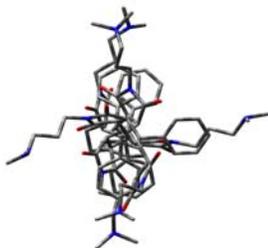
This presentation is concerned with studies carried out at the electronic and atomistic levels. A complete knowledge of interactions between atoms yields the determination of a forcefield. Such calculations are performed using the DFT, Hartree Fock and semi empirical method. Since *ab initio* calculation performed on one repeat unit of Nafion® will use too much CPU resources, the triflic acid is used as a model for the acidic functional group.

An accurate representation of the triflic acid has been developed for the OPLS force field. The validation of the forcefield was done by calculating IR spectra and density at different water uptake and different temperatures. This improved forcefield parameters for the acid group will be transferred to proton exchange membranes to enable the water uptake and conductivity of these membranes to be more accurately modeled.

## Modelling Can Tell You What to do, Even if it Cannot Tell You What You Did

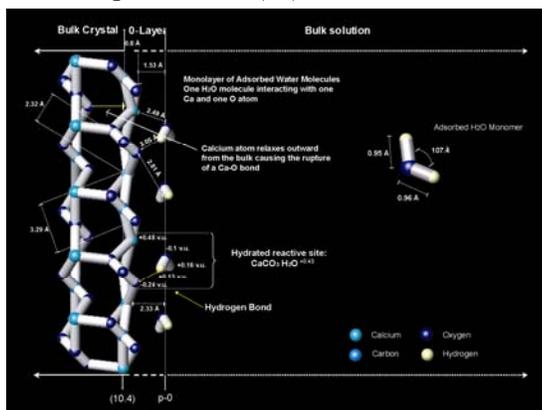
*Tony M.A. Whitehead, Thomas Lazzara, Rami Hourani and Adrian Villegas-Jiménez*  
 McGill University

Modelling of nano-tubes, dendritic structures, and surface interactions will be analysed for their predictive abilities. The problems of using modelling to explain reactions will be discussed; and the requirement of using relative results emphasised:



gas phase Hartree-Fock STO-3g hexamer optimization (SS)<sup>5</sup> of *SMI*

Sizes and shapes of dendrimers



Surface effects of water on calcite: a molecular approach to ex-foliation

# POSTERS

## Charge-ELF: Addressing Conformational Dependency of Small-molecule Atomic Charge for Biomolecular Simulations

*Daniel J. McKay and Christopher I. Bayly*  
*Merck Frosst Canada & Co.*

There are many methods for generating small molecule atom centered point charges for use in accurate biomolecular simulations (1, 2, 3). Many of these methods suffer from conformationally dependent charge variations that directly and significantly affect the critical electrostatic terms within the model and hence binding energies. The recommended approach of conformational averaging has the liability that it is not straightforward for the user to select for the electrostatically least-interacting conformers, as opposed to conformational diversity in the traditional sense. We present a fast, general and algorithmic method for selecting a minimal set of conformations to use in fitting a set of atom centered point charges for small molecules. This method has been used with AM1-BCC although it can be applied to any charge fitting scheme that suffers from conformational dependencies.

1: Jakalian A., Jack D., Bayly C. J. *Comp. Chem* 23 1623-1641

2: Cornell W., Cieplak P., Bayly C., Kollman P. J. *Am. Chem. Soc.* 115 9620-9631

3: Li J., Zhu T., Cramer C., Truhlar D. J. *Phys. Chem.* 102 1820-1831

## High-dimensional Wavepacket Methods using Lanczos Propagation

*Jason Cooper and Tucker Carrington, Jr.*  
*Université de Montréal*

We present our recent work on wavepacket techniques, in which quantum mechanical results are obtained by the propagation of one or more wavepackets in a model potential. Such methods can be viewed as employing a dynamic basis set; they therefore offer the opportunity to significantly reduce basis set size for some high-dimensional problems. Two new methods are presented, one employing a nonorthogonal gaussian basis, and one an orthogonal generalized gaussian basis. In both methods, Lanczos methods are used to efficiently propagate expansion coefficients, with the discrete variable representation used to allow for an arbitrary potential. We compare these new methods to Heller's frozen gaussian method for application in inelastic scattering, with a focus on their behaviour in the limit of many degrees of freedom.

### On the Electronic Structure of N-sulfinyl Amines, Hydrazines and Hydrazides, and the Relationship to their Hydrolysis Reaction

*Elena V. Ivanova and Heidi M. Muchall  
Concordia University*

Depending on the substituent R on the N=S=O moiety, N-sulfinyl compounds demonstrate a different behaviour towards water: aliphatic compounds are more reactive than aromatics and hydrazides, but hydrazines are inert and do not react with water. With the use of the B3LYP/6-31+G(2d,2p) model chemistry we studied the electronic structures of several compounds of interest and modelled the reaction of N-sulfinyl compounds with two water molecules in order to get insight into the nature of their reactivity. Similar to our previous studies, the model consists of concerted hydroxylation of sulphur and protonation of either nitrogen or oxygen of the N=S=O moiety. The major difference appears in the complexation of N-sulfinyl compounds: while N-sulfinyl- amines and hydrazides interact with water in a close to perpendicular orientation between the water dimer and the plane of the N=S=O group, complexes of hydrazines with two water molecules are rather planar. The electron density was analyzed for determination of the nature of bonding in the complexes and evaluation of atomic properties with use of the Quantum Theory of Atoms in Molecules (QTAIM). A trend between the charge on the electrophilic sulfur and the magnitude of the activation barriers for the hydrolysis reaction was found.

### A Quantum Chemical Investigation into the Observation of NA Tautomers in Isolated Base Pairs

*Petrina R.N. Kamyra and Heidi M. Muchall  
Concordia University*

According to Francis Crick, the hydrogens of bases do not have fixed locations; they are rather instantly hopping from between possible tautomeric positions. Many QC calculations conducted on isolated nucleic acid bases in the gas phase, as well as in micro-hydrated environments have shown evidence of NA bases existing in their tautomeric forms. We have devised a methodology that incorporates experimental geometries in an analysis of the stabilizing interactions between NA base pairs using Bader's quantum theory of atoms in molecules (QTAIM).

From our previous work we noted marked variations in the electron density at the hydrogen bond critical points of G•C base pairs that are not present in A•T base pairs. The patterns fall under 5 motifs that can be related to the tautomeric forms of G•C base pairs. This may be an example that shows the different tautomeric forms of NA bases within an oligonucleotide.

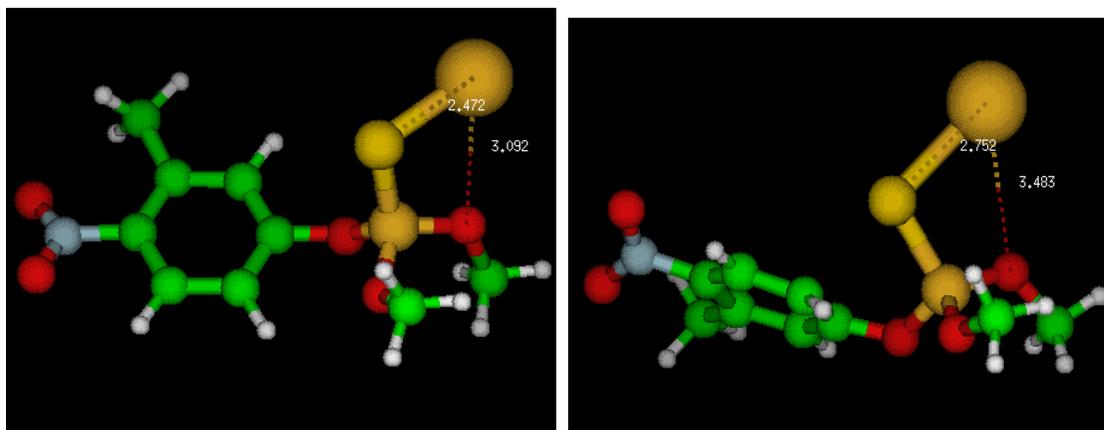
## Investigation into the $^{31}\text{P}$ NMR Chemical Shifts for Organophosphorus Esters and Organophosphorus-metal Complexes

*In S. Koo and Kiyull Yang*  
Gyeongsang National University, Korea & Queen's University

*Dildar Ali, Gary W. vanLoon, Erwin Buncel*  
Queen's University

As a part of our studies of organophosphorus pesticides stability,<sup>1</sup> we present the results of a calculational study of  $^{31}\text{P}$  NMR chemical shifts in the organophosphorus esters,  $(\text{RY-P}(=\text{X})(\text{OR})_2)$ ,  $\text{X}, \text{Y}=\text{O}$  or  $\text{S}$ ,  $\text{R}=\text{CH}_3$ ) and in the organophosphorus pesticides with metal ions ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ). The theoretical  $^{31}\text{P}$  NMR chemical shifts were calculated using absolute shielding constants and relative to  $\text{H}_3\text{PO}_4$  ( $\delta$  of  $^{31}\text{P}=\text{0.0}$ ). The calculations of absolute shielding constants have been performed using the Gauge-Independent Atomic Orbital (GIAO) perturbational method<sup>2</sup> with Hartree-Fock (HF) methods at 6-311+G(2d,p) level. For the larger molecules only HF method is used to compute absolute shielding constants.

The results reveal a decrease of  $^{31}\text{P}$  NMR chemical shifts for organophosphorus esters,  $\text{RS-P}(=\text{S})(\text{OR})_2$  (118.3 ppm) <  $\text{RO-P}(=\text{S})(\text{OR})_2$  (85.2 ppm) <  $\text{RS-P}(=\text{O})(\text{OR})_2$  (37.9 ppm) <  $\text{RO-P}(=\text{O})(\text{OR})_2$  (1.1 ppm). These calculated results are in good agreement with experimental  $^{31}\text{P}$  NMR chemical shifts and order. The calculated  $^{31}\text{P}$  NMR chemical shifts order for transition metal-fenitrothion complexes are in good agreement with experimental  $^{31}\text{P}$  NMR chemical shift order.



(a) Fenitrothion-Ag complex  
(b) Fenitrothion-Hg complex  
*B3LYP/6-31G(d) structures of Fenitrothion-Ag and Fenitrothion-Hg complexes*

Organophosphorus compounds used for the control of unwanted plants and insects. As these synthetic compounds are released into the environment it is important that methods for their removal from contaminated sites be developed. Recent research has highlighted the role of metal ions in abiotic degradation processes for the organophosphorus ester and thioester pesticides. The increase in hydrolysis rates were in the range of 20-3000 times in metal ion solutions, such as  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  that for the uncatalyzed controls. However, the former studies are not explained due to the role of metal ions in organophosphorus pesticide hydrolysis. There is no direct experimental evidence provided to show organophosphorus pesticide with metal ion interaction. In order to find direct experimental evidence interaction of organophosphorus pesticides with metal ion, we investigated experimental and theoretical  $^{31}\text{P}$  NMR chemical shifts studies and low energy CID MS/MS for transition metal-FN complexes. The calculations of absolute shielding constants have been performed using the Gauge-Independent Atomic Orbital (GIAO) perturbation method with Hartree-Fock (HF) methods at the 6-311+G(2d,p) level. For the larger molecules only HF method is used to compute absolute shielding constants.

From the experimental and theoretical  $^{31}\text{P}$  NMR chemical shifts studies and low energy CID MS/MS for transition metal-FN complexes, it may be possible to draw conclusion about the transition metal binding site and it may give insight into the hydrolysis mechanism.

We present the results of a calculation study of  $^{31}\text{P}$  NMR chemical shifts in the organophosphorus esters,  $(\text{RY-P}(=\text{X})(\text{OR})_2, \text{X}, \text{Y}=\text{O}$  or  $\text{S}, \text{R}=\text{CH}_3)$  and in the organophosphorus pesticides with metal ions ( $\text{Ag}^+, \text{Hg}^{2+}$ ). The theoretical  $^{31}\text{P}$  NMR chemical shifts was calculated using absolute shielding constants and  $\text{H}_3\text{PO}_4$  chemical shift ( $\delta$  of  $^{31}\text{P}=0.0$ ). The calculations of absolute shielding constants have been performed using the Gauge-Independent Atomic Orbital (GIAO) perturbation method with Hartree-Fock (HF) methods at the 6-311+G(2d,p) level. For the larger molecules only HF method is used to compute absolute shielding constants.

These results reveals the decrease in the following order,  $^{31}\text{P}$  NMR chemical shifts for OPs esters,  $\text{RS-P}(=\text{S})(\text{OR})_2(118.3 \text{ ppm}) < \text{RO-P}(=\text{S})(\text{OR})_2(85.2 \text{ ppm}) < \text{RS-P}(=\text{O})(\text{OR})_2(37.9 \text{ ppm}) < \text{RO-P}(=\text{O})(\text{OR})_2(1.1 \text{ ppm})$ . These calculated results are in good agreement with experimental  $^{31}\text{P}$  NMR chemical shifts and order. The calculated  $^{31}\text{P}$  NMR chemical shifts order for transition metal-FN and transition metal-PA complexes are in good agreement with experimental  $^{31}\text{P}$  NMR chemical shifts order.

1. Balakrishnan, V. K.; Han, X.; VanLoon, G. W.; Dust, J. M.; Toullec, J.; Buncl, E. *Langmuir*, **2004**, *20*, 6586.

2. Ruud, K.; Helgaker, T.; Bak, K. L.; Jørgensen, P.; Jensen, H. J. A. *J. Chem. Phys.* **1993**, *99*, 3847..

**Poster 6**

Sat. 4:00–6:00 PM

## **Molecular Modeling of the Glass Transition of Stereoregular Vinyl Polymers**

*Noureddine Metatla and Armand Soldera*  
*Université de Sherbrooke*

The glass transition remains one of great nature mysteries. To give a better understanding of such phenomenon the stereoregular vinyl polymers offer a special regard since the presence of the  $\alpha$ -methyl group imparts to the polymer a difference in the glass transition temperature ( $T_g$ ) according to its tacticity. Moreover, the substitution of the  $\alpha$ -methyl group by an hydrogen atom, does not give rise to a significant difference in the  $T_g$ s between the isomers. Molecular modeling is thus a perfect tool to study those polymers. Nevertheless, such studies can be envisioned only if molecular modeling accurately describes such variations. Insights can then be gained in the understanding of the reasons that give rise to this behaviour by comparing obtaining results to experimental data and theories. Consequently, it offers an atomistic viewpoint to the glass transition phenomenon. Numerous studies have been carried out to specifically understand the difference in the  $T_g$ s between stereoregular poly(methyl methacrylate), PMMA and polymethacrylate, PMA. However, it is worth noting that few studies on the glass transition phenomena on the homologous vinylic polymer where the methacrylate side-chain is substituted by a phenyl group, thus obtaining poly( $\alpha$ -methyl styrene), P $\alpha$ MS, and polystyrene, PS, respectively, have been carried out. Experimentally, difference in the  $T_g$ s is observed only between the isotactic and the atactic P $\alpha$ MS. In this presentation, the glass transition behavior differences between PMMA, PMA, PMS, and PS, and between their configurations, are exposed. More particularly, differences in local dynamics of polymer chains are looked at.

## Applications of the SSP (Source-Sink Potentials) Method to Molecular Electronics Devices

*Francois Goyer and Matthias Ernzerhof*  
*Université de Montréal*

The understanding of electron transport through molecular electronic devices (MEDs) is essential to create new types of circuits that might, one day, be of practical use. We present the formalism behind our newly developed SSP method and various results of calculations on model systems. In these small systems, phenomena, such as internal current interference, are studied to provide insight on their impact on the conductance of MEDs. Fano resonances are also discussed, and the reason for their appearance can be rationalised in terms of the structure of the systems under study. The overall understanding of these features is crucial to the designing of MEDs with specific properties, for example, conductance.

The systems studied range from small aromatic compounds to nanotubes. Taking advantage of SSP, we describe conductance in terms of internal current distribution as well as current carrying wave functions.

## An Analytic 3-Dimensional Potential Energy Surface for CO<sub>2</sub>-He and its Predicted Infrared Spectrum

*Hui Li and Robert J. Le Roy*  
*University of Waterloo*

A three-dimensional, analytic potential energy surface for CO<sub>2</sub>-He that explicitly incorporates its dependence on the Q<sub>3</sub> asymmetric-stretch normal-mode coordinate of the CO<sub>2</sub> monomer, has been obtained by least-squares fitting new *ab initio* interaction energies to a new potential form. The potential energy values were obtained from a supermolecule calculation performed at the CCSD(T) level using an aug-cc-pVQZ basis set supplemented with bond functions, and the full counterpoise correction was applied. These points were fitted to a 3-dimensional generalization of the "Morse/Long-Range" potential function form<sup>1</sup> which incorporates theoretically known angle-dependent long-range inverse-power dispersion coefficients. The three-dimensional discrete-variable representation method was employed to calculate the rovibrational eigenvalues, without separating the inter- and intramolecular nuclear motions, and our simulated infrared spectra in the  $\nu_3$  region of CO<sub>2</sub> is compared with experiment.<sup>2</sup> This three-dimensional surface will be used to predict the IR vibrational frequency shifts which have been observed for CO<sub>2</sub>-(He)<sub>N</sub> clusters with *N* up to 20.

<sup>1</sup>R.J. Le Roy and R.D.E. Henderson, *Mol. Phys.* **105**, 691 (2007).

<sup>2</sup>M.J. Weida, J.M. Sperhac and D.J. Nesbitt, *J. Chem. Phys.* **101**, 8351 (1994).

<sup>3</sup>J. Tang and A.R.W. McKellar, *J. Chem. Phys.* **121**, 181 (2004).

## Generalization of Equation of Motion Coupled Cluster Method to a State-Selective Internally Contracted Multireference Coupled Cluster Approach

*Ondrej Demel, K. R. Shamasudar and Marcel Nooijen*  
*University of Waterloo*

The Equation of Motion Coupled Cluster Method (EOMCC) has seen a large number of successful applications to excited states. This method is applicable primarily to singly excited states that have a ground state (or more generally a parent state) that is well described at the single reference level.

In this poster we discuss the generalization of EOMCC approach to systems that require a multiconfigurational description of the parent state. The parameterization of the wave function is reminiscent of EOMCC and employs a spin-adapted cluster operator  $T$ , that excites from occupied and active orbitals into the virtual space. The transformed Hamiltonian  $\exp(-T) H \exp(T)$  is subsequently diagonalized over an active space plus single excitations.

Key features of the method are:

The approach can be used to target a specific state or a small number of states in a state-averaged fashion. The cluster amplitudes are optimized precisely for the states of interest.

The occupied and active orbitals are defined in a Brueckner like fashion: the reference state is determined in the presence of dynamical correlation effects.

The approach is classified as an internally contracted multireference CC approach and is fully spin-adapted.

The most expensive part of the calculation is the diagonalization of a transformed Hamiltonian, which contains three-body interactions over an active space plus single excitations. This is accomplished by an efficient direct CI approach and a factorization of the three-body terms.

Further extensions of the approach akin to the similarity transformed EOMCC are possible.

## Correlation Factor Model

*Hilke Bahmann*  
*Université de Montréal*

The efficient calculation of properties, such as reaction barriers, geometries, charge distributions, binding energies, and molecular orbitals, is the main goal of quantum chemistry. To reach higher accuracy in these calculations, we need to better understand electron-electron interaction effects, which may be described in terms of a hole in the charge density around each electron. Our work is thus based on the key concept of the exchange-correlation hole. In a first step we construct a simple analytical model hole for systems with constant electron density, a common approximation for solids. In the second step, we design an exchange-correlation hole, based on the preceding results, which applies as well to atoms and molecules.

**Quantum Effects on the Solvation Structure of I-(H<sub>2</sub>O)<sub>n</sub> Clusters**

*Lisandro Hernández de la Peña and Gilles H. Peslherbe*  
*Concordia University*

Classical simulation methods have been extensively used to study aqueous clusters and the processes that occur in these clusters. While progress has been made and valuable information has been gained from these studies, the conventional implementation of Monte Carlo and molecular dynamics methods explicitly ignore the quantum nature of protons. It is however well known, from a number of studies, that the properties of liquid water and ice are significantly affected by the inclusion of proton quantum delocalization. It is therefore expected that protonic quantum effects will be of relevance in small low-temperature clusters.

In this work, we compare results from classical molecular dynamics and path integral molecular dynamics simulations of I-(H<sub>2</sub>O)<sub>n</sub> for n=1-6. A rigid and polarizable water model is used, and only the molecular rotational motion of the water molecules is explicitly quantized. Quantum effects are found to cause a drift of about 10% in the calculated cluster formation enthalpy, which suggests that the proton uncertainty is non-negligible. Furthermore, the clusters are found to be significantly less structured upon inclusion of quantum effects.

**Role of Polarization in Simulations of Excited-State Dynamics:  
NaI(H<sub>2</sub>O)<sub>n</sub> Photodissociation as a Case Study**

*Denise M. Koch and Gilles H. Peslherbe*  
*Concordia University*

Computer simulations of the real time-evolution of complex chemical systems in their electronically excited states, resulting for example from photoexcitation, represent many challenges for modern computational chemistry. One such challenge lies in the proper, dynamical description of the electronic structure of the system of interest in various electronic states during the chemical process. In this contribution, we will address the role of solvent polarization in realistic nonadiabatic simulations of the photodissociation dynamics of sodium iodide in water clusters.

Sodium iodide has long been a paradigm for ultrafast nonadiabatic dynamics and our interest focuses on the influence of solvation on this process. In this context, we will discuss Quantum Mechanics/Molecular Mechanics (QM/MM) nonadiabatic simulations of photoexcited NaI(H<sub>2</sub>O)<sub>n</sub> clusters, in which the electronic structure of sodium iodide is described by semiempirical valence-bond theory and the water molecules are represented by model potentials. The importance of employing polarizable model potentials and force fields to describe the ground-state structure and energetics of chemical and biochemical systems is now well recognized. We will show how a proper account of solvent polarization is also essential in performing realistic excited-state simulations of NaI(H<sub>2</sub>O)<sub>n</sub> relaxation, the results of which can then be compared to and used to interpret experimental results.

## A Density-Functional Theory Investigation of Cu(I) Complexes

Yan Li, Qadir Timerghazin, Ann English and Gilles H. Peslherbe  
Concordia University

S-nitrosothiols (RSNO) play a biological role as NO donors or carriers *in vivo*, and traces of Cu(I) metal ions have been shown to catalyze the decomposition of RSNOs in solution. We have reported the first theoretical evidence that complexation of S-nitrosothiols to Cu(I) promotes their degradation and NO release [1]. In an effort to properly model the solution catalysis of RSNO degradation by Cu(I) metal ions, a systematic benchmarking of Density-Functional Theory (DFT) has been performed for S-nitrosothiols and Cu(I) complexes. Both the Becke 3-parameter Lee-Yang-Parr and Perdew-Burke-Ernzerhof functionals have been tested. A basis set for first and second-row elements is first chosen in order to properly model the S-N bond length and dissociation energy of small RSNOs estimated by Coupled Cluster theory with Single, Double and linearized Triple excitations [CCSD(T)] extrapolated to the complete basis set limit. A basis set for Cu is then chosen on the basis of calculations of Cu(I) complexes with small molecules such as NH<sub>3</sub> or H<sub>2</sub>O, and with cysteine, and comparison with available experimental data [2]. Future work will involve Quantum Mechanics/Molecular Mechanics (QM/MM) simulations of the Cu(I)-catalysed degradation of RSNOs in solution, where Cu(I) and its first coordination sphere will be treated by the optimal DFT-based model chemistry found in this work.

<sup>1</sup>. Toubin, C.; Yeung, D.Y-H.; English, A.M.; Peslherbe, G.H. *J. Am. Chem. Soc.* **2002**, *124*, 14816.

<sup>2</sup>. Hoyau, S.; Ohanessian, G. *Chem. Phys. Lett.* **1997**, *280*, 266. *J. Am. Chem. Soc.* **1997**, *119*, 2016.

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Solid State Physics



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Theoretical Chemistry



Tony Whitehead



Theoretical Chemistry



Armand Soldera



Molecular Physical  
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Dongqing Wei

Tianjin Institute of  
Bioinformatics and Drug  
Discovery (China)

Theoretical Chemistry



Nicolas Moitessier



Organic Chemistry

## Upcoming New Members

Matthias Ernzerhof (Université de Montréal, Theoretical / Physical Chemistry)

James L. Gleason (McGill University, Organic Chemistry)

Radu Iftimie (Université de Montréal, Theoretical / Physical Chemistry)

Guillaume Lamoureux (Concordia University, Theoretical / Biophysical Chemistry)

Xavier Ottenwaelder (Concordia University, Inorganic Chemistry)

Peter Pawelek (Concordia University, Biochemistry)

Christian Reber (Université de Montréal, Inorganic Chemistry)